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## How much copper can the pearceite structure sustain? The case of cupropearceite from Tsumeb, Namibia

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### Abstract

The intriguing recovery of an extremely Cu-rich cupropearceite crystal (Cu = 7.62 a.p.f.u.) from Tsumeb, Namibia, allowed us to study the effect of the entry of Cu in the positions usually occupied by Ag in the B module layer in the structure of the minerals belonging to the pearceite-polybasite group. Electron microprobe analysis yields the formula  $[\text{Cu}_6(\text{As}_{1.89}\text{Fe}_{0.01})_{\Sigma=1.90}\text{S}_{7.05}][(\text{Ag}_{8.36}\text{Cu}_{0.62})_{\Sigma=8.98}\text{CuS}_{4.06}]$ . Lattice parameters are:  $a = 7.144(1)$ ,  $c = 11.745(2)$  Å,  $V = 519.1(2)$  Å<sup>3</sup>. The structure was refined in the space group  $P\bar{3}m1$  up to  $R = 0.0278$  using 489 observed reflections [ $2\sigma(I)$  level]. The entry of these elevated amounts of Cu in the structure does not induce a structural change and shows that pearceite is able to accommodate higher contents of Cu than previously thought. This allows hypothesis of the existence of an ideal  $[\text{Cu}_6\text{As}_2\text{S}_7][\text{Cu}_9\text{CuS}_4]$  end member in nature. Such a proposed Ag-free mineral would show the highest structural disorder so far observed for a pearceite structure and, consequently, the highest ionic conductivity and could find applications in silver photography as sensitizer or in optics and microelectronics as rewritable storage medium.

*Key words:* sulfosalts; crystal structure; chemical composition; copper; fast ionic conductor; Tsumeb.

### Introduction

The minerals belonging to the pearceite-polybasite group are among the most widespread Ag-sulfosalts in nature. They exhibit the general

formula  $[\text{M}_6\text{T}_2\text{S}_7][\text{Ag}_9\text{CuS}_4]$  with  $M = \text{Ag}, \text{Cu}$  and  $T = \text{As}, \text{Sb}$ , and their crystal structure can be described as the stacking, along the  $c$  axis, of two pseudo-layer modules: a  $[\text{M}_6\text{T}_2\text{S}_7]^{2-}$   $A$  module layer and a  $[\text{Ag}_9\text{CuS}_4]^{2+}$   $B$  module layer

(Bindi et al., 2007a and references therein). Cu occurs in one structural position of the *B* module layer and replaces Ag in the only fully occupied *M* position (labelled Ag1/Cu1; Bindi et al., 2006a) of the *A* module layer. Consequently, when the Cu content is  $> 4.00$  a.p.f.u., the Ag structural position of the *A* module layer becomes Cu-dominant and we have the minerals cupropearceite (Bindi et al., 2007b; Bindi and Pekov, 2009) and cupropolybasite (Bindi et al., 2007b), depending on the As/Sb ratio.

One of the open questions among crystallographers who work with sulfosalts has been: how much copper can the pearceite structure sustain? Or, in other words, what happens when the Cu content is  $> 7.00$  a.p.f.u.? The presence of such high amounts of Cu would be enough to completely fill the Ag1/Cu1 position of the *A* layer and the Cu2 position of the *B* layer. Excess of Cu over 7.00 a.p.f.u. would have to be hosted in the disordered portion of the structure of the *B* layer (the two partially occupied Ag positions) giving rise to a condition heretofore unobserved for this group of minerals. Moreover, if the Cu content were  $> 11.50$  a.p.f.u., it would imply the existence

of a so far non-contemplated new member of the pearceite-polybasite group having the ideal formula  $[\text{Cu}_6\text{As}_2\text{S}_7][\text{Cu}_9\text{CuS}_4]$ . Although the latter hypothesis seems unlikely, we have recently found cupropearceite crystals with Cu contents (in a.p.f.u.) in the range 7.00-8.00 from the Tsumeb mine, Tsumeb, Namibia. The rock sample containing the Cu-rich cupropearceite consists mainly of zincian tennantite crystals up to 1 cm with small enargite and pseudo-hexagonal cupropearceite crystals growing on it. Such Cu-rich cupropearceite crystals gave us the possibility to shed light on the structural role of Cu in the disordered part of the *B* layer by means of single-crystal structural and chemical data.

### Chemical composition

The chemical composition of two cupropearceite fragments (Figure 1) was determined using wavelength dispersive analysis (WDS) by means of a JEOL Hyperprobe JXA-8530F electron microprobe [25 kV, 20 nA, beam size 2  $\mu\text{m}$ ; standards and measured lines used: pure metal - Ag(L $\alpha$ ); chalcopyrite - Cu(K $\alpha$ ), Fe(K $\alpha$ ); lorándite - As(L $\alpha$ ); stibnite - Sb(L $\alpha$ ),

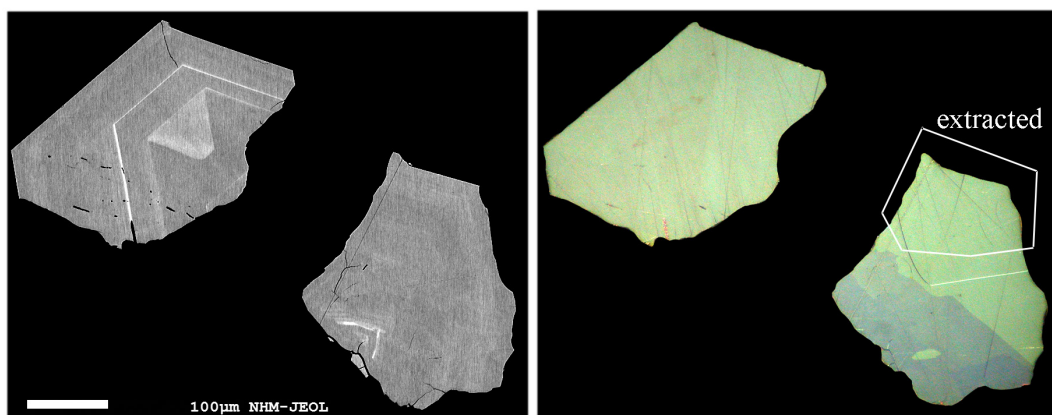


Figure 1. SEM-BSE and optical images of the two polished grains of cupropearceite from Tsumeb. On the right the fragment hand-picked for the structural study is highlighted. The narrow, bright zone in grain 2 (left) corresponds to cupropolybasite.



S(K $\alpha$ ); bismuthinite - Bi(L $\alpha$ ); galena - Pb(M $\alpha$ )]. No other elements were detected. The chemical compositions (12 to 9 analyses on the two grains, respectively) are reported in Table 1. The elements Bi, Fe and Pb are below the detection limits (0.15 wt% for Bi and Pb and 0.05 wt% for Fe) for the most of the analyzed points, and for this reason they were not included in the formula below. The brighter regions in Figure 1a correspond mainly to Sb-rich areas. The chemical formulae were calculated on the basis of 29 atoms. The chemical formula of the crystal selected for the X-ray single-crystal diffraction study (see below) can be written as  $[\text{Cu}_6(\text{As}_{1.89}\text{Fe}_{0.01})_{\Sigma=1.90}\text{S}_{7.05}] [(\text{Ag}_{8.36}\text{Cu}_{0.62})_{\Sigma=8.98}\text{CuS}_{4.06}]$  (it represents the average of analyses #13, 14 and 15 in Table 1).

### X-ray Crystallography

One fragment of cupropearceite was hand-picked from grain 2 (right in Figure 1b) and examined by means of an Oxford Diffraction Xcalibur 3 diffractometer, fitted with a Sapphire 2 CCD detector (see Table 2 for details). Intensity integration and standard Lorentz-polarization correction were performed with the *CrysAlis RED* (Oxford Diffraction, 2006) software package. The program ABSPACK in *CrysAlis RED* (Oxford Diffraction, 2006) was used for the absorption correction.

The program JANA2006 (Petříček et al., 2006) was used for the refinement of the structure which was carried out in the space group  $P\bar{3}m1$  starting from the atomic coordinates given by Bindi et al. (2006a) for the crystal structure of pearceite-*Tac*. With the introduction of anisotropic temperature factors for all the atoms and up to fourth-order non-harmonic Gram-Charlier tensors for the Debye-Waller description (Johnson and Levy, 1974; Kuhs, 1984) of the Ag2, Ag3, and S4 positions (to mimic the spread of electrons associated with silver along diffusion paths) the residual  $R$  value smoothly converged to the  $R = 0.0278$  value for 489 reflections [ $I > 2\sigma(I)$ ]

and  $R = 0.0325$  for all 897 unique reflections (Table 2).

Atomic parameters are given in Table 3. Bond distances are reported in Table 4. CIF and the list of structure factors are available from the Authors upon request.

### Results and discussion

The crystal structure of cupropearceite (Figure 2) consists of the stacking of  $[\text{Cu}_6\text{As}_2\text{S}_7]^{2-}$  (*A*) and  $[(\text{Ag,Cu})_9\text{CuS}_4]^{2+}$  (*B*) module layers along [001]; As forms isolated  $\text{AsS}_3$  pyramids typically occurring in sulfosalts, Cu fully replaces Ag in the threefold occupied position of the *A* module layer and links two S atoms in a linear coordination in the *B* layer, and Ag (with minor Cu) occupies sites with coordination ranging from quasi linear to almost tetrahedral in the *B* layer. In particular, in this layer the Ag cations are distributed along 2D diffusion paths

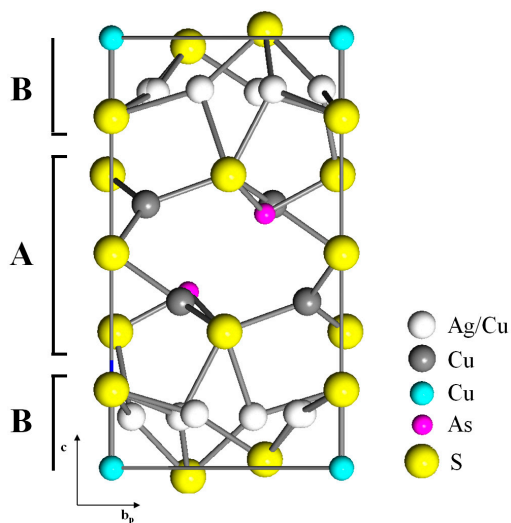


Figure 2. Projection of the cupropearceite-*Tac* structure along the  $a$  axis. The figure emphasizes the stacking of the  $[\text{Cu}_6\text{As}_2\text{S}_7]^{2-}$  *A* and  $[(\text{Ag,Cu})_9\text{CuS}_4]^{2+}$  *B* module layers.

Table 2. Details pertaining to the single-crystal X-ray data collection and structure refinement of cupropearceite.

*Crystal data*

space group	$P\bar{3}m1$ (#164)
cell parameters	$a = 7.144(1) \text{ \AA}$ $c = 11.745(2) \text{ \AA}$ $V = 519.1(2) \text{ \AA}^3$
<i>Z</i>	1
crystal color	black
crystal shape	block
crystal size (mm)	$0.040 \times 0.085 \times 0.110$
<i>Data collection</i>	
diffractometer	Oxford Diffraction Xcalibur 3
radiation type	MoK $\alpha$ ( $\lambda = 0.71073 \text{ \AA}$ )
monochromator	oriented graphite (002)
scan mode	$\varphi/\omega$
temperature (K)	298
detector to sample distance (cm)	5
number of frames	567
rotation width per frame (°)	0.20
measuring time (s)	75
maximum covered $2\theta$ (°)	69.94 ( $d \approx 0.65 \text{ \AA}$ )
range of $h, k, l$	$-11 \leq h \leq 11, -11 \leq k \leq 11, -18 \leq l \leq 18$
collected reflections	5013
$R_{\text{int}}$ before absorption correction	0.1084
$R_{\text{int}}$ after absorption correction	0.0299
<i>Refinement</i>	
refinement coefficient	$F^2$
No. of refl. in refinement	897
No. of observed refl.	489
No. of refined parameters	90
weighting scheme	$w = 1 / [\sigma^2(I) + (0.044 \times I)^2]$
$R^\dagger$ (obs) / $R^\dagger$ (all)	0.0278 / 0.0325
$wR^{2\dagger}$ (obs) / $wR^{2\dagger}$ (all)	0.0455 / 0.0774
$S$ (obs) / $S$ (all)	1.31 / 1.08
Secondary ext. coeff. $\ddagger$	0.019(6)
diff. Fourier ( $e^-/\text{\AA}^3$ )	[-0.68, 0.99]

Note:  $^\dagger R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ ;  $wR^2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w(|F_o|^4)]^{1/2}$ ;  $\ddagger$  Isotropic secondary extinction - Type I - Gaussian distribution (Becker and Coppens, 1974).

Table 3. Wyckoff positions, site occupation factors, fractional atomic coordinates, and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for the selected cupropearceite crystal.

atom	Wyckoff	s.o.f.	x	y	z	Uiso
Cu1	6i	1.000	0.3410(2)	0.1705(2)	0.3712(1)	0.0285(2)
Ag2	12j	0.346(5)	0.3612(3)	0.1599(2)	0.1252(3)	0.098(10)
Ag3	12j	0.384(5)	0.3004(3)	-0.0838(3)	0.1178(3)	0.111(3)
As	2d	1.000	0.3333	0.6667	0.40654(3)	0.0232(4)
Cu2	1a	1.000	0	0	0	0.0311(4)
S1	2c	1.000	0	0	0.1831(2)	0.0324(4)
S2	6i	1.000	0.01668(5)	0.50834(5)	0.31344(6)	0.0302(5)
S3	2d	1.000	0.6667	0.3333	0.0207(2)	0.0329(6)
S4	1b	1.000	0	0	0.5	0.105(3)

Table 4. Main interatomic distances ( $\text{\AA}$ ) for the selected cupropearceite crystal.

As	- S2	2.244(1)	Cu2	- S1	2.151(1)	Cu1 - S2	2.201(2)
	- S2	2.244(1)		- S1	2.151(1)	- S2	2.201(2)
	- S2	2.244(1)	<Cu2-S>		2.151	- S4 <sup>‡</sup>	2.249(5)
<As-S>		2.244				<Cu1-S>	2.217
Ag2	- S3	2.258(5)	Ag3	- S3	2.510(4)		
	- S1	2.341(4)		- S1	2.615(5)		
	- S2	2.920(6)		- S2	2.593(6)		
	- Cu2	2.679(5)		- Cu2	2.857(6)		

Note: <sup>‡</sup> the Cu1-S4 distance corresponds to the most probable distance calculated from the modes (maxima) of *jpdf* (joint probability density function) maps.

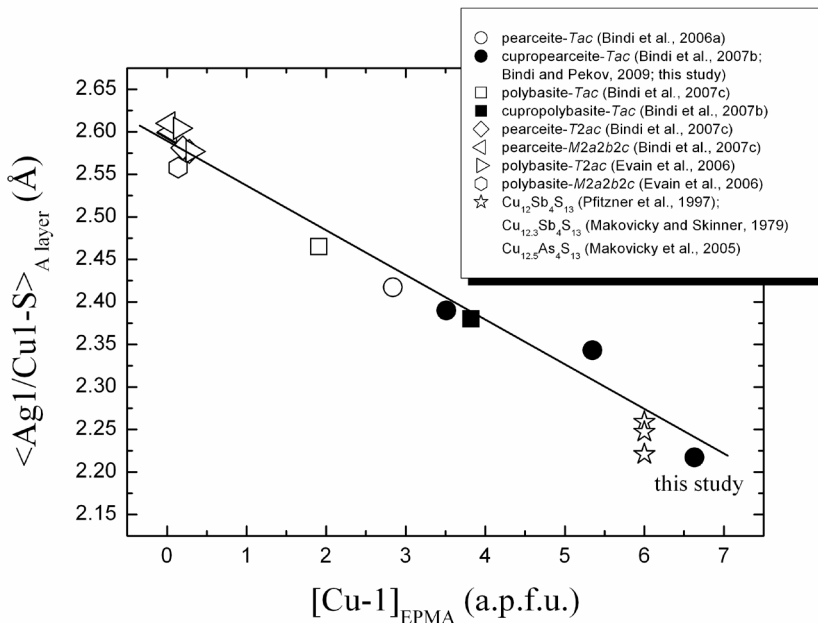


Figure 3. Relationship between the  $\langle \text{Ag1/Cu1-S} \rangle$  distance ( $\text{\AA}$ ) and  $[\text{Cu-1}]_{\text{EPMA}}$  (a.p.f.u.) for the different members of the pearceite-polybasite group ( $R^2 = 0.983$ ). The cupropearceite crystal studied here is indicated.

in a structure skeleton made of face-sharing tetrahedra around the linearly coordinated Cu atom.

The crystal structure refinement of cupropearceite showed that the Ag structural position of the *A* module is fully occupied by Cu. Cu atoms at this position exhibit a triangular coordination by sulfur atoms in a quasi-planar environment with a mean  $\langle \text{Cu1-S} \rangle$  distance of 2.217  $\text{\AA}$ . Taking into account all the Ag/Cu distances in the structures of all the members of the pearceite-polybasite group (Bindi et al., 2006a, 2007c; Evain et al., 2006) and those observed for synthetic  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  (Pfitzner et al., 1997), synthetic  $\text{Cu}_{12.3}\text{Sb}_4\text{S}_{13}$  (Makovicky and Skinner, 1979) and synthetic  $\text{Cu}_{12.5}\text{As}_4\text{S}_{13}$  (Makovicky et al., 2005), having Cu in a similar triangular environment, we can observe that the cupropearceite studied here shows the smallest value (Figure 3). The fact that it

shows a smaller value than those observed for synthetic compounds with a full occupancy of copper is not surprising given the presence of As only in the mineral. Indeed, the greater size of Sb with respect to As can induce a general enlargement of all of the structural topology. The strict relationship between Sb and Cu in the pearceite structure can be well represented by plotting the electron microprobe data (in a.p.f.u.) we obtained for the two grains (Figure 4). It appears evident that the greater the Cu content, the lower the Sb. The reason of such anti-correlation resides in the overall dimension of the *A* layer: the presence of high amounts of Cu replacing Ag provokes a smaller room for the trigonal pyramid, which preferentially hosts As. The situation is even more marked if, as in the present case, Cu partially replaces Ag also in the *B* layer. Obviously, for minor Cu contents in the *A* layer we can have also

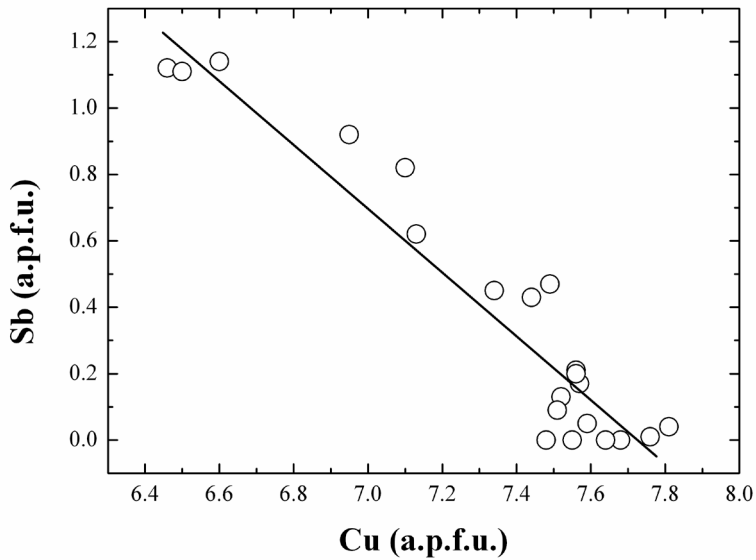


Figure 4. Relationship between the Sb and Cu contents (in a.p.f.u.) obtained with the electron microprobe for the two cupropearceite grains from Tsumeb ( $R^2 = 0.901$ ).

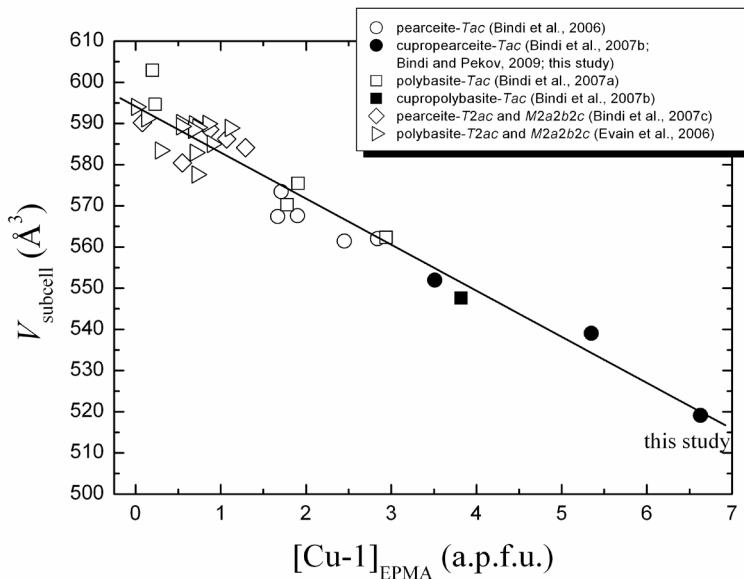


Figure 5. Relationship between the unit-cell volume of the hexagonal subcell ( $\text{\AA}^3$ ) and  $[\text{Cu-1}]_{\text{EPMA}}$  (a.p.f.u.) for the different members of the pearceite-polybasite group ( $R^2 = 0.931$ ). The cupropearceite crystal studied here is indicated.



a dominance of Sb over As, thus justifying the existence of the mineral cupropolybasite. However, the Sb contents are not very high in cupropolybasite (i.e.,  $[(\text{Cu}_{3.82}\text{Ag}_{2.42}\text{Zn}_{0.02}\text{Pb}_{0.01})_{\Sigma 6.27}(\text{Sb}_{1.19}\text{As}_{0.73})_{\Sigma 1.92}\text{S}_7][\text{Ag}_9\text{CuS}_4]$ ; Bindi et al., 2007b), being just slightly above 1 a.p.f.u.

In Figure 5 the variation of the hexagonal subcell parameters (i.e.,  $a \sim 7.5$ ,  $c \sim 12$  Å) is plotted as a function of  $[\text{Cu-1}]_{\text{EPMA}}$  to compare all the members belonging to the pearceite-polybasite group. The linear fit of the data gives rise to the following equation:  $V_{\text{subcell}} (\text{Å}^3) = 594(1) - 11.4(6)[\text{Cu-1}]_{\text{EPMA}}$ . It is worth noting that if we calculate the unit-cell volume from the equation above by using the copper content we obtained from the crystal structure refinement, i.e.  $[\text{Cu}_6\text{As}_2\text{S}_7][(\text{Ag}_{8.37}\text{Cu}_{0.63})\text{CuS}_4]$ , we find  $V_{\text{subcell}} = 518.4$  Å<sup>3</sup>. This value is in excellent agreement with that observed for the cupropearceite examined in this study (i.e., 519.1 Å<sup>3</sup>).

### Concluding Remarks

Bindi et al. (2006b) by means of complex impedance spectroscopy results showed that the pearceite-polybasite minerals are fast ionic conductors and that cupropearceite is the most conductive compound among the members of the group. This means that copper plays a crucial role in the stabilization of a disordered structure: the higher the Cu content, the higher the structural disorder. As discussed above, the disorder is mainly concentrated in the *B* layer of the structure, where the Ag cations are distributed in various sites corresponding to the most pronounced probability density function (*pdf*) locations (modes) of diffusion-like paths. These positions correspond to low-coordination sites, in agreement with the silver preference for such environments. Unfortunately, the scarce amount of material precludes a spectroscopic study on the cupropearceite from Tsumeb but we can infer that such a mineral, having

substantial Cu also in the *B* layer, should be the most conductive among the members of the group. As such, it could be very useful for important technological applications as in silver photography as sensitizers or in optics and microelectronics as rewritable storage media.

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