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The pearceite-polybasite group of minerals: Crystal chemistry and new nomenclature rules

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Abstract

The present paper reports changes to the existing nomenclature for minerals belonging to the pearceite-polybasite group. Thirty-one samples of minerals in this group from different localities, with variable chemical composition, and showing the 111, 221, and 222 unit-cell types, were studied by means of X-ray single-crystal diffraction and electron microprobe. The unit-cell parameters were modeled using a multiple regression method as a function of the Ag, Sb, and Se contents. The determination of the crystal structures for all the members of the group permits them to be considered as a family of polytypes and for all members to be named pearceite or polybasite. The main reason for doubling the unit-cell parameters is linked to the ordering of silver. The distinction between pearceite and polybasite is easily done with an electron microprobe analysis (As/Sb ratio). A hyphenated italic suffix indicating the crystal system and the cell-type symbol should be added, if crystallographic data are available. Given this designation, the old names antimonpearceite and arsenpolybasite are abandoned here and the old names pearceite and polybasite, previously defined on a structural basis (i.e., 111 and 222), are redefined on a chemical basis. The old name pearceite will be replaced by pearceite-*Tac*, antimonpearceite by polybasite-*Tac*, arsenpolybasite-221 by pearceite-*T*2*ac*, arsenpolybasite-222 by pearceite-*M*2*a*2*b*2*c*, polybasite-221 by polybasite-*T*2*ac*, and polybasite-222 by polybasite-*M*2*a*2*b*2*c*. Since all polytypes are composed of two different layers stacked along [001]: layer A, with general composition $[(Ag,Cu)_6(As,Sb)_2S_7]^{2-}$, and layer B, with general composition $[Ag_9CuS_4]^{2+}$, the chemical formulae of pearceite and polybasite should be written as $[Ag_9CuS_4][(Ag,Cu)_6(As,Sb)_2S_7]$ and $[Ag_9CuS_4][(Ag,Cu)_6(Sb,As)_2S_7]$, respectively, instead of $(Ag,Cu)_{16}(As,Sb)_2S_{11}$ and $(Ag,Cu)_{16}(Sb,As)_2S_{11}$, as is currently accepted. The new nomenclature rules were approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

Keywords: Pearceite-polybasite, nomenclature rules, crystal chemistry, X-ray data, chemical composition

Introduction

Sulfosalts belonging to the pearceite-polybasite group are relatively common in nature and were originally discovered in the 19th century (pearceite, Penfield 1896; polybasite, Rose 1829), while the new names antimonpearceite and arsenpolybasite were introduced by Frondel in 1963. The names pearceite and polybasite are grandfathered whereas the names antimonpearceite and arsenpolybasite were approved by the IMA Commission (see report of the IMA-CNMMN, 1967). According to Frondel (1963), these four minerals can be divided on structural basis into two series: the first one, formed by pearceite $(Ag,Cu)_{16}(As,Sb)_2S_{11}$ and antimonpearceite $(Ag,Cu)_{16}(Sb,As)_2S_{11}$, characterized by "small" unit cell (labeled 111) and high Cu content, and, the second one, formed by polybasite $(Ag,Cu)_{16}(Sb,As)_2S_{11}$ and arsenpolybasite $(Ag,Cu)_{16}(As,Sb)_2S_{11}$, with double cell parameters (labeled 222) and low Cu content. The chemical and crystallographic details of the four minerals are given in Table 1. Soon after Frondel's (1963) study, Harris et al. (1965) pointed out the existence of an intermediate type of unit cell labeled 221 for a sample of polybasite from the Las Chispas deposit, Sonora, Mexico. They observed that the intermediate cell 221 was present in some areas of the sample analyzed and was closely associated with the small cell 111, which is present in other seemingly identical areas of the same sample. The same intermediate type of unit cell (i.e., 221) was subsequently reported by Edenharter et al. (1971) and by Minčeva-Stefanova et al. (1979). Phase relations for the system $(Ag,Cu)_{16}(As,Sb)_2S_{11}$–$(Ag,Cu)_{16}(Sb,As)_2S_{11}$ were investigated experimentally by Hall (1967) who hypothesized that the variation of Cu content in different samples might play a key role in favoring chemical order-disorder phenomena and, therefore, to be the driving force in stabilizing the different unit cells.

From a chemical standpoint, the members of both series are generally pure containing only minor amounts of Bi, Pb, Zn, and Fe. However, Harris et al. (1965) reported the occurrence of an antimonpearceite sample from the San Carlos mine, Guanajuato, Mexico, containing up to 8.7 wt% Se but limited their study to the determination of the unit-cell parameters and chemical characterization only.

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Table 1. List of minerals belonging to the pearceite-polybasite group

Name	Chemical formula	Unit-cell parameters		Range of Cu content
		monoclinic setting	hexagonal setting	
pearceite	$(Ag,Cu)_{16}(As,Sb)_2S_{11}$	$a \approx 12.59$, $b \approx 7.27$, $c \approx 11.81$ Å, $\beta = 90.0°$	$a \approx 7.27$, $c \approx 11.81$ Å	5.5–19.7 wt%
antimonpearceite	$(Ag,Cu)_{16}(Sb,As)_2S_{11}$	$a \approx 12.81$, $b \approx 7.41$, $c \approx 11.91$ Å, $\beta = 90.0°$	$a \approx 7.41$, $c \approx 11.91$ Å	7.9–18.2 wt%
arsenpolybasite	$(Ag,Cu)_{16}(As,Sb)_2S_{11}$	$a \approx 26.08$, $b \approx 15.04$, $c \approx 23.84$ Å, $\beta = 90.0°$	$a \approx 15.04$, $c \approx 23.84$ Å	3.0–5.2 wt%
polybasite	$(Ag,Cu)_{16}(Sb,As)_2S_{11}$	$a \approx 26.17$, $b \approx 15.11$, $c \approx 23.89$ Å, $\beta = 90.0°$	$a \approx 15.11$, $c \approx 23.89$ Å	3.1–7.6 wt%

Notes: The transformation matrix from monoclinic to the trigonal unit cell is [½–½0, 010, 001]. The unit-cell values are taken from Strunz and Nickel (2001). The ranges of the copper content are taken from Hall (1967).

Several authors (Peacock and Berry 1947; Frondel 1963; Harris et al. 1965; Hall 1967; Sugaki et al. 1983) considered the members of the pearceite-polybasite group as monoclinic, space group $C2/m$, although dimensionally pseudo-hexagonal. On the other hand, Edenharter et al. (1971) determined the Laue symmetry as trigonal $\bar{3}m$. Despite the fact that these minerals are relatively common in nature, their crystal structure has yet to be characterized.

Harris et al. (1965), Minčeva-Stefanova (1979), and Guinier et al. (1984) have all pointed out problems associated with the classification scheme of Frondel (1963). Harris et al. (1965), for example, noted that the doubled dimensions, manifested as weak intermediate layer lines on rotation photographs, represented less-than-fundamental differences; the basic structural unit and the external crystal form are the same for all the members of the pearceite-polybasite group. Therefore, Harris et al. (1965) proposed to maintain the original classification with the addition of a symbol to signify the type of the cell. Pearceite (1–1–1) has As > Sb and unit-cell parameters of the basic structural unit (i.e., $a \sim 13$, $b \sim 7.5$, $c \sim 12$ Å, $\beta \sim 90°$), polybasite (2–2–2) has Sb > As and unit-cell parameters doubled with respect to the basic structural unit (i.e., $a \sim 26$, $b \sim 15$, $c \sim 24$ Å, $\beta \sim 90°$), whereas polybasite (2–2–1) has a and b doubled with respect to the basic structural unit (i.e., $a \sim 26$, $b \sim 15$, $c \sim 12$ Å, $\beta \sim 90°$).

More recently, Guinier et al. (1984), in a report for the International Union of Crystallography dealing with the nomenclature of polytype structures, proposed a new polytype symbolism for minerals belonging to the pearceite-polybasite group. Since these minerals had been previously described as exhibiting a strongly pseudohexagonal symmetry, Guinier et al. (1984) suggested adding a hyphenated italic symbol, such as ψ*H*, where the Greek letter ψ is the abbreviation of pseudo-, to the root names (i.e., pearceite and polybasite). Thus, pearceite would be written as pearceite-ψ*Habc* and arsenpolybasite as pearceite-ψ*H*2*a*2*b*2*c*.

Despite Guinier et al.'s (1984) proposal, systematic mineralogy books such as Strunz and Nickel (2001) and Mandarino and Back (2004) still maintain the classification scheme of Frondel (1963) for minerals of the pearceite-polybasite group. This is, in large part, due to the fact that no complete crystal structure characterization of this group has yet to be published in the literature.

In the course of a study dealing with the characterization of structurally complex silver-bearing minerals, we analyzed 31 samples belonging to the pearceite-polybasite group and solved the crystal structure for all of its members. On the basis of information gained from this characterization new nomenclature rules for this group of minerals are proposed.

The current study complements studies of the crystal structural data that have been published elsewhere (Bindi et al. 2006a, 2006b; Evain et al. 2006a, 2006b).

Experimental methods

A list of the samples investigated here together with their provenance and the unit-cell type (expressed, for clarity, in hexagonal setting for all the members) is given in Table 2. We studied six samples of pearceite, five samples of antimonpearceite, five samples of arsenpolybasite, and 15 samples of polybasite. Among the specimens of arsenpolybasite and polybasite we found several with the 221 unit-cell type (Table 2). All crystals were analyzed by X-ray single-crystal diffraction and with an electron microprobe.

X-ray single-crystal diffraction

The diffraction quality of the single crystals was initially checked by means of an Enraf-Nonius CAD4 single-crystal diffractometer equipped with a conventional point detector. Then, the unit-cell type was carefully investigated by means of an Oxford Diffraction "Xcalibur 2" single-crystal diffractometer (enhanced X-ray source, X-ray radiation Mo$K\alpha$, $\lambda = 0.71073$ Å) fitted with a Sapphire 2 CCD detector. A total of 100 frames of data were collected at room temperature as 3 sets of omega runs with an exposure time of 100 s per frame and a frame width of 0.75°. Data frames were processed using the *CrysAlis* software package running on the Xcalibur 2 control PC. For samples 45895/G (pearceite), 171541 (antimonpearceite), 2453/I (Se-rich antimonpearceite), 17002/38 (polybasite-222), 2503/I (polybasite-221), AW634 (arsenpolybasite-222), and AB6829 (arsenpolybasite-221), a complete collection of X-ray data was obtained.

Electron microprobe analyses

Qualitative chemical analysis using energy dispersive spectrometry, performed on the crystal fragments used for the structural study, did not indicate the presence of elements ($Z > 9$) other than S, Fe, Cu, Zn, As, Se, Ag, Sb, Te, Au, Pb, and Bi. Quantitative chemical compositions were then determined using wavelength dispersive analysis (WDS) by means of a JEOL JXA-8200 electron microprobe. Concentrations of major and minor elements were determined at an accelerating voltage of 20 kV and a beam current of 40 nA, with 10 s as the 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$L\beta$, Te$L\alpha$, Au$M\alpha$, Pb$M\alpha$, Bi$M\beta$. The standards employed were: native elements for Cu, Ag, Au, and Te, 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, synthetic ZnS for Zn, and synthetic $PtSe_2$ for Se. The crystal fragments were found to be homogeneous within analytical error. The average chemical compositions (four to six analyses on each grain) are reported in Table 3. The chemical formulae were calculated on the basis of 29 atoms.

Results

Unit-cell parameters

In Figure 1, the variation in unit-cell parameters is reported as a function of the at% of Ag in the (Ag,Cu) position (Figs. 1a, 1c, and 1e) and of the at% of Sb in the (Sb, As) position (Figs. 1b, 1d, and 1f). To compare samples, the variation of the subcell parameters (i.e., $a \sim 7.5$, $c \sim 12$ Å) was considered. It appears evident that both the a and c parameters are strongly influenced by the Ag content whereas the influence of the Sb content is very minor. However, to take into account all the effects of any chemical substitutions in these minerals (i.e., Ag ↔ Cu, Sb ↔ As, S ↔ Se), a multiple regression model was conducted. The following equations were obtained:

TABLE 2. Location, unit-cell parameters, old name, new name, and unit-cell type of samples studied

	Sample	Provenance	Unit-cell parameters (Å)	Old names	New names	Unit-cell type
(A)	1652/2	Montana, U.S.A.	a = 7.408(1) c = 11.939(1)	pearceite	pearceite-*Tac*	1:1:1
(B)	2399/I	Sarbay, Kazakhstan	a = 7.306(1) c = 11.860(1)	pearceite	pearceite-*Tac*	1:1:1
(B)	2260/I	Clara Mine, Schwarzwald, Germany	a = 7.418(1) c = 11.910(1)	pearceite	pearceite-*Tac*	1:1:1
(B)	45895/G	Clara Mine, Schwarzwald, Germany	a = 7.3876(4) c = 11.8882(7)	pearceite	pearceite-*Tac*	1:1:1
(C)	D21651	Silver King, Australia	a = 7.382(1) c = 11.896(2)	pearceite	pearceite-*Tac*	1:1:1
(D)	M49352	Clara Mine, Germany	a = 7.442(2) c = 11.954(2)	pearceite	pearceite-*Tac*	1:1:1
(A)	1649/5	Sarrabus, Sardinia, Italy	a = 7.455(1) c = 11.847(1)	antimonpearceite	polybasite-*Tac*	1:1:1
(B)	17004/80	Pachuca, Hidalgo, Mexico	a = 7.569(1) c = 11.984(1)	antimonpearceite	polybasite-*Tac*	1:1:1
(B)	2453/I	De Lamar Mine, Idaho, U.S.A.	a = 7.598(1) c = 12.059(1)	antimonpearceite	polybasite-*Tac*	1:1:1
(D)	M32151	Silback Premier, Canada	a = 7.399(2) c = 11.860(3)	antimonpearceite	polybasite-*Tac*	1:1:1
(E)	171541	Eagle Mine, Colorado, U.S.A.	a = 7.478(1) c = 11.881(2)	antimonpearceite	polybasite-*Tac*	1:1:1
(F)	AB6829	Freiberg, Germany	a = 14.9556(9) c = 11.9886(6)	arsenpolybasite	pearceite-*T2ac*	2:2:1
(F)	L2283	Quespisizd, Perù	a = 15.105(2) c = 11.946(2)	arsenpolybasite	pearceite-*T2ac*	2:2:1
(F)	K1422	Mangani mine, Sumatra	a = 15.045(7) c = 12.010(9)	arsenpolybasite	pearceite-*T2ac*	2:2:1
(F)	AW634	St.Joachim Sthal, Bohemia	a = 26.007(8) b = 15.015(6) c = 24.02(1) β = 90.02(5)	arsenpolybasite	pearceite-*M2a2b2c*	2:2:2
(F)	L4250	Sadomine, Japan	a = 26.00(4) b = 15.01(6) c = 23.95(9) β = 90.01(5)	arsenpolybasite	pearceite-*M2a2b2c*	2:2:2
(B)	2503/I	Zacatecas, Mexico	a = 15.123(1) c = 11.945(1)	polybasite	polybasite-*T2ac*	2:2:1
(B)	17003/38	Pachuca, Hidalgo, Mexico	a = 15.102(1) c = 11.951(1)	polybasite	polybasite-*T2ac*	2:2:1
(C)	D4356	Chile	a = 15.013(6) c = 11.946(5)	polybasite	polybasite-*T2ac*	2:2:1
(D)	M34095	Double Rainbow, U.S.A.	a = 15.045(2) c = 11.939(1)	polybasite	polybasite-*T2ac*	2:2:1
(D)	M44605	Junction Mine, Australia	a = 15.111(1) c = 11.920(1)	polybasite	polybasite-*T2ac*	2:2:1
(A)	1651/5	Colorado, U.S.A.	a = 15.107(1) c = 11.938(1)	polybasite	polybasite-*T2ac*	2:2:1
(A)	1661/7	Sonora, Mexico	a = 26.197(2) b = 15.125(1) c = 23.877(1) β = 90.03(1)	polybasite	polybasite-*M2a2b2c*	2:2:2
(A)	6693/10	Freiberg, Germany	a = 26.090(2) b = 15.063(1) c = 23.979(1) β = 90.00(2)	polybasite	polybasite-*M2a2b2c*	2:2:2
(B)	17000/38	Pachuca, Hidalgo, Mexico	a = 25.925(1) b = 14.968(1) c = 23.817(1) β = 90.04(2)	polybasite	polybasite-*M2a2b2c*	2:2:2
(B)	17001/38	Pachuca, Hidalgo, Mexico	a = 26.116(3) b = 15.078(1) c = 23.970(1) β = 90.05(2)	polybasite	polybasite-*M2a2b2c*	2:2:2
(B)	17002/38	Pachuca, Hidalgo, Mexico	a = 26.130(2) b = 15.086(1) c = 23.911(1) β = 90.01(2)	polybasite	polybasite-*M2a2b2c*	2:2:2
(A)	1650/6	Las Chispas, Mexico	a = 26.220(2) b = 15.138(1) c = 23.946(1) β = 90.06(2)	polybasite	polybasite-*M2a2b2c*	2:2:2
(F)	AA6029	Lasphe, Germany	a = 26.119(4) b = 15.080(1) c = 23.940(3) β = 90.01(3)	polybasite	polybasite-*M2a2b2c*	2:2:2
(F)	AK831	Schemnitz, Slovak Republic	a = 26.015(8) b = 15.020(2) c = 23.888(9) β = 90.05(2)	polybasite	polybasite-*M2a2b2c*	2:2:2
(C)	D20293	Durango, Mexico	a = 26.114(5) b = 15.077(1) c = 23.902(4) β = 90.03(2)	polybasite	polybasite-*M2a2b2c*	2:2:2

Note: The letters in the first column indicate the Institutions that provided us with pearceite-polybasite samples; in detail: (A) Dipartimento Geomineralogico, Università di Bari, Italy; (B) Museo di Storia Naturale, Università di Firenze, Italy; (C) Australian Museum, Sydney, Australia; (D) Department of Mineralogy and Petrology, Museum Victoria, Australia; (E) Smithsonian Institution, Washington, D.C.; (F) Naturhistorisches Museum of Vienna, Austria.

$$a_{pred} = 6.67(9) + 0.009(1)Ag(\%) + 0.0005(2)Sb(\%) + 0.002(1)Se(\%)$$

$$c_{pred} = 11.35(5) + 0.0073(6)Ag(\%) - 0.0007(1)Sb(\%) + 0.0045(8)Se(\%)$$

$$V_{pred} = 426(15) + 1.8(2)Ag(\%) + 0.05(3)Sb(\%) + 0.5(2)Se(\%)$$

The good agreement between the observed and predicted unit-cell parameters of the hexagonal subcell is shown in Figure 2.

Crystal structure of the members having the 111 unit-cell type

The careful structural studies performed on minerals of the pearceite-polybasite group suggest that the reason for the lack of structural information for these complex minerals is probably related to the difficulty in describing the Ag or Cu electron density, which is influenced by the strong ionic conductivity of these minerals (Bindi et al. 2006c). It was shown that for such a description, a non-harmonic model based upon a development of the atomic displacement factor is the best approach to solving the structure (Kuhs and Heger 1979; Boucher et al. 1992, 1993; Evain et al. 1998).

The crystal structures of members of the pearceite-polybasite group that possess the 111 unit-cell type [i.e., pearceite, sample 45895/G, Bindi et al. (2006a), and antimonpearceite, sample 171541, Bindi et al. (2006b)] have been solved and refined at 300 K in the space group type $P\bar{3}m1$. The refinement of the structure leads to residual factors of R = 0.0464 (pearceite) and R = 0.0405 (antimonpearceite). Basically, their crystal structure (Fig. 3) can be described as a regular alternation of two types of layers stacked along [001]: layer "A" with the general composition $[(Ag,Cu)_6(As,Sb)_2S_7]^{2-}$, and layer "B" with the general composition $(Ag_9CuS_4)^{2+}$. In this structure, atoms of As and Sb form isolated $(As,Sb)S_3$ pyramids that are common in sulfosalts, copper cations link two sulfur atoms in a linear coordination, and silver cations are found in a fully occupied position and in various sites corresponding to the most pronounced probability density function locations of diffusion-like paths. These positions correspond to low coordination (2, 3, and 4) sites, in agreement with the preference of silver for such environments. The distribution of d^{10} silver ions was deduced by means of a combination of a Gram-Charlier development of the atomic displacement factors

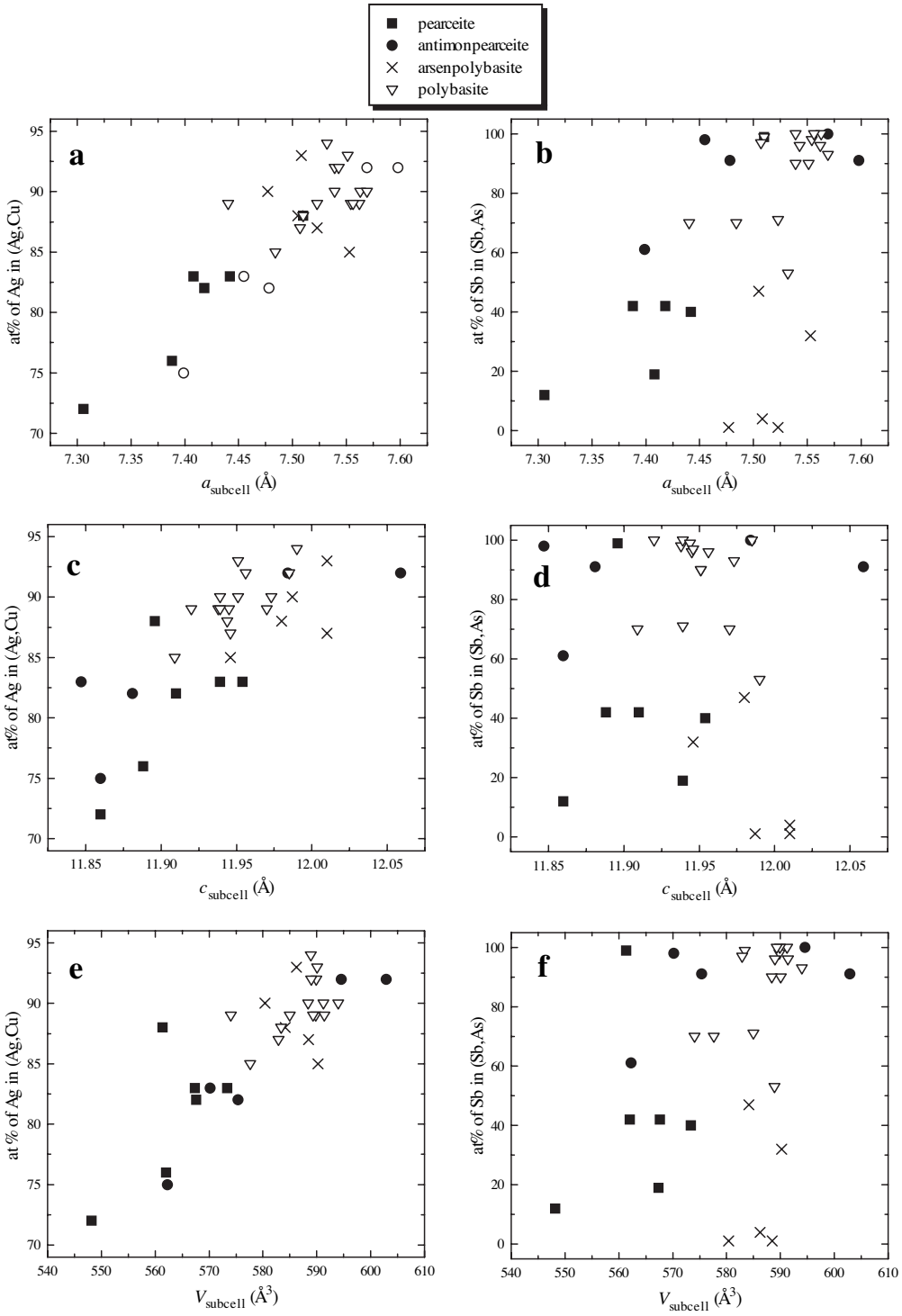

FIGURE 1. Relationship between the at% of Ag in (Ag,Cu) and the unit-cell parameters of the hexagonal subcell (**a**, **c**, and **e**), and between the at% of Sb in (Sb,As) and the unit-cell parameters of the hexagonal subcell (**b**, **d**, and **f**).

and a split-atom model.

We also refined the crystal structure of a Se-rich variety of antimonpearceite to $R = 0.0489$ (sample 2453/I; Evain et al. 2006a). At room temperature, it shows the same structural arrangement found in pure antimonpearceite but with one Se atom ordered in a specific structural position. Based on the nomenclature rules we have introduced for Se-free members of the pearceite-polybasite group (see below), the chemical formula of the Se-rich antimonpearceite analyzed here would be written as $[(Ag,Cu)_6(Sb,As)_2(S,Se)_7][Ag_9Cu(S,Se)_2Se_2]$.

TABLE 3. Electron microprobe analyses (in wt% of elements) and atomic ratios (calculated on the basis of 29 atoms) of the selected crystals

	1652/2	2399/I	2260/I	45895/G	D21651	M49352	1649/5	17004/80	2453/I	M32151	171541	AB6829	L2283
Ag	67.42	60.72	66.18	62.34	64.41	66.75	66.24	67.90	66.17	61.85	64.64	72.64	68.40
Cu	7.93	14.03	8.64	11.60	10.43	8.02	7.92	3.46	3.19	11.74	8.46	4.53	6.77
Bi	0.10	0.00	0.39	0.00	0.00	0.00	0.00	0.09	0.09	0.10	0.00	0.19	0.10
Pb	0.10	0.00	0.00	0.00	0.00	0.10	0.00	0.09	0.09	0.10	0.00	0.00	0.19
Zn	0.06	0.00	0.06	0.00	0.00	0.06	0.00	0.03	0.03	0.06	0.03	0.03	0.03
Fe	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.02	0.07	0.00	0.03	0.00	0.00
Au	n.a.	n.a.	n.a.	n.a.	0.00	0.00	n.a.	n.a.	n.a.	0.00	0.00	0.09	0.00
Sb	1.94	1.43	4.56	4.82	3.53	4.25	10.21	10.93	9.47	6.51	9.64	0.06	3.29
As	5.26	6.31	3.86	4.19	4.55	3.87	0.13	0.00	0.60	2.53	0.59	6.06	4.39
S	16.61	17.30	16.60	16.77	16.96	16.55	15.28	15.44	11.36	16.45	16.23	16.15	16.68
Se	0.00	0.00	0.00	0.00	0.00	0.04	0.00	2.03	8.42	0.00	0.00	0.04	0.04
Te	n.a.	n.a.	n.a.	n.a.	0.00	0.06	n.a.	n.a.	n.a.	0.00	0.06	0.06	0.12
Total	99.42	99.82	100.29	99.72	99.88	99.70	99.78	99.99	99.49	99.34	99.68	99.85	100.01
Ag	13.37	11.50	13.09	12.15	12.52	13.29	13.69	14.23	14.67	12.22	13.10	14.64	13.63
Cu	2.67	4.51	2.90	3.84	3.45	2.71	2.78	1.23	1.20	3.94	2.91	1.56	2.29
Bi	0.01	0.00	0.04	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.02	0.01
Pb	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.00	0.00	0.02
Zn	0.02	0.00	0.02	0.00	0.00	0.02	0.00	0.01	0.01	0.02	0.01	0.01	0.01
Fe	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.00	0.01	0.00	0.00
Au	/	/	/	/	0.00	0.00	/	/	/	0.00	0.00	0.01	0.00
Sb	0.34	0.24	0.80	0.83	0.62	0.75	1.87	2.03	1.86	1.14	1.73	0.01	0.58
As	1.50	1.72	1.10	1.18	1.28	1.11	0.04	0.00	0.19	0.72	0.17	1.77	1.26
S	11.08	11.02	11.05	11.00	11.13	11.09	10.62	10.89	8.47	10.94	11.06	10.96	11.17
Se	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.58	2.55	0.00	0.00	0.01	0.01
Te	/	/	/	/	0.00	0.01	/	/	/	0.00	0.01	0.01	0.02
	K1422	AW634	L4250	2503/I	17003/38	D4356	M34095	M44605	1651/5	1661/7	6693/10	17000/38	17001/38
Ag	69.68	72.84	69.25	68.15	70.74	67.88	68.51	67.99	67.94	68.63	71.91	66.68	69.95
Cu	6.11	3.16	5.36	4.76	3.16	6.03	4.93	5.24	4.90	4.30	2.88	6.98	3.52
Bi	0.10	0.10	0.10	0.09	0.00	0.00	0.09	0.09	0.09	0.00	0.09	0.00	0.09
Pb	0.10	0.10	0.00	0.09	0.00	0.09	0.09	0.00	0.00	0.00	0.09	0.00	0.09
Zn	0.00	0.00	0.00	0.00	0.06	0.00	0.09	0.00	0.09	0.03	0.03	0.00	0.03
Fe	0.00	0.03	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.03	0.00
Au	0.00	0.09	0.00	n.a.	n.a.	0.00	0.09	0.00	n.a.	n.a.	n.a.	n.a.	n.a.
Sb	0.06	0.45	4.90	10.73	9.56	9.59	7.20	10.69	11.01	10.76	5.84	7.46	11.22
As	6.38	5.99	3.38	0.27	0.66	0.20	1.83	0.00	0.13	0.00	3.16	2.00	0.00
S	16.66	16.46	15.88	15.29	15.37	15.96	16.24	15.71	15.73	15.31	15.91	16.02	14.33
Se	0.00	0.00	0.04	0.56	0.00	0.00	0.00	0.00	0.00	0.38	0.00	0.00	0.89
Te	0.00	0.18	0.23	n.a.	n.a.	0.12	0.17	0.06	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.09	99.40	99.14	99.94	99.55	99.87	99.29	99.78	99.89	99.41	99.91	99.17	100.12
Ag	13.89	14.77	14.22	14.27	14.94	13.98	14.08	14.15	14.14	14.47	14.87	13.62	14.98
Cu	2.07	1.08	1.87	1.69	1.13	2.11	1.72	1.85	1.73	1.54	1.01	2.42	1.28
Bi	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.01
Pb	0.01	0.01	0.00	0.03	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.01
Zn	0.00	0.00	0.00	0.00	0.02	0.00	0.03	0.00	0.03	0.01	0.01	0.00	0.01
Fe	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.01	0.00
Au	0.00	0.01	0.00	/	/	0.00	0.01	0.00	/	/	/	/	/
Sb	0.01	0.09	0.89	1.99	1.79	1.76	1.32	1.98	2.02	2.01	1.07	1.35	2.13
As	1.84	1.76	1.00	0.08	0.20	0.06	0.54	0.00	0.04	0.00	0.94	0.59	0.00
S	11.17	11.23	10.96	10.77	10.92	11.06	11.23	11.00	11.02	10.86	11.08	11.01	10.32
Se	0.00	0.00	0.01	0.16	0.00	0.00	0.00	0.00	0.00	0.11	0.00	0.00	0.26
Te	0.00	0.03	0.04	/	/	0.02	0.03	0.01	/	/	/	/	/

Note: n.a. means not analyzed.

continued on next page

Using our approach, the name of the Se-rich mineral would be selenopolybasite-*Tac*.

Crystal structure of the members having the 221 unit-cell type

The crystal structures of members of the pearceite-polybasite group that possess the 221 unit-cell type [i.e., arsenpolybasite-221, sample AB6829, Bindi et al. (2006b), and polybasite-221, sample 2503/I, Evain et al. (2006b)] have been solved and refined in the space group type *P*321, with twinning [first-degree twin, $\bar{3}$'2 / m'1 polychromatic point group, (Nespolo 2004 and references therein)]. At the beginning, the data collections (full diffraction sphere) were carried out at room temperature. In the *P*321 space group type, the refinements smoothly converged toward residual $R \approx 0.07$ values (for both arsenpolybasite-221 and polybasite-221), however, large positive residuals (up to 4 $e^-/Å^3$) were observed almost on top of all heavy atoms of the $[(Ag,Cu)_6Sb_2S_7]^{2-}$ A pseudo layer and in the vicinity of Ag atoms of the $[Ag_9CuS_4]^{2+}$ B pseudo layer. These residuals could be taken into account by introducing a stacking fault, that is, the presence of a minor component (ca. 10%) related to the cell content by an inversion center (introduced in Jana2000 with rigid bodies), but not by the introduction of an inversion twin law. However, although without any significant residuals left in the difference Fourier synthesis maps, the correlations were still very high and prevented convergence of the refinement (even with a very small damping factor). New data collections were then performed on the same crystals and the same diffractometer at 120 K. The refinements largely improved with a residual R value of ≈0.04 and without the presence of significant positive residuals in the difference Fourier synthesis. The refinement of the structure leads

TABLE 3.—*Continued*

	17002/38	1650/6	AA6029	AK831	D20293
Ag	69.22	68.93	69.48	68.17	69.71
Cu	3.63	4.71	4.87	5.41	4.39
Bi	0.10	0.09	0.09	0.00	0.19
Pb	0.09	0.00	0.09	0.09	0.09
Zn	0.00	0.00	0.00	0.03	0.00
Fe	0.00	0.00	0.00	0.00	0.05
Au	n.a.	0.00	0.00	0.00	0.00
Sb	10.70	9.14	7.30	9.87	9.29
As	0.30	0.43	1.88	0.04	0.60
S	15.82	15.27	16.05	15.97	16.01
Se	0.00	0.77	0.04	0.00	0.00
Te	n.a.	0.06	0.06	0.00	0.06
Total	99.86	99.40	99.86	99.58	100.39
Ag	14.48	14.47	14.28	14.12	14.40
Cu	1.29	1.68	1.70	1.90	1.54
Bi	0.01	0.01	0.01	0.00	0.02
Pb	0.01	0.00	0.01	0.01	0.01
Zn	0.00	0.00	0.00	0.01	0.00
Fe	0.00	0.00	0.00	0.00	0.02
Au	/	0.00	0.00	0.00	0.00
Sb	1.98	1.70	1.33	1.81	1.70
As	0.09	0.13	0.56	0.02	0.18
S	11.14	10.78	11.09	11.13	11.12
Se	0.00	0.22	0.01	0.00	0.00
Te	/	0.01	0.01	0.00	0.01

Note: n.a. means not analyzed.

to residual factors of $R = 0.0531$ (arsenpolybasite-221) and $R = 0.0359$ (polybasite-221). The structure of the 221 members is obtained from the polybasite-222 structure (see below) by selecting half its cell content along the **c** axis, that is either the A-B (or A'-B') double module layer or the A/2-B-A'/2 (or A'/2-B'-A/2) double module layer, since A and A' approximately correspond to each other by a ½ translation along the **c** axis (Fig. 4). The selected double module layer approximately fulfills a trigonal symmetry, space group type *P*321, except for one sulfur atom that appears as disordered (out of the threefold axis) in the 221-structure. The coordination of the atoms is very similar to that for members having the 111 unit-cell type. The reason for doubling the *a* parameter is linked to the ordering of silver (Fig. 4).

Crystal structure of the members having the 222 unit-cell type

The crystal structures of members of the pearceite-polybasite group that possess the 222 unit-cell type [i.e., arsenpolybasite-222, sample AW634, Bindi et al. (2006b), and polybasite-222, sample 17002/38, Evain et al. (2006b)] were solved and refined at 300 K in the space group type *C*2/*c*, with a second-degree twin with the polychromatic point group:

$$K_{WB}^{(p)} = \left(\frac{6^{(6)}}{m^{(2)}} \frac{2^{(2,2)}}{m^{(2,2)}} \frac{2^{(2)}}{m^{(2)}} \right)^{(6)}$$

(Nespolo 2004 and references therein). The refinement of the structure leads to residual factors of $R = 0.0700$ (arsenpolybasite-222) and $R = 0.0500$ (polybasite-222). The structure of the 222 members (Fig. 5) can be described as a succession along the **c** axis of two module layers: the $[(Ag,Cu)_6Sb_2S_7]^{2-}$ A (or A') module layer and the $[Ag_9CuS_4]^{2+}$ B (or B') module layer (A/B and A'/B' being related by a *c* glide mirror symmetry operation). The coordination of the atoms is very similar to that for members having the 111 unit-cell type. The reason for doubling the unit-cell parameters is linked to the ordering of silver (Fig. 5).

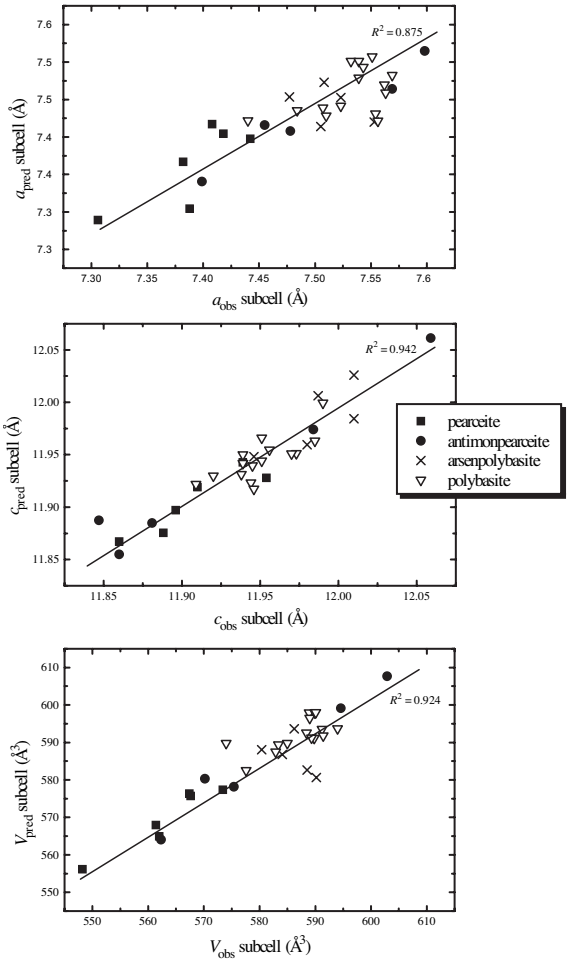

FIGURE 2. Relationship between the observed unit-cell parameters of the hexagonal subcell and the predicted values.

Changes to the existing nomenclature

We report here that minerals in the pearceite-polybasite group exhibit three unit-cell types (i.e., 111, 222, and 221) that correspond to three separate structures (space group types $P\bar{3}m1$, *P*321, and *C*2/*c* for 111, 221, and 222, respectively). Hence, it is evident that only careful crystallographic studies permit the characterization of unit-cell type. Moreover, as Harris et al. (1965) pointed out, unit-cell types may be different in various parts of the same sample. Therefore, without precise X-ray data the most practical nomenclature is to use only two names, pearceite and polybasite, since their compositions are easily obtained by microprobe analysis (As/Sb ratio). If crystallographic data are available (it is sufficient to determine unit-cell parameters without carrying out a complete crystal structure refinement), a hyphenated italic suffix, indicating the crystal system with the cell-type symbol, should be added to the names pearceite or polybasite. With the introduction of these new nomenclature rules we also avoid the problem of requiring two new mineral names for species possessing the 221 unit-cell type.

In short, the old names antimonpearceite and arsenpolybasite should be abandoned and the former names pearceite and

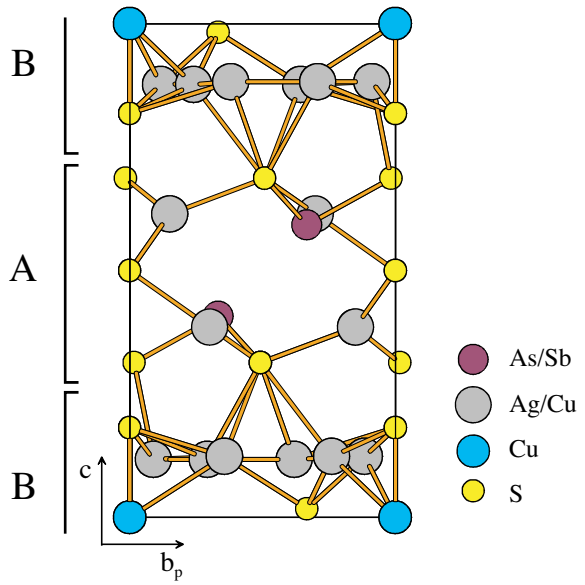

FIGURE 3. Projection of the 111-structure along the hexagonal *a* axis, emphasizing the succession of the $[(Ag,Cu)_6Sb_2S_7]^{2-}$ A (A') and $[Ag_9CuS_4]^{2+}$ B (B') module layers.

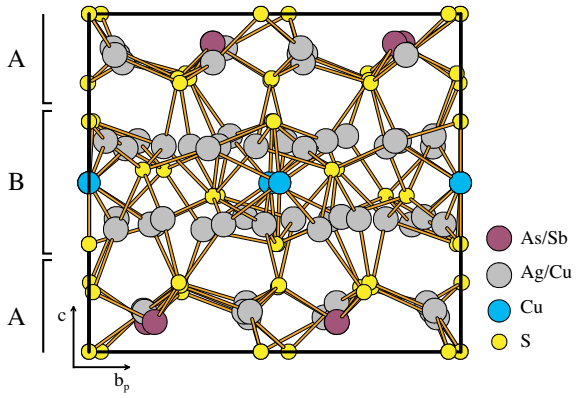

FIGURE 4. Projection of the 221-structure along the hexagonal *a* axis, emphasizing the succession of the $[(Ag,Cu)_6Sb_2S_7]^{2-}$ A (A') and $[Ag_9CuS_4]^{2+}$ B (B') module layers.

polybasite, previously defined on a structural basis (i.e., 111 and 222), are redefined on a chemical basis. The crystal structures of all members of the pearceite-polybasite group allow them to be considered as a family of polytypes, since they are built up by layers stacked along the **c** axis of nearly identical structure and composition. The old accepted names of members of the pearceite-polybasite group together with the new names are given in Table 4. In addition to the revision in mineral names it is also recommended here that the formulae of these minerals be changed. All crystal structures of pearceite-polybasite group minerals consist of two different layers: layer A $[(Ag,Cu)_6(As,Sb)_2S_7]^{2-}$, and layer B $[Ag_9CuS_4]^{2+}$. Therefore, chemical formulae should be written as $[Ag_9CuS_4][(Ag,Cu)_6(As,Sb)_2S_7]$ and $[Ag_9CuS_4][(Ag,Cu)_6(Sb,As)_2S_7]$ instead of $(Ag,Cu)_{16}(As,Sb)_2S_{11}$ and $(Ag,Cu)_{16}(Sb,As)_2S_{11}$ for pearceite and polybasite, respectively. The new nomenclature rules were approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

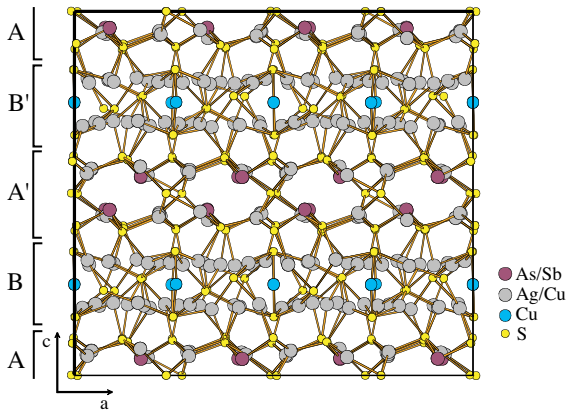

FIGURE 5. Projection of the 222-structure along the monoclinic *b* axis, emphasizing the succession of the $[(Ag,Cu)_6Sb_2S_7]^{2-}$ A (A') and $[Ag_9CuS_4]^{2+}$ B (B') module layers.

Members with the 111 unit-cell type: Polytypes or polytypoids?

It was noted in the Introduction that the Cu content of members having the 111 unit-cell type is generally high whereas those exhibiting the 221 and 222 cell type possess low Cu contents. This raises the question concerning whether both pearceite-*Tac* and polybasite-*Tac* are polytypoids rather than polytypes, where the term polytypoids indicates substances in which more than 0.25 atoms per formula unit differs in at least one component as proposed by the IMA-IUCr Joint Committee on Nomenclature (Bailey et al. 1977). This aspect considers only those members possessing the 111 cell type, as those with the 221 and 222 cell type must be classified as polytypes (almost identical chemical composition). It is our opinion that pearceite-polybasite group minerals that have 111 cell type should also be considered as polytypes. In Figure 6, the composition of samples studied here are plotted on a diagram originally constructed by Hall (1967; Fig. 1). It is evident from Figure 6 that some samples of arsenpolybasite show a copper content similar to that of some samples of pearceite. Moreover, some polybasite samples exhibit a copper content almost the same as that present in samples of antimonpearceite. It is worth noting that two samples of antimonpearceite (i.e., 2453/I and 17004/80) fall in the polybasite field thus indicating that the copper content of pearceite-polybasite group minerals could be very low if selenium is present.

CONCLUDING STATEMENTS

In summary, if only the chemical composition is available:

(1) the name pearceite is applied to minerals having As > Sb; old formula: $(Ag,Cu)_{16}(As,Sb)_2S_{11}$—new formula: $[Ag_9CuS_4][(Ag,Cu)_6(As,Sb)_2S_7]$

(2) the name polybasite is applied to minerals having Sb > As old formula: $(Ag,Cu)_{16}(Sb,As)_2S_{11}$—new formula: $[Ag_9CuS_4][(Ag,Cu)_6(Sb,As)_2S_7]$.

If crystallographic data are also available a hyphenated italic suffix, indicating the crystal system with the cell-type symbol, has to be added to the names pearceite or polybasite. Consequently,

TABLE 4. New nomenclature for minerals belonging to the pearceite-polybasite group

Old name	Old formula	New name	New formula	Space group type
pearceite (111)	$(Ag,Cu)_{16}(As,Sb)_2S_{11}$	pearceite-*Tac*	$[Ag_9CuS_4]$ $[(Ag,Cu)_6(As,Sb)_2S_7]$	$P\bar{3}m1$
antimonpearceite (111)	$(Ag,Cu)_{16}(Sb,As)_2S_{11}$	polybasite-*Tac*	$[Ag_9CuS_4]$ $[(Ag,Cu)_6(Sb,As)_2S_7]$	$P\bar{3}m1$
arsenpolybasite (222)	$(Ag,Cu)_{16}(As,Sb)_2S_{11}$	pearceite-*M2a2b2c*	$[Ag_9CuS_4]$ $[(Ag,Cu)_6(As,Sb)_2S_7]$	*C*2/*c*
arsenpolybasite (221)	$(Ag,Cu)_{16}(As,Sb)_2S_{11}$	pearceite-*T2ac*	$[Ag_9CuS_4]$ $[(Ag,Cu)_6(As,Sb)_2S_7]$	*P*321
polybasite (222)	$(Ag,Cu)_{16}(Sb,As)_2S_{11}$	polybasite-*M2a2b2c*	$[Ag_9CuS_4]$ $[(Ag,Cu)_6(Sb,As)_2S_7]$	*C*2/*c*
polybasite (221)	$(Ag,Cu)_{16}(Sb,As)_2S_{11}$	polybasite-*T2ac*	$[Ag_9CuS_4]$ $[(Ag,Cu)_6(Sb,As)_2S_7]$	*P*321

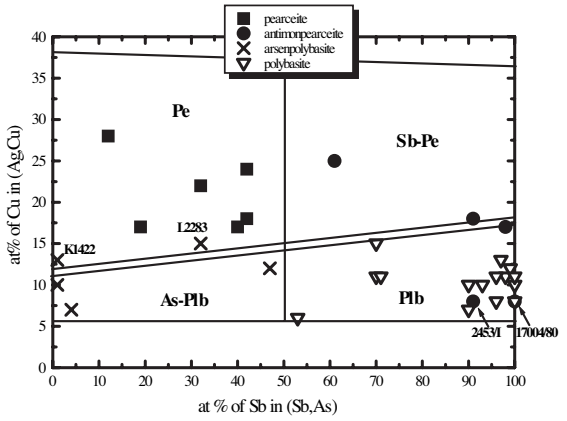

FIGURE 6. Relationship between the at% of Sb in (Sb,As) and the at% of Ag in (Ag,Cu) after Hall (1967).

the following names are applied to the known polytypes:

(3) pearceite-*Tac* (As > Sb—unit-cell type 111—old name: pearceite)

(4) polybasite-*Tac* (Sb > As—unit-cell type 111—old name: antimonpearceite)

(5) pearceite-*T2ac* (As > Sb—unit-cell type 221—old name: arsenpolybasite)

(6) pearceite-*M2a2b2c* (As > Sb—unit-cell type 222—old name: arsenpolybasite)

(7) polybasite-*T2ac* (Sb > As—unit-cell type 221—old name: polybasite)

(8) polybasite-*M2a2b2c* (Sb > As—unit-cell type 222—old name: polybasite)

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