

## ISODIMORPHISM OF THE POLYBASITE AND PEARCEITE SERIES

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## ABSTRACT

The arsenic analogue of polybasite and the antimony analogue of pearceite are shown to occur in nature. The new names arsenopolybasite and antimonpearceite are given to these minerals. Polybasite-arsenopolybasite and pearceite-antimonpearceite probably form complete solid solution series,  $(\text{Ag}, \text{Cu})_{16}(\text{Sb}, \text{As})_2\text{S}_{11}$ - $(\text{Ag}, \text{Cu})_{16}(\text{As}, \text{Sb})_2\text{S}_{11}$ . The two series are isodimorphous, analogous to enargite-stibioenargite and luzonite-famatinite, both  $\text{Cu}_3(\text{As}, \text{Sb})\text{S}_4$ - $\text{Cu}_3(\text{Sb}, \text{As})\text{S}_4$ . The members of both series are monoclinic, although dimensionally pseudo-hexagonal, with the space group  $C2/m$ . The cell dimensions of the polybasite-arsenopolybasite series ( $a \sim 26 \text{ \AA}$ ,  $b \sim 15$ ,  $c \sim 24$ ,  $\beta 90^\circ$ ) are all double those of the pearceite-antimonpearceite series ( $a \sim 13 \text{ \AA}$ ,  $b \sim 7.4$ ,  $c \sim 12$ ,  $\beta 90^\circ$ ). X-ray and chemical data are given for members of these series from 25 localities. Antimonpearceite from Sonora, Mexico, has the composition Ag 62.54, Cu 8.90, Fe 0.05, As 1.43, Sb 9.65, S 17.62, total 100.19%, with As:Sb=1:4.15; G 6.35;  $a$  12.81  $\text{ \AA}$ ,  $b$  7.41,  $c$  11.91,  $\beta$  90°. Arsenopolybasite from the Neuer Morgenstern mine, Freiberg, Saxony, has Ag 71.20, Cu 3.26, Fe 0.38, As 6.87, Sb 0.80, S 17.37, total 99.8%, with Sb:As=1:13.9; specific gravity 6.18;  $a$  26.08  $\text{ \AA}$ ,  $b$  15.04,  $c$  23.84,  $\beta$  90°.

## INTRODUCTION

Polybasite,  $(\text{Ag}, \text{Cu})_{16}(\text{Sb}, \text{As})_2\text{S}_{11}$ , and pearceite,  $(\text{Ag}, \text{Cu})_{16}(\text{As}, \text{Sb})_2\text{S}_{11}$ , have been accepted in view of their close morphological and chemical similarities as members of a single solid solution series. More recently, Peacock and Berry (1947) have shown by x-ray single-crystal study that these minerals are in fact not isostructural, but that all of the cell dimensions of polybasite are doubled as compared to those of pearceite (Table 1). Both minerals have the same space group,  $C2/m$ . The structural significance of the dimensional differences is not known.

The x-ray work of Peacock and Berry was done on specimens that chanced to be near one or the other of the end-compositions. The numerous chemical analyses reported of these minerals, however, indicate a large and possibly complete mutual substitution of Sb and As. The question thus exists of the extent of the two distinct series that stem from polybasite and pearceite, respectively.

In the present study, museum specimens of these minerals from 22 localities were examined by x-ray powder diffraction methods. X-ray single-crystal measurements were made by the Weissenberg and precession methods in certain instances. Complete chemical analyses have been reported in the literature on material from 9 of these localities, and two new complete chemical analyses have been obtained. The approximate content of Sb and As of all specimens also was determined by x-ray

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TABLE 1. UNIT CELL DIMENSIONS OF MEMBERS OF THE POLYBASITE-ARSENOPOLYBASITE AND PEARCEITE-ANTIMONPEARCEITE SERIES  
 Monoclinic, prismatic-2/m. Space group C 2/m  
 Pseudohexagonal cells: polybasite-arsenopolybasite,  $a \sim 7.4$ ,  $c \sim 11.9$  Å  
 pearceite-antimonpearceite,  $a \sim 15.1$ ,  $c \sim 25.9$  Å

Name	Locality	Ref.	a	b	c	$\beta$	Atomic per cent:	
							Sb in (Sb,As)	Ag in (Ag,Cu)
Polybasite	Beaverdell, B. C.	6	26.17 Å	15.11 Å	23.94 Å	90°00'	91.0	91.7
Polybasite	South Lorrain, Ont.	6	26.17	15.11	23.89	90°00'	71.0	94.3
Polybasite	Ouray, Colorado	6	26.17	15.11	23.93	90°00'	—	—
Polybasite	Cobalt, Ontario	6	26.29	15.18	23.95	90°00'	—	—
Arsenopolybasite	Quespisiza, Chile	Present study	26.08	15.04	23.84	90°00'	44.9	86.8
Arsenopolybasite	Freiberg, Saxony	Present study	26.08	15.04	24.00	90°00'	6.8	91.9
Pearceite	Sierra Mojada, Mex.	Present study	12.59	7.27	11.81	90°00'	Tr.	69.0
Pearceite	Aspen, Colorado	6	12.64	7.29	11.90	90°00'	2.5	69.3
Pearceite	Silver, Montana	6	12.80	7.38	11.94	90°00'	—	—
Antimonpearceite	Sonora, Mexico	Present study	12.81	7.41	11.91	90°00'	81.1	80.4
Antimonpearceite	Guanajuato, Mex.	5	13.02	7.52	11.97	90°00'	92.8	88.7

TABLE 2. PARTIAL X-RAY POWDER DATA FOR THE POLYBASITE-ARSENOPOLYBASITE AND PEARCEITE-ANTIMONPEARCEITE SERIES

(Å) range for both series	Relative intensities	Polybasite-arsenopolybasite hkl	Pearceite-antimonpearceite hkl
3.18-3.05	50-90	2244	1122
2.99-2.95	100	0008	0004
2.90-2.86	85-40	3252	absent
2.87-2.78	80	4044	2022
2.77-2.73	15	1128	absent
2.69-2.64	60	{3146 3254}	absent
2.56-2.53	15	4154	absent
2.52-2.47	45	4046	2023
2.42-2.34	20-30	4262	2131
2.33-2.30	40-20	2248	1124
2.20-2.16	25	4048	2024

spectrography. In addition, chemical and *x*-ray data given by Peacock and Berry for material from 3 localities have been included. A number of analyzed occurrences of so-called polybasite and pearceite remain for which *x*-ray data are lacking, and many occurrences are known for which both chemical and *x*-ray data are lacking.

As shown by Peacock and Berry, the *x*-ray powder patterns of polybasite and pearceite as redefined have a number of strong lines in common, as a consequence of the crystallographic and dimensional similarities, but with some distinct differences that allow these minerals to be readily distinguished. The diagnostic strong lines in the two types of pattern are listed in Table 2. Complete *x*-ray powder data are given by Berry and Thompson (1962). The actual *d*-spacings vary slightly accompanying variation in the Sb:As and Ag:Cu ratios. The range of variation is indicated in the table. The indexing is based on the pseudo-hexagonal cells of Peacock and Berry. The relative line or peak intensities also vary considerably with composition. In polybasite {2244} and {4044} are of comparable intensity, but in pearceite {1122} generally is weaker than {2022}. The {3146} {3254} reflection of polybasite-arsenopolybasite is strong and sharp, and is the best of the diagnostic lines listed.

The results of this survey, summarized in Fig. 1 and Table 3, show that the traditional polybasite and pearceite actually are members of two separate solid solution series in which Sb and As substitute mutually. Each series probably is complete. The name polybasite is retained in its original sense for material with Sb > As in atomic per cent, and the new

TABLE 3. LIST OF SPECIMENS

The content of Sb is given in atomic per cent in the (Sb,As) position. Analyses cited from the literature are tabulated by Peacock and Berry (1947). The new approximate determinations of Sb and As were made with a Philips broad-focus x-ray spectrograph using a LiF crystal in a helium path and a flow proportional counter. The  $\text{AsK}\alpha_1$  and  $\text{SbL}\alpha_1$  lines were measured. Calibration graphs based on synthetic standards of the composition  $\text{Ag}_{16}(\text{Sb,As})_2\text{S}_{11}$  were employed, the varying substitution of Cu for Ag being disregarded. In some instances only small samples were available, below 100 mg. in weight. The precision of the measurements, estimated from results obtained on natural specimens of known composition, is about 15 per cent of the amount of (Sb,As) present in the range from 10 to 90 per cent Sb and decreases rapidly beyond these limits (see list).

Pearceite. Sierra Mojada, Mexico. Contains less than Sb 2, with S.G. 6.10 and  $c$  11.81 Å. Sample analyzed and described by Van Horn and Cook (1911) [with Sb lacking and S.G. 6.062]. Large coarse crystals.

Pearceite. Aspen, Colorado. Data of Peacock and Berry (1947), analysis of Penfield and Pearce (1892) with Sb 2.5 and S.G. about 6.07;  $c$  11.90 Å.

Pearceite. Neihart, Montana. Sb  $4 \pm 2$ ;  $c$  11.92 Å. Thick tabular isolated crystal.

Pearceite. Pozos, Mexico. Sb  $6 \pm 2$ ;  $c$  11.80 Å. Group of coarse crystals, with chalcopyrite.

Pearceite. Sierra Juarez, Mexico. Sb  $7 \pm 2$ ;  $c$  11.84 Å. Large crystal.

Pearceite. Tuscarora, Nevada. Sb  $\sim 34$ ;  $c$  11.95 Å. The material from this locality is somewhat variable in composition, in part with higher As content. Thin scales with pyrite.

Pearceite. Mangani mine, Sumatra. Sb  $\sim 43$ ;  $c$  11.84 Å. Thin scales on drusy quartz.

Pearceite. Schemnitz, Hungary. Sb  $\sim 46$ ;  $c$  11.88 Å.

Antimonpearceite. Sonora, Mexico. Sb 81.1; G. 6.35;  $c$  11.91 Å. Analysis given in Table 4, cell dimensions in Table 1; described in text.

Antimonpearceite. Guanajuato, Mexico. Sb 92.8. Analyzed by Prior (1890), cited in Table 4; G. 6.33;  $c$  11.91 Å. The sample here examined, too small for precise measurement, had Sb greatly in excess of As. Associated with argentite and amethyst.

Arsenopolybasite. Neuer Morgenstern mine, Freiberg, Saxony. Sb 6.7; G. 6.18;  $c$  24.0 Å. Analysis given in Table 4, cell dimensions in Table 1; described in text.

Arsenopolybasite. Quespisiza, Peru. Sb 44.9;  $c$  23.84 Å. Material analyzed and described by Bodländer (1895), cited in Table 4; cell dimensions cited in Table 1.

Polybasite. Gersdorf, Saxony. Sb  $\sim 51$ ;  $c$  23.75 Å. Large crystal, with pyrite.

Polybasite. Cobalt, Ontario. Sb  $\sim 52$ ;  $c$  23.90 Å. Associated with proustite, smaltite and safflorite.

Polybasite. Durango, Mexico. Sb  $\sim 62$ ;  $c$  23.79 Å. Six different specimens examined from this general locality varied in Sb content between 62 and 90 atomic per cent (see beyond).

Polybasite. Las Chiapis, Sonora, Mexico. Sb  $\sim 67$ ;  $c$  23.82 Å. Probably the same material as analyzed as Ungemach (1910) with Sb 73.6. Thick tabular crystals.

Polybasite. Keeley mine, South Lorraine, Ontario. Data of Peacock and Berry (1947), with Sb 71.0,  $c$  23.84 Å, G. 6.27.

Polybasite. Arizpe, Sonora, Mexico. Sb  $\sim 78$ ;  $c$  23.84 Å. Probably the same material as analyzed by Ungemach (1910) with Sb 83.6.

Polybasite. Himmelfahrt mine, Freiberg, Saxony. Sb  $\sim 83$ ;  $c$  23.84 Å. Material analyzed from this locality by Rose (1833) had Sb 81.1. Small pseudohexagonal plates, with chalcopyrite.

Polybasite. Voigtsberg near Freiberg, Saxony. Sb  $\sim 88$ ;  $c$  23.84 Å.

TABLE 3.—(Continued)

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Polybasite. Durango, Mexico. Sb~90; $c$ 23.82 Å.
Polybasite. Creede, Colorado. Sb~90; $c$ 23.86 Å. Small sample; thin plates with pyrrargyrite and pyrite.
Polybasite. Beaverdell, British Columbia. Data of Peacock and Berry (1947), with Sb 91.0, S.G. 6.26, $c$ 23.89 Å.
Polybasite. Batopilas, Mexico. Sb~95, $c$ 23.82 Å.
Polybasite. Příbram, Bohemia. Sb~95; $c$ 23.9 Å. Probably the same material analyzed by Reuss (1860) with Sb 100 and G. 6.03. With argentite and pyrite.

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name arsenopolybasite is used to designate material in this series with As > Sb in atomic per cent. Similarly, pearceite and the new name antimonpearceite are employed for the parallel series, with halved cell dimensions, with As > Sb and Sb > As in atomic per cent, respectively. These isodimorphous series are analogous to enargite-stibioenargite and luzonite-famatinitite.

#### POLYBASITE-ARSENOPOLYBASITE SERIES

Most of the 15 specimens found by  $x$ -ray study to be of the polybasite structural type with  $c \sim 23.9$  Å have Sb > As, conforming to the traditional polybasite, but two specimens have As > Sb in atomic per cent. The maximum content of As was found in a specimen from the Neuer Morgenstern mine near Freiberg, Saxony. A complete analysis of this material, cited in Table 4, shows a content of 93.2 atomic per cent As in the (As, Sb) position. The unit cell dimensions are given in Table 1; specific gravity 6.18. The crystals are rough pseudo-hexagonal plates up to 6 cm across

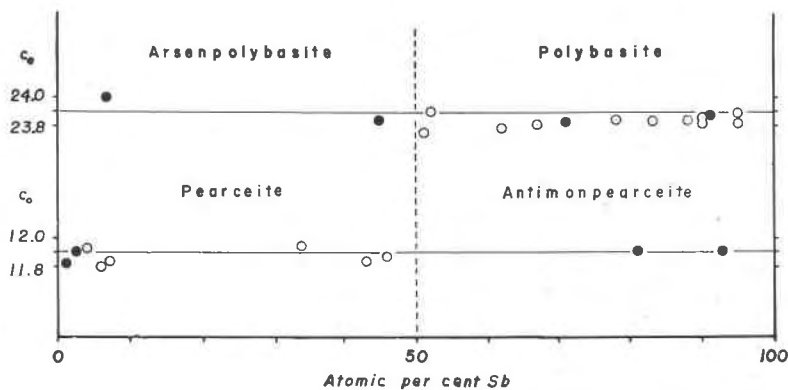


FIG. 1. Sb content and  $c$  value for members of the pearceite-antimonpearceite and polybasite-arsenopolybasite series. Solid circles represent specimens for which complete analyses are available, open circles represent partial analyses by  $x$ -ray spectrography (Tables 3, 4).

and are associated with argentite and chalcopyrite. This mineral is dimorphous with pearceite, and is here designated by the name arsenopolybasite.<sup>1</sup> It is intended that this name refer to all material in the series with polybasite that has  $As > Sb$  in atomic per cent.

The material from the Neuer Morgenstern mine was analyzed by Brandes in 1818, who found it to contain As and to lack Sb (Table 4). The analysis is only of historical interest. The Harvard specimen here analyzed, obtained in 1828, is of the same vintage. In Brandes' time the mineral was classed among Werner's *Sprödglasserz*. With the separation of this group into stephanite and polybasite by H. Rose in 1829, it was placed by Breithaupt (1829) and others with the antimony mineral polybasite. After the formal description of the arsenic analogue pearceite in 1896 it would have been referred to that species but seems to have escaped notice. It now reappears as a new species.

The so-called polybasite from Quespisiza, Peru, analyzed by Bodländer (anal. 3, Table 4) has As slightly in excess of Sb, with 55.1 atomic per cent As, and is here classed as arsenopolybasite. The measured unit cell dimensions of this material are given in Table 1.

#### PEARCEITE-ANTIMONPEARCEITE SERIES

Two of the 10 specimens found on  $x$ -ray study to be of the pearceite structural type with  $c \sim 11.9 \text{ \AA}$  and  $Sb > As$  in atomic per cent. The largest content of Sb was found in a specimen from Guanajuato, Mexico. This material is identical with the so-called polybasite from Guanajuato analyzed by Prior (1890), with 92.8 atomic per cent Sb in the (Sb, As) position (anal. 5, Table 4). It is evidently also identical with the so-called polybasite from Guanajuato  $x$ -rayed by Gossner and Kraus (1934), who found the halved cell dimensions (Table 1), here verified, that are now known to be consistent with the pearceite-antimonpearceite series rather than the polybasite-arsenopolybasite series.

Another specimen with the pearceite structure was found to contain 81.1 atomic per cent Sb in the (As, Sb) position. A complete analysis of this material, from an unknown locality in Sonora, Mexico, is given in

<sup>1</sup> The name arsenopolybasite already exists in mineralogical literature, but in circumstances that should not cause confusion with the present use. In 1895, Penfield used the term "arsenical polybasite" in passing reference to a mineral from Aspen, Colorado, that he showed to be chemically similar to material from Montana for which the specific name pearceite was then proposed. This study, originally published in English in the American Journal of Science, was republished in German in the Zeitschrift für Kristallographie. The term "arsenical polybasite" here appears in translation as arsenopolybasit. This inadvertent name has since been recorded as a synonym of pearceite. (The Aspen material was shown by Peacock and Berry to be structurally identical with pearceite, but the structural identity of the Montana material is not known.)

TABLE 4. ANALYSES OF ARSENPOLYBASITE AND ANTIMONPEARCEITE

	1	2	3	4	5
Ag	71.20	65.50	67.95	62.54	68.39
Cu	3.26	3.75	6.07	8.90	5.13
Fe	0.38	5.46		0.05	
As	6.87	3.30	3.88	1.43	0.50
Sb	0.80		5.15	9.65	10.64
S	17.37	19.40	16.37	17.62	15.43
Rem.		1.00	0.76		
Total	99.88	98.41	100.18	100.19	100.09
G.	6.18	6.15	6.23	6.35	6.33

1. Arsenpolybasite. Neuer Morgenstern mine, Freiberg, Saxony. J. Ito, analyst, 1961. No Zn or Ge.
2. Arsenpolybasite. Neuer Morgenstern mine, Freiberg, Saxony. Analysis of Brandes (1818). Rem. is gangue.
3. Arsenpolybasite. Quespisiza, Chile. Analysis of Bodländer (1895). Rem. is Pb.
4. Antimonpearceite. Sonora, Mexico. J. Ito, analyst, 1961. No Zn or Ge.
5. Antimonpearceite. Guanajuato, Mexico. Analysis of Prior (1890).

Table 4. The unit cell dimensions are given in Table 1; specific gravity 6.35. The crystals are pseudo-hexagonal tablets, up to 2 cm across, arranged in subparallel and rosette-like groups. The luster is submetallic, brighter than in pearceite or arsenpolybasite, and the color is black. This mineral, and that from Guanajuato, are dimorphous with polybasite and are here designated by the new name antimonpearceite. This name is intended to refer to all material in the series with pearceite that has  $Sb > As$  in atomic per cent.

Morphological measurements could not be obtained by optical goniometry on either the Guanajuato or Sonora material. The detailed morphological data reported for so-called pearceite by Penfield (1896) on crystals from the Drumlummon mine, Marysville, Montana, are of uncertain relevance because  $x$ -ray evidence of the structural type are lacking. The morphology of polybasite as redefined is well established through the work of Penfield and Berry (1947) and others on material that has been verified by  $x$ -ray work. In general, the minerals of the pearceite-antimonpearceite and polybasite-arsenpolybasite series can not be distinguished by morphological means, because of the crystallographic and dimensional similarities, and the morphological measurements show no significant deviation from hexagonal (pseudo) symmetry.

The unit cell volume of the members of these series would be expected to increase with increasing substitution of Sb for As. The relation is com-

plicated by a variation in the ratio of Cu to Ag in the (Ag, Cu) position, with Fe, <sup>206</sup>Pb, <sup>66</sup>Zn and Bi also sometimes present, and the precise relations between the bulk composition and the cell volume and specific gravity are not known. The content of copper ranges roughly between 5 and 35 atomic per cent Cu in the (Ag, Cu) position.

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