

# Structural role of copper in the minerals of the pearceite-polybasite group: the case of the new minerals cupropearceite and cupropolybasite

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## ABSTRACT

The pearceite-polybasite group of minerals, general formula  $[M_6T_2S_7][Ag_9CuS_4]$  with  $M = Ag, Cu$ ; and  $T = As, Sb$ , show a crystal structure which can be described as the succession, along the  $c$  axis, of two pseudo-layer modules: a  $[M_6T_2S_7]^{2-}$   $A$  module layer and a  $[Ag_9CuS_4]^{2+}$   $B$  module layer. Copper is present in one structural position of the  $B$  module layer and replaces Ag in the only fully occupied  $M$  position of the  $A$  module layer. When the Cu content is  $>4.00$  a.p.f.u., the structural position of the  $A$  module layer becomes Cu-dominant and, consequently, the mineral deserves its own name. In this paper we report the crystal-chemical characterization of two Cu-rich members exhibiting the 111 unit-cell type (corresponding to the  $Tac$  polytype). One sample (space group  $P\bar{3}m1$ ,  $a$  7.3218(8),  $c$  11.8877(13) Å,  $V$  551.90(10) Å<sup>3</sup>,  $Z = 1$ ) having As  $>$ Sb and with the structural position of the  $A$  module layer dominated by Cu, has been named cupropearceite and the other sample (space group  $P\bar{3}m1$ ,  $a$  7.3277(3),  $c$  11.7752(6) Å,  $V$  547.56(8) Å<sup>3</sup>,  $Z = 1$ ) having Sb  $>$ As has been named cupropolybasite.

Both the new minerals and mineral names have been approved by the IMA-CNMNC.

**KEYWORDS:** cupropearceite, cupropolybasite, new mineral, crystal structure, chemical composition.

## Introduction

THE minerals of the pearceite-polybasite group are relatively widespread in nature. They exhibit the general formula  $[M_6T_2S_7][Ag_9CuS_4]$  with  $M = Ag, Cu$  and  $T = As, Sb$ , and their crystal structure can be described as the succession, along the  $c$  axis, of two pseudo-layer modules: a  $[M_6T_2S_7]^{2-}$   $A$  module layer and a  $[Ag_9CuS_4]^{2+}$   $B$  module

layer (Bindi *et al.*, 2007a and references therein). From a chemical point of view, the members of this group are generally pure, containing only minor amounts of Bi, Pb, Zn and Fe. Nonetheless, Bindi *et al.* (2007b) proved the existence of a Se-rich end-member having two structural positions of sulphur dominated by selenium. Bindi *et al.* named this mineral selenopolybasite to indicate the Se-dominant analogue of polybasite.

In the present paper, we investigate the structural role of Cu in the minerals of the pearceite-polybasite group. Copper is present in one structural position of the  $B$  module layer and replaces Ag in the only fully occupied  $M$  position

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(labelled Ag1/Cu1; Bindi *et al.*, 2006a) of the *A* module layer. It appears evident that when the Cu content is  $>4.00$  a.p.f.u., the structural position Ag1/Cu1 of the *A* module layer becomes Cu-dominant and, consequently, the mineral deserves its own name. Here, we report the crystal-chemical characterization of two Cu-rich members (samples 2399/I and M12128) of the pearceite-polybasite group (with 111 unit-cell type corresponding to the polytype *Tac*; Bindi *et al.*, 2007a). Sample 2399/I, having  $As > Sb$  and the structural position Ag1/Cu1 of the *A* module layer dominated by Cu, has been named cupropearceite to indicate the Cu-dominant analogue of pearceite. Moreover, as it exhibits the 111 unit-cell type, the full name for the polytype is cupropearceite-*Tac*, the Cu-dominant analogue of pearceite-*Tac*. The type-material is housed in the Mineralogical Collection of the Museo di Storia Naturale, Università di Firenze, Italy. However, as sample M12128 has  $Sb > As$  and the structural position of the *A* module layer dominated by Cu, this has been named cupropolybasite to indicate the Cu-dominant analogue of polybasite. In addition, as it exhibits the 111 unit-cell type, the full name for the polytype is cupropolybasite-*Tac*, the Cu-dominant analogue of polybasite-*Tac*. The type-material for this mineral is deposited in the Mineralogical Collection of the Royal Ontario Museum, Department of Natural History, Ontario (Canada).

Both the new minerals and mineral names have been approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (IMA CNMNC) (IMA 2007-046 and IMA 2008-004 for cupropearceite and cupropolybasite, respectively).

## Occurrence

### Cupropearceite

Cupropearceite (sample 2399/I) is from the Sarbay deposit situated in the Kustanai region (Valerianovsky belt), north Kazakhstan. Geological and metallogenetic data concerning this deposit were reported by Dymkin (1966), Chuguevskaya (1969), and Pekov and Karpenko (1997). Cupropearceite is typically associated with tetrahedrite to form subhedral to anhedral grains up to 300  $\mu\text{m}$  in size. Other minerals spatially associated with cupropearceite are pyrite, quartz and calcite.

### Curopolybasite

Curopolybasite (sample M12128) is from the Premier mine which is one of British Columbia's largest epithermal silver-gold deposits. It is hosted by early Jurassic andesitic to dacitic volcanic rocks of the Unuk River Formation. Ore minerals include pyrite, sphalerite and galena with minor tetrahedrite, chalcopyrite, arsenopyrite and local pyrrhotite. Geological and metallogenetic data are reported in Panteleyev (1991). The type specimen is a mass of native silver with cupropolybasite and quartz, fitting the description of supergene ore from the Premier Mine by Burton (1926). Cupropolybasite exhibits a subhedral to anhedral grain morphology and does not show any inclusions or intergrowths with other minerals. The maximum grain-size of the cupropolybasite is  $\sim 350$   $\mu\text{m}$ . Other minerals spatially associated with cupropolybasite are native silver and quartz.

## Physical and optical properties

Cupropearceite and cupropolybasite are opaque with a metallic lustre. They possess a black streak and are brittle; neither fracture nor cleavage were observed. Unfortunately, density could not be measured due to the small grain-size of the samples; the calculated density (on the basis of the empirical formula) is 6.134  $\text{g}/\text{cm}^3$  and 6.310  $\text{g}/\text{cm}^3$  for cupropearceite and cupropolybasite, respectively. Micro-indentation measurements carried out with a VHN load of 100 g gave a mean value of 117  $\text{kg}/\text{mm}^2$  (range 112–128) for cupropearceite and a mean value of 129  $\text{kg}/\text{mm}^2$  (range 121–137) for cupropolybasite, corresponding to a Mohs hardness of 3–3.5. In plane-polarized reflected light, both minerals are moderately birefractant and weakly pleochroic from light-grey to a blue grey. Between crossed polars, the minerals are anisotropic, without characteristic rotation-tints and internal reflections.

Reflectance measurements for the two new minerals were made in air with an MPM-200 Zeiss microphotometer equipped with an MSP-20 system processor on a Zeiss Axioplan ore microscope. The filament temperature was  $\sim 3350$  K. Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The spot-size diameter was 0.1 mm. Reflectance percentages ( $R_{\text{min}}$  and  $R_{\text{max}}$ ) for cupropearceite for the four standard COM wavelengths are 31.7, 32.8 (471.1 nm), 29.1,

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31.5 (548.3 nm), 28.8, 30.8 (586.6 nm) and 28.5, 29.9 (652.3 nm), respectively; the values for cupropolybasite are 32.4, 33.3 (471.1 nm), 31.2, 32.7 (548.3 nm), 30.8, 31.9 (586.6 nm) and 29.6, 30.5 (652.3 nm).

**X-ray crystallography**

*Cupropearceite*

A detailed description of the crystal structure of cupropearceite (space group  $P\bar{3}m1$ ;  $a = 7.3218(8)$ ,

TABLE 1. Calculated powder XRD data for cupropearceite and cupropolybasite.

Cupropearceite				Cupropolybasite			
<i>I</i>	$d_{calc}$	<i>h</i>	<i>k</i> <i>l</i>	<i>I</i>	$d_{calc}$	<i>h</i>	<i>k</i> <i>l</i>
<b>53.54</b>	<b>11.8877</b>	<b>0</b>	<b>0</b> <b>1</b>	<b>42.55</b>	<b>11.7752</b>	<b>0</b>	<b>0</b> <b>1</b>
15.73	6.3409	1	0 0	10.80	6.3460	1	0 0
6.83	5.9439	0	0 2	9.37	5.8876	0	0 2
7.68	3.6609	1	1 0	5.19	3.6639	1	1 0
4.67	3.4988	1	1 1	14.58	3.4984	1	1 1
11.93	3.1704	2	0 0	7.03	3.1730	2	0 0
11.22	3.1171	1	1 2	17.02	3.1107	1	1 2
28.00	3.0634	0	2 1	20.33	3.0637	0	2 1
<b>37.62</b>	<b>3.0634</b>	<b>2</b>	<b>0</b> <b>1</b>	<b>45.41</b>	<b>3.0637</b>	<b>2</b>	<b>0</b> <b>1</b>
<b>100.00</b>	<b>2.9719</b>	<b>0</b>	<b>0</b> <b>4</b>	<b>100.00</b>	<b>2.9438</b>	<b>0</b>	<b>0</b> <b>4</b>
7.24	2.7974	0	2 2	10.88	2.7932	0	2 2
<b>44.02</b>	<b>2.7974</b>	<b>2</b>	<b>0</b> <b>2</b>	<b>55.77</b>	<b>2.7932</b>	<b>2</b>	<b>0</b> <b>2</b>
4.80	2.6890	1	1 3	18.30	2.4676	0	2 3
13.00	2.4756	0	2 3	<b>39.13</b>	<b>2.4676</b>	<b>2</b>	<b>0</b> <b>3</b>
<b>44.96</b>	<b>2.4756</b>	<b>2</b>	<b>0</b> <b>3</b>	5.14	2.3503	1	2 1
6.17	2.3966	2	1 0	<b>35.84</b>	<b>2.3503</b>	<b>2</b>	<b>1</b> <b>1</b>
<b>45.09</b>	<b>2.3494</b>	<b>2</b>	<b>1</b> <b>1</b>	<b>40.64</b>	<b>2.2948</b>	<b>1</b>	<b>1</b> <b>4</b>
<b>37.40</b>	<b>2.3073</b>	<b>1</b>	<b>1</b> <b>4</b>	5.04	2.2079	0	1 5
<b>42.12</b>	<b>2.1683</b>	<b>0</b>	<b>2</b> <b>4</b>	<b>38.10</b>	<b>2.1581</b>	<b>0</b>	<b>2</b> <b>4</b>
20.49	2.0507	1	2 3	10.31	2.1153	3	0 0
18.54	1.9939	1	1 5	8.92	2.0820	3	0 1
8.71	1.9915	0	3 2	13.79	2.0467	1	2 3
9.18	1.9021	2	0 5	10.33	1.9907	0	3 2
<b>49.72</b>	<b>1.8305</b>	<b>2</b>	<b>2</b> <b>0</b>	24.19	1.9811	1	1 5
7.05	1.6879	2	1 5	9.39	1.8911	2	0 5
11.01	1.6802	2	0 6	7.62	1.8621	0	3 3
9.28	1.5713	0	4 1	<b>37.75</b>	<b>1.8319</b>	<b>2</b>	<b>2</b> <b>0</b>
12.13	1.5713	4	0 1	10.65	1.8102	2	2 1
17.81	1.5585	2	2 4	8.07	1.6804	2	1 5
7.85	1.4970	2	0 7	12.05	1.6691	2	0 6
7.28	1.4860	0	0 8	7.64	1.6600	2	2 3
19.74	1.4718	0	4 3	5.62	1.5723	0	4 1
5.86	1.4718	4	0 3	7.18	1.5723	4	0 1
9.36	1.4130	3	2 2	7.14	1.5554	2	2 4
6.73	1.4130	2	3 2	6.17	1.4862	2	0 7
8.45	1.3987	4	0 4	6.72	1.4719	0	0 8
9.91	1.3455	0	2 8	13.30	1.4709	0	4 3
7.69	1.2409	2	3 5	7.12	1.4460	2	2 5
7.13	1.1923	4	2 1	8.39	1.3966	4	0 4
7.67	1.1588	0	4 7	7.11	1.3352	0	2 8
				5.03	1.1542	0	4 7

The calculated powder XRD pattern for cupropearceite was computed with the atomic coordinates and the occupancy factors reported in Bindi *et al.* (2006b), whereas those for cupropolybasite were determined with the atomic coordinates and the occupancy factors reported in Table 3. Numbers in bold indicate the strongest XRD peaks of these minerals.

TABLE 2. Details pertaining to the single-crystal XRD data collection and structure refinement of cupropolybasite.

Crystal data	
Space group	$P\bar{3}m1$ (#164)
Cell parameters	$a = 7.3277(3)$ (Å) $c = 11.7752(6)$ (Å) $V = 547.56(8)$ (Å <sup>3</sup> )
Z	1
Crystal colour	Black
Crystal shape	Block
Crystal size (mm)	0.045 × 0.055 × 0.070
Data collection	
Diffractometer	Oxford Diffraction Xcalibur 3
Radiation type	Mo-K $\alpha$ ( $\lambda = 0.71073$ )
Monochromator	oriented graphite (002)
Scan mode	$\varphi/\omega$
Temperature (K)	298
Detector to sample distance (cm)	5
Number of frames	674
Rotation width per frame (°)	0.20
Measuring time (s)	120
Maximum covered $^{\circ}2\theta$	69.75 ( $d = 0.65$ Å)
Range of $h, k, l$	$-11 \leq h \leq 11, -11 \leq k \leq 11, -18 \leq l \leq 18$
Collected reflections	4987
R <sub>int</sub> before absorption correction	0.1189
R <sub>int</sub> after absorption correction	0.0312
Refinement	
Refinement coefficient	$F^2$
F(000)	945
No. of reflections in refinement	906
No. of observed reflections	578
No. of refined parameters	92
Weighting scheme	$w = 1/[\sigma^2(I) + (0.0446 \times I)^2]$
R <sub>obs</sub> <sup>†</sup> /R <sub>all</sub> <sup>†</sup>	0.0340/0.0537
wR2 <sub>obs</sub> <sup>†</sup> /wR2 <sub>all</sub> <sup>†</sup>	0.0863/0.0881
S <sub>obs</sub> /S <sub>all</sub>	1.42/1.12
Secondary ext. coeff. <sup>‡</sup>	0.03(1)
Difference Fourier (e <sup>-</sup> /Å <sup>3</sup> )	[-0.85, 1.06]

$$^{\dagger}R = \Sigma||F_o| - |F_c||/\Sigma|F_o|; wR^2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^4)]^{1/2}$$

<sup>‡</sup> Isotropic secondary extinction – Type I: Gaussian distribution (Becker and Coppens, 1974).

$c = 11.8877(13)$  Å,  $V = 551.90(10)$  Å<sup>3</sup>,  $Z = 1$ ) as well as the experimental details of the data collection and refinement, have already been published by Bindi *et al.* (2006b), where the mineral was reported as a Cu-rich variety of pearceite. Table 1 reports the calculated powder X-ray diffraction (XRD) pattern for cupropearceite computed with the atomic coordinates and the occupancy factors given in Bindi *et al.* (2006b).

#### Cupropolybasite

Several crystals of cupropolybasite were selected from sample M12128 and examined by means of a Bruker P4 single-crystal diffractometer using graphite-monochromatized Mo-K $\alpha$  radiation. Unit-cell dimensions were determined by least-squares refinement using the setting angles of 30 high- $\theta$  reflections ( $25^\circ < \theta_{\text{Mo-K}\alpha} < 30^\circ$ ) giving nearly identical unit-cell values for all the crystals

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

Atom	Wyckoff	s.o.f.	x	y	z	$U_{iso}$
Ag1	6i	0.451(11)	0.2954(3)	0.14769(13)	0.38437(13)	0.0518(9)
Cu1	6i	0.549	0.2954	0.14769	0.38437	0.0518
Ag2	12j	0.356(7)	0.3568(6)	0.113(5)	0.1236(4)	0.312(18)
Ag3	12j	0.394(7)	0.3046(9)	-0.0841(7)	0.1186(4)	0.139(3)
Sb	2d	0.691(12)	0.3333	0.6667	0.41428(6)	0.0245(2)
As	2d	0.309	0.3333	0.6667	0.41428	0.0245
Cu2	1a	1.000	0	0	0	0.0320(5)
S1	2c	1.000	0	0	0.1833(2)	0.0322(7)
S2	6i	1.000	0.0100(2)	0.50499(11)	0.31516(14)	0.0269(5)
S3	2d	1.000	0.6667	0.3333	0.0202(3)	0.0463(9)
S4	1b	1.000	0	0	0.5	0.113(4)

investigated. Since the crystals were identical to each other, we decided to carry out data collection on the one which showed the best diffraction quality. The data collection was carried out with 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 JANA2000 (Petříček *et al.*, 2000) 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 Ag1/Cu1, Ag3 and S4 positions, to mimic the spread of electrons associated with silver along diffusion paths, the residual  $R$  value smoothly converged to the  $R = 0.0340$  value for 578 reflections ( $I > 2\sigma(I)$ ) and  $R = 0.0537$  for all 906 unique reflections (Table 2).

Atomic parameters are reported in Tables 3–5. Bond distances are reported in Table 6. The calculated powder XRD pattern for cupropolybasite, computed with the atomic coordinates and the occupancy factors reported in Table 3, is given in Table 1, together with that of cupropearceite.

### Chemical composition

The chemical composition was determined using wavelength dispersive spectroscopy (WDS) by means of a JEOL JXA-8200 electron microprobe

TABLE 4. Anisotropic displacement parameters  $U_{ij}$  ( $\text{\AA}^2$ ) for the selected cupropolybasite crystal.

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ag1/Cu1	0.0620(12)	0.0384(9)	0.0627(14)	0.0310(6)	-0.0052(7)	-0.0026(4)
Ag2	0.0401(13)	0.73(4)	0.0510(13)	0.103(7)	0.0064(10)	0.020(8)
Ag3	0.230(4)	0.177(4)	0.057(2)	0.137(3)	-0.0329(19)	-0.030(2)
Sb/As	0.0253(3)	0.0253(3)	0.0228(4)	0.01265(15)	0	0
Cu2	0.0396(7)	0.0396(7)	0.0168(8)	0.0198(3)	0	0
S1	0.0408(9)	0.0408(9)	0.0150(10)	0.0204(5)	0	0
S2	0.0221(6)	0.0247(5)	0.0330(8)	0.0110(3)	0.0016(6)	0.0008(3)
S3	0.0484(11)	0.0484(11)	0.0421(18)	0.0242(5)	0	0
S4	0.146(4)	0.146(4)	0.047(8)	0.073(2)	0	0

TABLE 5. Higher-order displacement parameters  $^{\dagger\dagger}$  for the selected cupropolybasite crystal.

	Ag1/Cu1	Ag3	S4
<i>C111</i>	0.0383(17)	0.12(2)	0
<i>C112</i>	0.0191(9)	-0.152(14)	0
<i>C113</i>	-0.0096(6)	0.021(4)	0
<i>C122</i>	0.0067(6)	-0.149(11)	0
<i>C123</i>	-0.0048(3)	0.020(3)	0
<i>C133</i>	0.0032(3)	-0.0039(10)	0
<i>C222</i>	0.0004(10)	-0.085(10)	0
<i>C223</i>	-0.0020(3)	0.023(2)	0
<i>C233</i>	0.00159(16)	-0.0015(9)	0
<i>C333</i>	-0.0046(3)	-0.0005(4)	0
<i>D1111</i>	-0.004(4)	-0.13(4)	-0.51(3)
<i>D1112</i>	-0.0018(18)	-0.25(2)	-0.255(14)
<i>D1113</i>	0.0035(10)	0.051(7)	0.008(7)
<i>D1122</i>	-0.0023(13)	-0.183(11)	-0.255(14)
<i>D1123</i>	0.0018(5)	0.037(4)	0.004(3)
<i>D1133</i>	-0.0022(5)	-0.0071(14)	-0.006(3)
<i>D1222</i>	-0.002(2)	-0.164(11)	-0.255(14)
<i>D1223</i>	0.0011(4)	0.029(3)	-0.004(3)
<i>D1233</i>	-0.0011(2)	-0.0056(11)	-0.0030(15)
<i>D1333</i>	0.0010(3)	0.0006(5)	0
<i>D2222</i>	-0.0032(19)	-0.196(13)	-0.51(3)
<i>D2223</i>	0.0008(6)	0.032(3)	-0.008(7)
<i>D2233</i>	-0.0008(3)	-0.0042(10)	-0.006(3)
<i>D2333</i>	0.00049(15)	0.0006(5)	0
<i>D3333</i>	-0.0002(3)	0.0012(4)	0.003(2)

$^{\dagger}$  Third-order tensor elements  $C_{ijk}$  are multiplied by 103.

$^{\ddagger}$  Fourth-order tensor elements  $D_{ijkl}$  are multiplied by 104.

(EMP). Concentrations of major and minor elements were determined at an accelerating voltage of 20 kV and a beam current of 40 nA, with a 10 s counting time. For the WDS analyses, the following lines were used: S- $K\alpha$ , Fe- $K\alpha$ ,

Cu- $K\alpha$ , Zn- $K\alpha$ , As- $L\alpha$ , Se- $L\alpha$ , Ag- $L\alpha$ , Sb- $L\beta$ , Pb- $M\alpha$  and Bi- $M\beta$ . The standards employed were: native elements for Cu and Ag, galena for Pb, pyrite for Fe and S, synthetic  $Sb_2S_3$  for Sb, synthetic  $As_2S_3$  for As, synthetic  $Bi_2S_3$  for Bi,

TABLE 6. Main interatomic distances ( $\text{\AA}$ ) for the selected cupropolybasite crystal.

Sb	-S2	2.361(1)	Cu2-S	-S1	2.159(2)	Ag1/Cu1	-S2	2.415(2)
	-S2	2.361(1)		-S1	2.159(2)		-S2	2.415(2)
	-S2	2.361(1)		<Cu2-S>	2.159		-S4 $^{\ddagger}$	2.310(2)
<Sb-S>		2.361				<Ag1/Cu1-S>		2.380
Ag2	-S3	2.362(9)	Ag3	-S3	2.536(8)			
	-S1	2.419(9)		-S1	2.705(9)			
	-S2	2.799(9)		-S2	2.615(6)			
	-Cu2	2.733(8)		-Cu2	2.946(9)			

$^{\ddagger}$  the Ag1/Cu1-S4 distance corresponds to the most probable distance calculated from the modes (maxima) of  $jpdf$  (joint probability density function) maps.

synthetic ZnS for Zn, and synthetic PtSe<sub>2</sub> for Se. The crystal fragments were found to be homogeneous within analytical error. The average chemical compositions (8 analyses on different spots), together with the amounts (ranges) of each element, are reported in Table 7. On the basis of 29 atoms and according to the revised chemical formula obtained on the basis of the structural results (Bindi *et al.* 2006*b* for cupropearceite and this study for cupropolybasite), the chemical formulae for cupropearceite and for cupropolybasite can be written as [(Cu<sub>3.51</sub>Ag<sub>2.50</sub>Fe<sub>0.01</sub>)<sub>Σ6.02</sub>(As<sub>1.72</sub>Sb<sub>0.24</sub>)<sub>Σ1.96</sub>S<sub>7</sub>][Ag<sub>9</sub>CuS<sub>4</sub>] and [(Cu<sub>3.82</sub>Ag<sub>2.42</sub>Zn<sub>0.02</sub>Pb<sub>0.01</sub>)<sub>Σ6.27</sub>(Sb<sub>1.19</sub>As<sub>0.73</sub>)<sub>Σ1.92</sub>S<sub>7</sub>][Ag<sub>9</sub>CuS<sub>4</sub>], respectively.

**Structure description and discussion**

The crystal structures of cupropearceite and cupropolybasite (Fig. 1) consist of the stacking of [M<sub>6</sub>T<sub>2</sub>S<sub>7</sub>]<sup>2-</sup> (*A*) and [Ag<sub>9</sub>CuS<sub>4</sub>]<sup>2+</sup> (*B*) module layers (where *M* = Ag, Cu, and *T* = As, Sb) along

[001]. The (As,Sb) form isolated TS<sub>3</sub> pyramids which typically occur in sulphosalts; Cu replaces Ag in the only fully occupied *M* position of the *A* module layer and links two S atoms in a linear coordination in the *B* layer. Silver occupies sites with coordination ranging from quasi-linear to almost tetrahedral. Notably, in the *B* module layer, the Ag cations are distributed along 2D diffusion paths in a structure skeleton made of face-sharing tetrahedra around the Cu atom. The structural disorder observed in the *B* layer (2D diffusion paths) is strongly related to the fast ion-conduction character exhibited by the minerals of the pearceite-polybasite group (Bindi *et al.*, 2006*b*).

The crystal structure refinement of cupropearceite showed that the Ag1/Cu1 structural position of the *A* module is dominated by Cu. The Ag/Cu atoms in this position are triangularly coordinated by S atoms in a quasi-planar environment with a mean <Ag1/Cu1-S> distance of 2.390 Å. The same distance in the structure of cupropolybasite

TABLE 7. Electron microprobe analysis (EMPA) results (means, ranges and standard deviations in wt.% of elements) and atomic ratios (on the basis of 29 atoms) for cupropearceite and cupropolybasite.

	Wt.%	Range	σ	Atom	Atomic ratios
Cupropearceite (sample 2399/I)					
Ag	60.72	60.44–61.22	0.16	Ag	11.50
Cu	14.03	13.80–14.66	0.10	Cu	4.51
Bi	0.00	0.00–0.03	0.01	Bi	0.00
Pb	0.00	0.00–0.05	0.01	Pb	0.00
Zn	0.00	0.00–0.03	0.01	Zn	0.00
Fe	0.03	0.00–0.06	0.01	Fe	0.01
Sb	1.43	1.25–1.59	0.03	Sb	0.24
As	6.31	6.01–6.74	0.05	As	1.72
S	17.30	16.99–17.80	0.10	S	11.02
Se	0.00	0.00–0.02	0.01	Se	0.00
Total	99.82	98.96–100.68		Σatoms	29.00
Cupropolybasite (sample M12128)					
Ag	58.86	58.35–59.93	0.20	Ag	11.42
Cu	14.63	14.34–14.85	0.13	Cu	4.82
Bi	0.00	0.00–0.02	0.01	Bi	0.00
Pb	0.10	0.07–0.16	0.02	Pb	0.01
Zn	0.06	0.00–0.09	0.01	Zn	0.02
Fe	0.01	0.00–0.03	0.01	Fe	0.00
Sb	6.95	6.80–7.17	0.02	Sb	1.19
As	2.62	2.45–2.78	0.04	As	0.73
S	16.51	16.30–16.72	0.08	S	10.81
Se	0.01	0.00–0.03	0.01	Se	0.00
Total	99.75	99.23–100.73		Σatoms	29.00

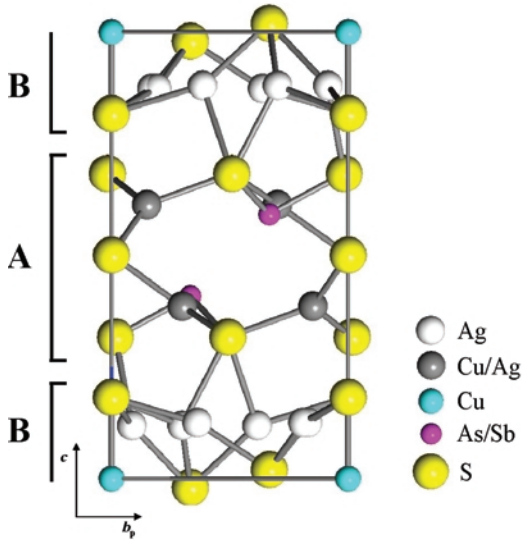


FIG. 1. Projection of the cupropearceite-*Tac* (cupropolybasite-*Tac*) structure along the  $a$  axis. The figure emphasizes the succession of the  $[(\text{Cu},\text{Ag})_6(\text{As},\text{Sb})_2\text{S}_7]^{2-}$   $A$  and  $[\text{Ag}_9\text{CuS}_4]^{2+}$   $B$  module layers.

is 2.380 Å (Table 6). 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 tetrahedrite,

$\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  (Pfitzner *et al.*, 1997), and synthetic  $\text{Cu}_{12.3}\text{Sb}_4\text{S}_{13}$  (Makovicky and Skinner, 1979) having Cu in a similar triangular environment, the following linear equation is obtained:  $\langle \text{Ag1/Cu1-S} \rangle$  (Å) =  $2.595(5) - 0.058(1) [\text{Cu-1}]_{\text{EMPA}}$  (Fig. 2). This indicates that if a mean bond distance smaller than 2.421 Å (calculated with  $[\text{Cu-1}]_{\text{EMPA}} = 3.00$  a.p.f.u.) is observed for the Ag1/Cu1 position, the mineral will be named cupropearceite or cupropolybasite depending on its As/Sb ratio. If structural data are lacking, a chemical criterion should be used to properly name a member. Provided that the name cupropearceite (or cupropolybasite) should be reserved for samples Cu-dominant in the Ag1/Cu1 structural site of the  $A$  layer, samples with  $\text{Cu} > 4.00$  a.p.f.u. ( $\text{Ag} < 12.00$  a.p.f.u.) should be named cupropearceite (or cupropolybasite), whereas the name pearceite (or polybasite) is for members with  $\text{Cu} < 4.00$  a.p.f.u. ( $\text{Ag} > 12.00$  a.p.f.u.). Similar considerations can be obtained from the data plotted in Fig. 3 where, to compare all the members belonging to the pearceite-polybasite group, the variation of the hexagonal subcell parameters (i.e.  $a \sim 7.5$  Å;  $c \sim 12$  Å) as a function of  $[\text{Cu-1}]_{\text{EMPA}}$  was considered. The equation obtained from the linear fit of the data (i.e.  $V_{\text{subcell}} (\text{Å}^3) = 595(1) - 12.0(8)[\text{Cu-1}]_{\text{EMPA}}$ ) allows a determination of the  $[\text{Cu-1}]_{\text{EMPA}}$  value directly by the unit-cell

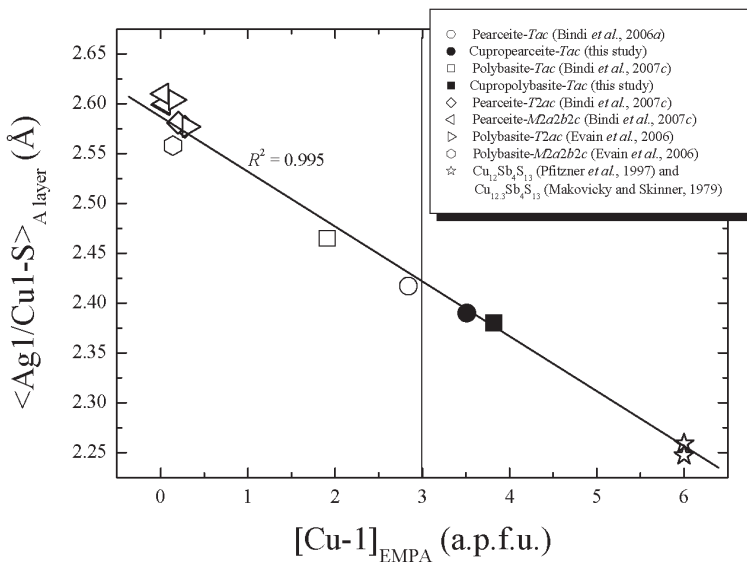


FIG. 2. Relationship between the  $\langle \text{Ag1/Cu1-S} \rangle$  distance (Å) and  $[\text{Cu-1}]_{\text{EMPA}}$  (a.p.f.u.) for the different members of the pearceite-polybasite group.



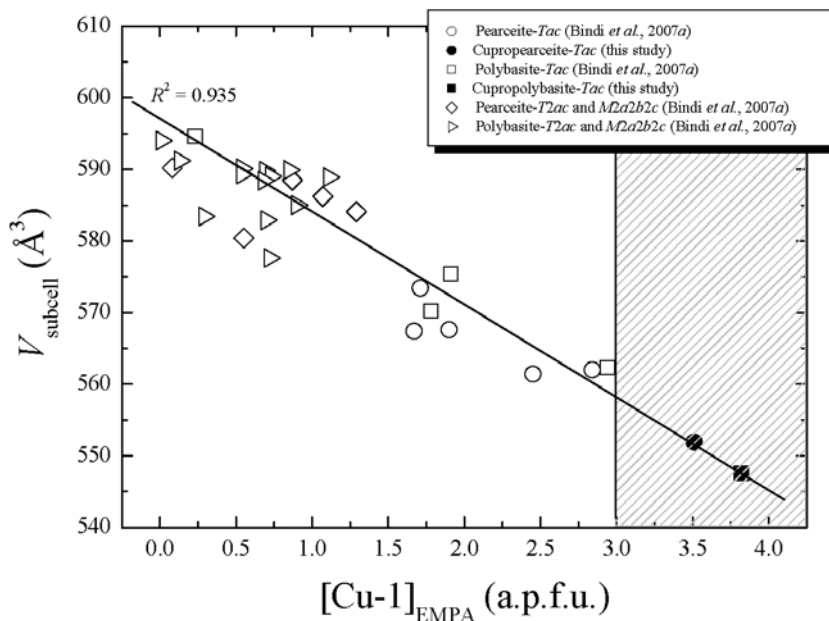


FIG. 3. Relationship between the unit-cell volume of the hexagonal subcell ( $\text{\AA}^3$ ) and  $[\text{Cu-1}]_{\text{EMPA}}$  (a.p.f.u.) for the different members of the pearceite-polybasite group. The dashed area indicates the field of cupropearceite and cupropolybasite.

parameters, which are easily obtained by a powder XRD investigation. It appears evident that when a mineral shows a  $V_{\text{subcell}} < 559 \text{ \AA}^3$  (calculated with  $[\text{Cu-1}]_{\text{EMPA}} = 3.00$  a.p.f.u. in the equation above), it should be named cupropearceite or cupropolybasite depending on its As/Sb ratio. It is worth noting that Petruk *et al.* (1971) reported an unusually Cu-rich polybasite from the Foster mine, Ontario, Canada. The mineral studied by Petruk *et al.* shows  $\text{Sb} > \text{As}$  and a Cu content of 5.63 a.p.f.u. If we write the chemical formula according to the criteria introduced by Bindi *et al.* (2007a), we obtain  $[(\text{Cu}_{4.63}\text{Ag}_{1.37})_{\Sigma 6.00}(\text{Sb}_{1.33}\text{As}_{0.68})_{\Sigma 2.01}\text{S}_7][\text{Ag}_9\text{CuS}_4]$ . This means that the Cu-rich polybasite from the Foster mine should be classified as cupropolybasite. Moreover, Petruk *et al.* (1971) carried out a powder XRD investigation on the mineral and found that the polybasite from the Foster mine shows the 111 hexagonal unit-cell type ( $a$  7.33;  $c$  11.77  $\text{\AA}$ ); hence, the full name for the polytype is cupropolybasite-*Tac*. Calculation of the unit-cell volume of the mineral studied by Petruk *et al.* (1971), shows a  $V_{\text{subcell}} = 547.7 \text{ \AA}^3$ . This value is in fairly good agreement with that obtained from the equation proposed in this study (i.e.  $\sim 540 \text{ \AA}^3$ ).

### Concluding remarks

The complex impedance spectroscopy (CIS) results indicated cupropearceite to be the most conductive compound among the members of the pearceite-polybasite group (Bindi *et al.*, 2006b). This means that Cu plays a crucial role in the stabilization of a disordered structure, the greater the Cu content, the greater the structural disorder. It appears evident that cupropearceite and cupropolybasite could be very useful for important technological applications. If these minerals are also fast ionic conductors, they could find applications in silver photography as sensitizers or in optics and microelectronics as rewritable storage media.

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