THE AMERICAN MINERALOGIST, VOL. 52, SEPTEMBER-OCTOBER, 1967

# THE PEARCEITE AND POLYBASITE SERIES[1]

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## ABSTRACT

Experimental study of the phases pearceite $(Ag, Cu)_{16}As_2S_{11}$ and polybasite $(Ag, Cu)_{16}Sb_2S_{11}$ has shown that copper is an essential component and that these phases are end members of two distinct series: pearceite-antimonpearceite and polybasite-arsenpolybasite. Synthetic arsenpolybasite is homogeneous over a compositional interval which extends from 3.0 to 5.2 weight percent copper at 200°C. Its antimony analog, polybasite, is stable from 3.1 to 7.6 weight percent copper at 200°C. Synthetic pearceite is homogeneous from 5.5 to 19.7 weight percent copper at 200°C; whereas, its antimony analog is homogeneous from 7.9 to 19.2 weight percent copper at 200°C. A narrow two-phase field separates the two solid solution series. At about 360°C arsenpolybasite inverts to a high temperature polymorph, X-arsenpolybasite. The compositional limits of copper for the two synthetic series corresponds with that found in natural material.

## INTRODUCTION

Pearceite and polybasite, with similar pseudohexagonal or monoclinic form and similar composition, $8(Ag, Cu)_2S \cdot (As, Sb)_2S_3$ and $8(Ag, Cu)_2S \cdot (Sb, As)_2S_3$, have generally been regarded as the arsenic and antimony end-members respectively, of a single solid solution series. Copper replaces silver in considerable and varying amounts in both minerals, and in polybasite there may also be substantial replacement of antimony by arsenic.

Although most of the specific properties of polybasite and pearceite are known, there are still some gaps and uncertainties in the descriptions. The purpose of this investigation was to determine experimentally the stability range and compositional limits of pearceite and polybasite.

## PREVIOUS DESCRIPTIONS

Peacock and Berry (1947) were the first to determine the unit cell of pearceite. They obtained values of

$$a = 12.64, \qquad b = 7.29, \qquad c = 11.90 \text{ Å}, \qquad \beta = 90°$$

from rotation and Weissenberg films with [001] and [010] or [110] as the rotation axes on a crystal from Aspen, Colorado. The photographs showed hexagonal symmetry as regards the position of reflections, but only monoclinic symmetry as regards their intensities.

The unit cell of polybasite had previously been determined by Gossner and Kraus (1934) on unanalyzed material from the Guanajuato district in Mexico:

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[1] Part of a dissertation presented to the faculty of Brown University in candidacy for the Degree of Doctor of Philosophy.

$$a = 13.02, \qquad b = 7.52, \qquad c = 11.97 \text{ Å}, \qquad \beta = 90°.$$

Peacock and Berry made rotation and Weissenberg studies of polybasite crystals from five additional localities. The photographs showed the same hexagonal geometry and monoclinic symmetry as pearceite with roughly the same dimensions as reported by Gossner and Kraus on polybasite, but weak intermediate layer lines proved that all the crystals except one, have double these dimensions:

$$a \sim 26, \qquad b \sim 15, \qquad c \sim 24 \text{ Å}, \qquad \beta = 90°.$$

The exception was a specimen of polybasite from the Las Chispas mine, Sonora, Mexico on which they found only $a$ and $b$ dimensions are doubled:

$$a = 26.17, \qquad b = 15.11, \qquad c = 11.94 \text{ Å}, \qquad \beta = 90°.$$

In the 17 analyses of polybasite available to Peacock and Berry, arsenic ranged from zero to over one-half of the (Sb, As) component. On the other hand, antimony comprised only a small fraction of the (As, Sb) component in the six available pearceite analyses, although the analyses represented only five localities, Peacock and Berry decided that the chemical data did not indicate complete solid solution from arsenian polybasite to pearceite and concluded that it was proper to recognize the minerals as distinct species rather than end-members of a series. The pearceite of Peacock and Berry, therefore, has the cell dimensions $a \sim 13$, $b \sim 7.5$, $c \sim 12$ Å, $\beta = 90°$, a cell content of $Z[8(\mathrm{Ag, Cu})_2\mathrm{S} \cdot (\mathrm{As, Sb})_2\mathrm{S}_3]$ in which $Z = 2$, and the (As, Sb) component is largely arsenic. Their polybasite has cell dimensions $a \sim 26$, $b \sim 15$, $c \sim 12$ or 24 Å, $\beta = 90°$ (if the data of Gossner and Kraus are disregarded), but a pronounced pseudocell has $a \sim 13$, $b \sim 7.5$, $c \sim 12$ Å, $\beta = 90°$ like pearceite. The cell contents are $Z[8(\mathrm{Ag, Cu})_2\mathrm{S} \cdot (\mathrm{Sb, As})_2\mathrm{S}_3]$ in which $Z = 8$ or 16 in the true cells, and arsenic varies from zero to more than one-half of the (Sb, As) component.

In a study of pearceite and polybasite from 22 localities, Frondel (1963) confirmed the existence of the Gossner-Kraus polybasite cell, found a pearceite with all dimensions doubled and presented evidence to show that possibly complete mutual substitution of antimony and arsenic occurs in both the small and double cell. This led Frondel to divide these minerals into two series (see Fig. 1). He redefined the mineral pearceite as the arsenic end-member of one series characterized by the cell: $a \sim 13$, $b \sim 7.4$, $c \sim 12$ Å, and proposed the name antimonpearceite for the antimony analog. Similarly he redefined polybasite in terms of a second series with the double cell ($a \sim 26$, $b \sim 15$, $c \sim 24$ Å), and called its arsenic analog arsenpolybasite.

The original specimen from the Las Chispas mine studied by Peacock and Berry was reexamined by Harris, Nuffield, and Frohberg (1965) and the existence of the intermediate cell was confirmed, but they discovered that while some areas of the specimen give this cell, other seemingly identical areas are characterized by the small cell. Frondel had also examined crystals from this mine and obtained a value of 23.82 Å for *c*, rather than the reported value near 12 Å. The Las Chispas material therefore, crystallized with the small, the double, and an intermediate cell. Harris, *et al.* decided that the weak intermediate layer lines on rotation photographs represent "less-than-fundamental" differences, and concluded that it is desirable to recognize their basic similarity and return to the original classification in which pearceite and polybasite are regarded as the arsenic and antimony end-members of one series. They proposed that the series is based on a structural unit with dimensions:

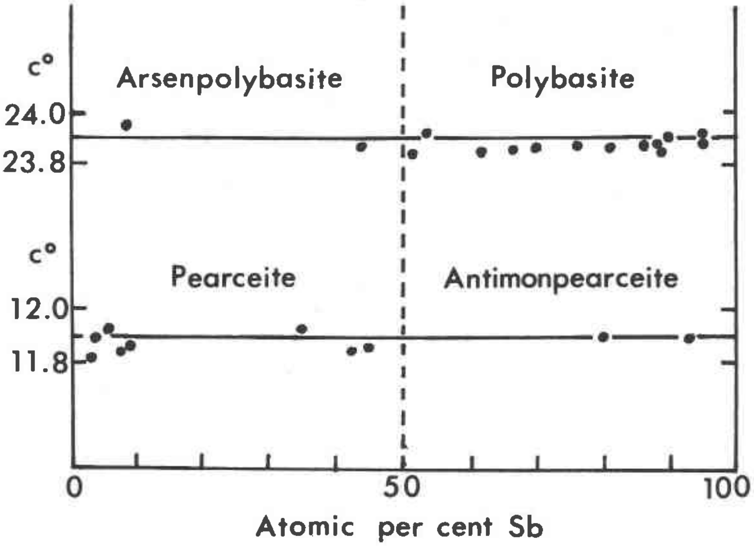

FIG. 1. Classification of 25 pearceite-polybasite specimens according to the values of *c* and the atomic percent of Sb (after Frondel, 1963).

$$a \sim 13, \quad b \sim 7.5, \quad c \sim 12\ \text{Å}, \quad \beta = 90°$$

and composition

$$(Ag, Cu)_{32}(Sb, As)_4S_{22}.$$

From the distribution of double- and single-celled crystals as determined by Frondel, Harris *et al.*, suggested that the doubling is a consequence of the presence of antimony in the structure and that the basic structure accommodates arsenic more readily than antimony.

## PREVIOUS EXPERIMENTAL WORK

Previous attempts to synthesize pearceite and polybasite have either not been successful (Jensen, 1947; Jaeger and van Klooster, 1912; Barstad, 1959; and Somanchi, 1963) or the identification of the products is not conclusive, (Gaudin and McGlashan, 1938; Béland, 1946; and Weil *et al.*, 1954). Hall (1965) has shown that the products prepared by Gaudin and McGlashan, Béland, and Weil, *et al.* in the systems Ag-As-S and Ag-Sb-S were most probably the two new silver sulfosalts pseudopearceite ($Ag_7AsS_6$) and pseudopolybasite ($Ag_7SbS_6$).

Gaudin and McGlashan in their investigation of the quaternary system Ag-Cu-Sb-S reported a phase *C* which does not occur in the Ag-Sb-S system and whose optical properties fit for polybasite. From estimates of the relative abundances of the various phases, the composition of phase *C* was believed to be $Ag_{13}Cu_3Sb_2S_{12}$. The authors, therefore, tentatively correlated phase *C* with polybasite, although the composition is not the same as that determined for the mineral polybasite, it is the only mineral which contains these four elements.

## MATERIALS, EQUIPMENT, AND TECHNIQUES

All syntheses were carried out in sealed, evacuated, silica-glass tubes. The sealed charges were heated in nichrome-wound horizontal furnaces. Temperatures were measured potentiometrically by chromel-alumel thermocouples. The temperature uncertainty does not exceed 5°C.

Standard X-ray and optical techniques were used to identify the phases. When an accurate measurement of a particular reflection was desired, eight oscillations were made with a Norelco diffractometer using Lake Toxaway quartz ($d_{(101)}=3.3432$ Å) as an internal standard.

All synthetic products were prepared from the pure elements. The arsenic, antimony, and copper used in these experiments were obtained from the American Smelting and Refining Co. The arsenic (lot no. P-6923), antimony (lot no. 168), and copper have a reported purity of 99.999+percent, exclusive of dissolved gases. The sulfur supplied by the Freeport Sulfur Co., Port Sulfur, Louisiana has 0.007 percent impurities, substantially all of which is carbonaceous material (see Skinner, Barton, and Kullerud, 1959). The silver that was used has a reported purity of 99.999+percent and was obtained from the United Mineral and Chemical Company.

## RESULTS

In order to establish the phase relations in the silver-rich portion of the $Ag_{16}As_2S_{11}$-$Cu_{16}As_2S_{11}$ and $Ag_{16}Sb_2S_{11}$-$Cu_{16}Sb_2S_{11}$ systems, samples were prepared from the elements and melted at 600°C for a period of from two to three days, annealed at an appropriate temperature for a period of one to thirty days, and quenched to room temperature. A portion of each sample was prepared for X-ray study and another portion was utilized for polished section study. The limits of solid solution were determined by plotting the variation of values for the major peak (004 or 008) as a function of composition. The terms employed to designate the phases are those defined by Frondel (1963).

*Polybasite-Antimonpearceite.* The results of experiments on the antimony system are shown in Figure 2. Because it is not possible by the methods used in this study to quench the liquid; the liquidus curves could not be determined. The upper curve, therefore, represents the first appearance of liquid.

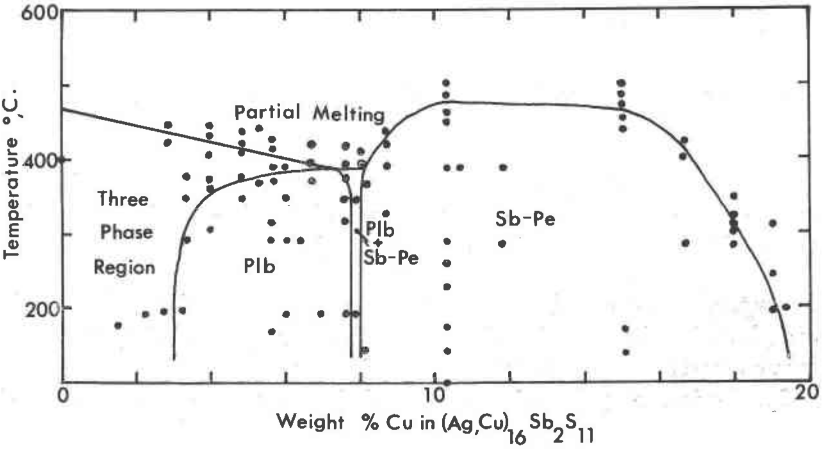

FIG. 2. Temperature-composition diagram of the Ag-rich portion of the system $Ag_{16}Sb_2S_{11}$ $-Cu_{11}Sb_2S_{16}$. The upper curve represents the first appearance of liquid.

As can be seen in Figure 2, synthetic polybasite (Plb) is homogeneous over a compositional interval that extends from about 3.1 to 7.6 weight percent copper at 200°C. Antimonpearceite (Sb-Pe) is not a polymorph of polybasite, but rather a distinct and separate compound that is homogeneous from about 7.9 to 19.2 weight percent copper at 200°C. A very narrow two-phase field separates the solid solution regions.

Figure 3 shows $d_{(008)}$ for polybasite and $d_{(004)}$ for antimonpearceite as a function of composition for samples quenched from 200°C. There is a sharp decrease in the $c$ dimension for polybasite with increase in copper content, but the difference between the $c$ dimension of polybasite and antimonpearceite is very small at the two-phase region.

Despite the basic similarity, small cells can be easily distinguished from doubled cells. The (322) and (316) (324) reflections of polybasite

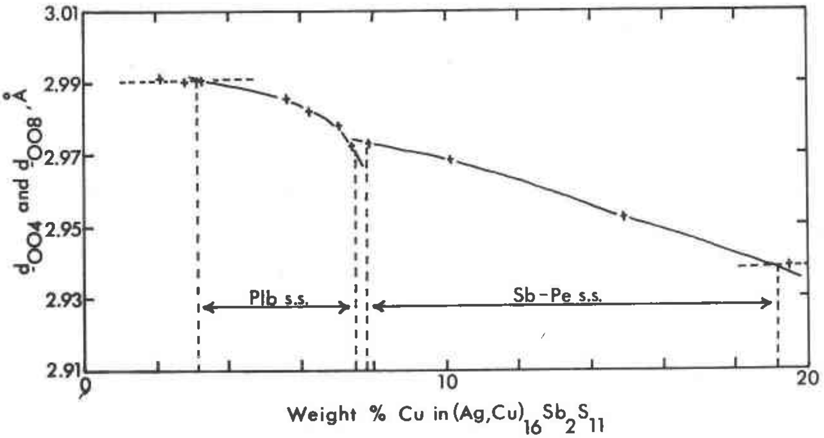

FIG. 3. Variation of $d_{(004)}$ and $d_{(008)}$ as a function of the composition of polybasite and antimonpearceite, respectively, annealed at 200°C.

are strong and sharp, whereas, these reflections are missing in antimonpearceite. Optically polybasite has a distinctive red internal reflection which is not present in antimonpearceite.

*Arsenpolybasite-Pearceite.* The results for arsenpolybasite and pearceite are given in Figure 4. As with polybasite-antimonpearceite, the upper curve represents the first appearance of melts.

Synthetic arsenpolybasite (As-Plb) is homogeneous over a composi-

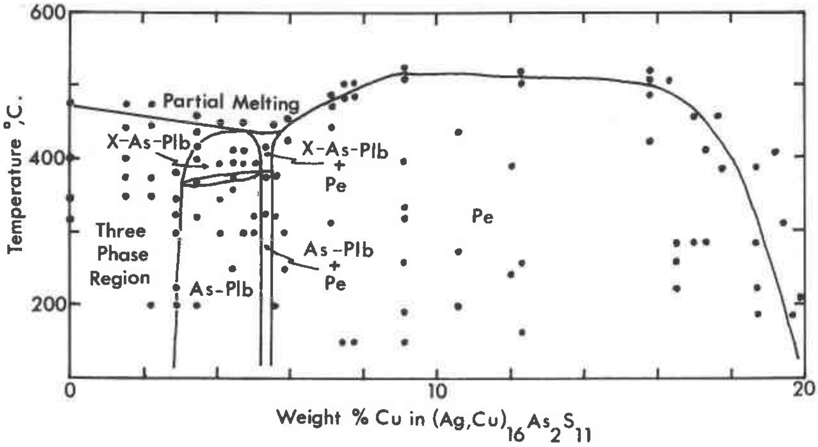

FIG. 4. Temperature-composition diagram of the Ag-rich portion of the system $Ag_{16}As_2S_{11}$ $-Cu_{16}As_2S_{11}$. The upper curve represents the first appearance of liquid.

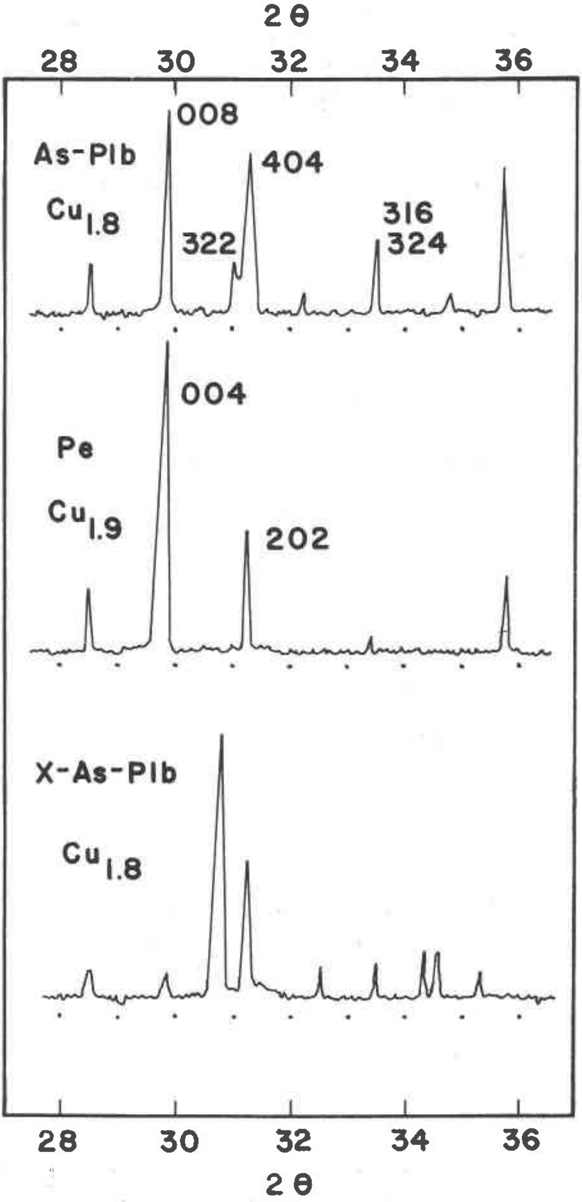

FIG. 5. A portion of X-ray powder patterns of synthetic arsenpolybasite, X-arsenpolybasite, and pearceite. All patterns were obtained on a Norelco diffractometer with Cu radiation.

tional interval that extends from about 3.0 to 5.2 weight percent copper at 200°C. Pearceite is homogeneous from about 5.5 to 19.7 weight percent copper at 200°C. A very narrow two-phase field separates the solid solutions regions. At 365±5°C arsenpolybasite inverts to a high temperature polymorph, X-arsenpolybasite (X-As-Plb), not reported occurring in nature.

The same reflections that were used to distinguish polybasite from antimonpearceite were employed to differentiate between pearceite and arsenpolybasite; that is the (322) and (316) (324). A portion of the X-ray powder patterns of synthetic pearceite, arsenpolybasite, and X-arsenpolybasite are shown in Figure 5.

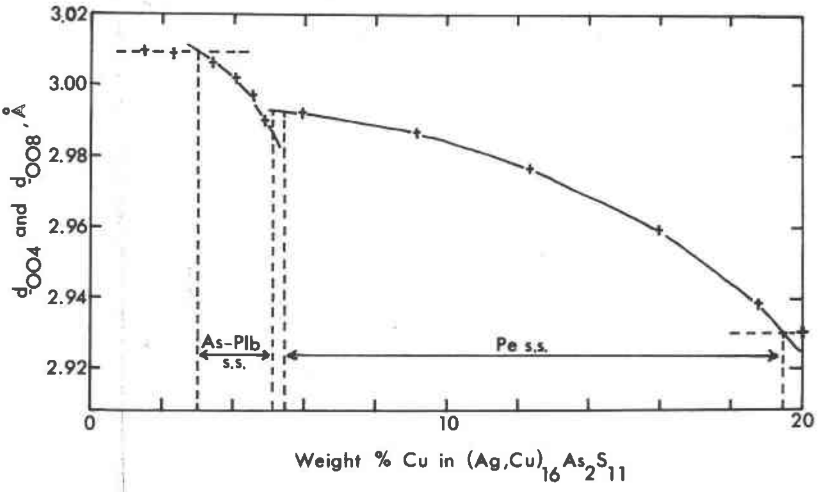

FIG. 6. Variation in $d_{(004)}$ and $d_{(008)}$ as a function of the composition of pearceite and arsenpolybasite, respectively, annealed at 200°C.

A plot of $d_{(008)}$ of arsenpolybasite and $d_{(004)}$ of pearceite as a function of composition is given in Figure 6. The curves are very similar to those for the antimony system.

*Polybasite-arsenpolybasite and antimonpearceite-pearceite series.* Only two runs were prepared in which both antimony and arsenic were present. Mixtures of polybasite plus arsenpolybasite with 5.66 weight percent copper and pearceite plus antimonpearceite with 10.21 weight percent copper were homogenized at 600°C and annealed at 200°C. The mixtures were approximately 50 formula percent of the end-members. Both runs were homogeneous and had intermediate $d_{(008)}$ and $d_{(004)}$

values, respectively. This indicates that there is complete mutual solubility of antimony and arsenic in both the small and double cell; as was shown to be true for natural material by Frondel (1963).

## DISCUSSION

In this study powder X-ray techniques were used to identify the products; therefore, it was not possible to observe the intermediate cell. The significance of such a cell is not known. It may be related to an order-disorder effect or due to mixture of members of the two series.

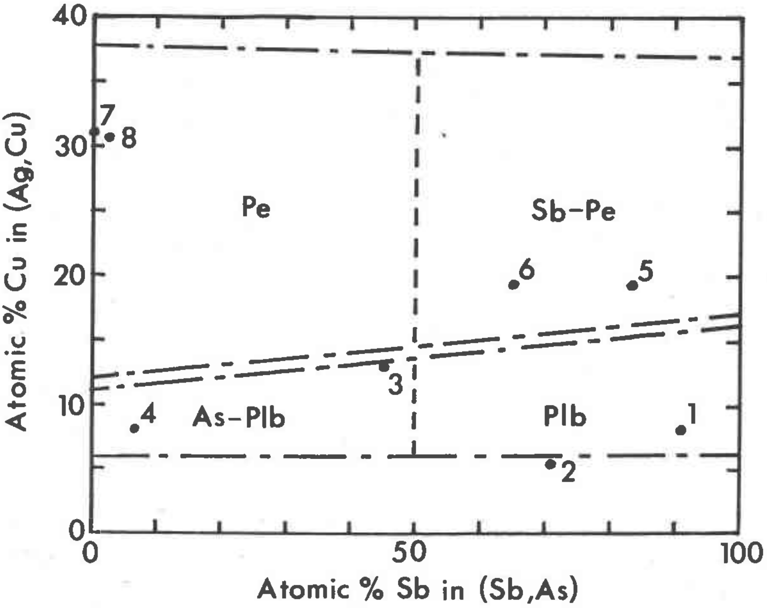

FIG. 7. Composition of natural pearceite-polybasite compared with solid solution in synthetic systems. Numbers correspond to the analyzed specimens listed in Table 1.

For the sake of comparison the present results are given in Figure 7 together with analyzed natural samples reported by Frondel; the data are given in Table 1. The solubility limits of copper for the two series, in the synthetic systems corresponds closely with that found in the natural material. There is also agreement with a recently analyzed sample of Se-rich antimonpearceite from the San Carlos mine, Guanajuato, Mexico; described by Harris *et al.* (1965).

In conclusion, the results of this study substantially confirm the observations made by Frondel (1963). They show that the traditional polybasite and pearceite actually are members of two separate solid

TABLE 1. COMPARISON OF MEMBERS OF THE POLYBASITE-ARSENPOLYBASITE AND PEARCEITE-ANTIMONPEARCEITE SERIES

| No. | Name[1] | Locality | Atomic Percent | |
|---|---|---|---|---|
| | | | Sb in (Sb, As) | Cu in (Ag, Cu) |
| 1 | Plb | Beaverdell, B. C. | 91.0 | 8.3 |
| 2 | Plb | South Lorrain, Ont. | 71.0 | 5.7 |
| 3 | As-Plb | Quespisiza, Chile | 44.9 | 13.2 |
| 4 | As-Plb | Freiberg, Saxony | 6.8 | 8.1 |
| 5 | Sb-Pe | Sonora, Mexico | 81.1 | 19.6 |
| 6[2] | Sb-Pe | Guanajuato, Mexico | 65.0 | 19.4 |
| 7 | Pe | Sierra Majada, Mexico | Tr. | 31.0 |
| 8 | Pe | Aspen, Colorado | 2.5 | 30.7 |

[1] The names are those reported by Harris, *et al.* (1965) and Frondel (1963).

[2] Analysis taken from Harris, *et al.* (1965) all other analyses taken from Frondel (1963).

solution series in which antimony and arsenic substitute mutually. But, these parallel series are not dimorphous as was suggested by Frondel and copper is a necessary component.

## ACKNOWLEDGEMENTS

This study was done at Brown University using the laboratory facilities of Dr. R. A. Yund. Dr. Yund gave freely of his time for discussions during all phases of the study and his assistance is gratefully acknowledged.

I am especially grateful to Brown University for a University Fellowship (1963–64) and for a Research Assistantship (1964–65).

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*Manuscript received, October 3, 1966; accepted for publication, October 6, 1966.*