STUDIES OF MINERAL SULPHO-SALTS:
XIX—SELENIAN POLYBASITE

D. C. HARRIS,1 E. W. NUFFIELD,2 AND M. H. FROHBERG3

Abstract

A study of a rich Au-Ag ore from the La Guadalupe Arcos mine, Zacualpan, Mexico has led to the discovery of a se]enian polybasite associated with a number of silver-bearing minerals. A cleavable variety of pyrite is a feature of the ore. The mineral occurs as minute grains but about 1 milligram was concentrated from a more favourable material from the San Carlos mine, Guanajuato, Mexico. This gave the cell dimensions: \(a\) 13.00, \(b\) 7.50, \(c\) 11.99 Å, \(\beta\) 90° and, by x-ray spectroscopy, the approximate cell contents:

\[(\text{Ag}_{28.0}\text{Cu}_{4.2})(\text{Sb}_{0.8}\text{As}_{1.4})(\text{S}_{17.2}\text{Se}_{8.0}).\]

This study has led to a reclassification of the polybasite-pearceite minerals. Frondel's classification into two series, according to whether the cell is small \((a \sim 13, b \sim 7.5, c \sim 12)\), or double this, is untenable. The basic structural unit and external crystal form is the same for all polybasites and pearceites. Doubled dimensions, which manifest themselves as weak intermediate layer lines on rotation photographs, represent less-than-fundamental differences. This is illustrated by a coarsely-crystallized specimen from the Las Chispas mine, Mexico. Some areas give the small cell while other, seemingly-identical areas give an intermediate cell \((a \sim 26, b \sim 15, c \sim 12)\). Frondel has reported that material from this mine gives the double cell.

The original classification into one series, with polybasite as the Sb > As end-member and pearceite as the As analogue, is preferable because it recognizes the basic similarity of all polybasite-pearceite minerals. We advocate the addition of a symbol to signify the type of cell. Thus: pearceite (1-1-1) when \(\text{As} > \text{Sb}\) and the cell is identical with the basic structural unit \((a \sim 13, b \sim 7.5, c \sim 12)\); polybasite (2-2-2), when \(\text{Sb} > \text{As}\) and the cell dimensions are doubled; polybasite (2-2-1), when \(\text{Sb} > \text{As}\) and only the \(a\) and \(b\) dimensions are doubled.

Recently one of us (M. H. F.) collected ore specimens from the La Guadalupe Arcos mine, Zacualpan, Mexico which offered an unusually intriguing mineralogical study. Although grab specimens gave phenomenally high assays for gold and silver, no gold was visible even under a high power binocular microscope. Later, no gold was observed in polished sections. The report that high gold values were invariably associated with significant amounts of selenium added to the interest.

Silver has been mined near Zacualpan in the southwest portion of the State of Mexico since the early days of the Spanish colonization. Since the beginning of this century, mining in the area has been on the decline and in 1959 the La Guadalupe Arcos property was the only mine in

1Dept. of Mineralogy, Royal Ontario Museum.
2Dept. of Geological Sciences, University of Toronto.
3Consulting geologist, Toronto.
production. Some of the veins in the Zacualpan district, including those of the La Guadalupe Arcos and El Alacran mines, were known to carry in places high values in gold, but such occurrences were somewhat of a mystery to the mine operators since no identifiable minerals seemed to account for the gold content.

The material for the present study was obtained from the La Trinidad vein on the La Guadalupe Arcos property, from a pocket in an exploratory winze some 125 feet below the Socavon Llave haulage level. Striking nearly due north and dipping steeply to the west, the La Trinidad vein is one of a set of fissure type veins which have been followed underground for a length exceeding 1,500 feet and to a depth of more than 800 feet below the outcrop. Host rock, of the La Trinidad vein is a more or less altered andesitic volcanic which according to Robles Ramos (1937) is probably Oligocene in age. It is not known whether this rock represents a massive lava flow or is intrusive into a series of highly folded sediments occurring nearby.

The veins of the La Guadalupe Arcos mine are composed of quartz, carbonates, wall rock inclusions and a number of ore minerals, of which seven are silver bearing. The veins show crustified banding, cockade structures and cavities lined with crystals of calcite, quartz and sulphides—clusters of well-formed crystals of stephanite, intimately associated with wire silver, pyrargyrite, polybasite and acanthite occur in vugs in rich vein sections. The crustified texture is characterized by distinct bands of pyrite, mostly next to the wall-rock contacts, and by more or less distinct bands of sphalerite, galena, finely disseminated polybasite and massive silver. A cleavable variety of pyrite is commonly observed in high grade ore and is regarded by local miners as an indicator of appreciable gold values. In polished sections this variety has a crystallographic replacement texture, formed by the arrangement of numerous rounded to vein-like microscopic inclusions of acanthite, electrum, polybasite, galena, chalcopyrite and sphalerite (in order of abundance) along unusually well-developed cubic cleavage planes (Fig. 1).

Pyrite appears to represent the first stage in the formation of the veins. After a distinct time interval, deposition of the other minerals shown in the Robertson-Van de Veer diagram (Fig. 2) resulted in fracturing and replacement of the pyrite. The occurrence of the well-formed crystals of stephanite and pyrargyrite, and the wire silver in the cavities suggest a third stage of mineralization.

There is little if any evidence of oxidation by circulating surface waters on the Socavon Llave haulage level, and the general appearance of the veins suggests that the minerals observed below that horizon are primary in origin.
The occurrence of gold

In an effort to locate the gold, a 3-inch specimen of rich ore from the La Trinidad vein was broken in two. One half was reserved for a fire assay
while representative slices of the other half were fashioned into polished sections. A microscopic study of the sections revealed no gold although the fire assay returned a value of 24.3 oz. of gold (and 3500 oz. of silver) per ton. The assay rejects were then superpanned and the fractions tested for gold by x-ray spectroscopy. This showed, as expected, that the gold was concentrated in the tail. The gold-bearing grains were concentrated by testing the tail in 5 to 10 milligram lots, and handpicking and re-testing those lots which gave positive results. It was established with this procedure, that the gold is alloyed with the massive silver and therefore the silver is actually electrum. Later, the silver was found to have a cell edge of 4.08 Å. This represents a composition of about 5 atomic per cent gold when referred to the cell edge vs Ag/Au ratio data of Sachs & Weerts (1930), re-plotted on the basis of Swanson & Tatge’s (1953) modern values for the cell edges of gold and silver. Presumably this accounts for all of the gold. It was found that the presence of gold could be detected in samples weighing as little as 1 to 2 milligrams (Fig. 3), comprising only 4 or 5 grains, and consequently likely portions of the superpanner tail were tested almost grain by grain.

Fig. 3. Part of characteristic spectrum from 1.6 mgs. of electrum; 40 kv/30 ma, W, SF 4, TC 2, Scan speed 1/2°/min.
The occurrence of selenium

None of the minerals mentioned above accounts for the presence of selenium in the ore. Separate fractions of quartz, pyrite and silver all gave positive tests for selenium by x-ray spectroscopy, but close scrutiny of these materials invariably showed very fine inclusions. One additional ore mineral was found by systematically extracting these inclusions and identifying them by x-ray powder photography. This mineral's powder pattern does not appear in Berry & Thompson (1962) but the pattern is identical with one in the University of Toronto files, which had been obtained by Earley (1950) from a “brittle metallic mineral” associated with aguilarite (Ag₄SeS) on a specimen from the San Carlos mine, Guanajuato, Mexico (ROM-M 3832). Earley identified this mineral as pearceite which, in the terminology of Peacock & Berry (1947) implied a mineral with (ideal) cell contents

\[(\text{Ag,Cu})_{32}(\text{As,Sb})_{4}S_{22}\]

(in which As is greatly in excess of Sb) and the cell dimensions \(a \approx 13\), \(b \approx 7.5\), \(c \approx 12\), \(\beta = 90^\circ\). Our examination of the pattern showed that it is indeed very similar to the patterns of pearceite and polybasite in the University files, but small differences, and the mineral's association with a known selenide in the Earley specimen suggested that it was a seleniferous variety of the pearceite-polybasite series and therefore responsible for the selenium in the gold ore from Zacualpan, Mexico.

The mineral occurs only as finely disseminated grains in the Zacualpan ore, and therefore the material could not be used for a detailed study. Fortunately the Earley specimen was available to us. It yielded about one milligram of clean mineral on which almost all of the subsequent work was performed.

**The Selenium-bearing “Pearceite”**

The mineral is very brittle, making it easy to separate it by hand-picking from the associated, highly-sectile aguilarite. Fragments are iron black and like pearceite, but unlike polybasite, practically opaque, even on thin splinters. The luster is sub-metallic to adamantine on fresh surfaces, tarnishing dull with an occasional bluish cast. The mineral has one extremely difficult cleavage yielding plane surfaces, which allows grains to be oriented on an optical goniometer. Subsequent x-ray studies disclosed that the cleavage is parallel to \{001\}.

**Structural crystallography**

Cleavage fragments gave rotation and Weissenberg photographs which are identical with those reported by Peacock & Berry (1947) for pearceite,
as described below. The lattice is geometrically hexagonal, but the symmetry is monoclinic. The conventional cell has the dimensions:

\[ a = 13.00, \quad b = 7.50, \quad c = 11.99 \text{ Å}, \quad \beta = 90^\circ \]

**X-ray spectrographic analysis**

The apparatus used in the analysis of the mineral consisted of a Norelco x-ray spectrograph equipped with a vacuum sample chamber (in which the sample is inverted), a pulse height analyzer (with the baseline set at 6 volts, and the window inoperative, for all measurements) and a scintillation detector (operated at 850 volts).

About 3/4 milligrams of cleaned material was ground under alcohol to a fine powder, sucked up into a pipette and slowly dripped onto the center of the Mylar cover on the inside of a sample holder. By following a procedure of allowing the alcohol to evaporate between drops, the material was concentrated within a circular area, about 10 mm. in diameter. Figs. 4 & 5 show reproductions of the intensity vs \(2\theta\) charts obtained by traversing the counter slowly across three pertinent angular ranges of the spectrum from this sample. The peaks are well-resolved by the use of a fine (0.005") parallel plate collimator. They prove the presence of selenium and provide at sight, from a knowledge of the sensitivity of the elements, a rough estimate of the relative proportions of the major elements in the sample: Ag predominates, followed by Cu, then Sb or Se, and lastly As.

The mineral was analyzed by comparing the net peak intensity ratios Cu\(K\alpha/AgK\alpha^2\), Sb\(K\alpha/AsK\alpha\) and Cu\(K\alpha/SeK\alpha\), with the ratios obtained on standards. Both natural and synthetic pearceites were used as standards. The synthetic pearceites were prepared from mixtures of the elements (including sulphur) in stoichiometrical proportions calculated to straddle the composition of the new mineral. The mixtures were inserted in silica glass tubes, which were then evacuated and sealed. The charges were heated to melting, held at this temperature for a short period and slowly cooled. They were then ground to a fine powder to assure that the portion used for the x-ray standard was truly representative. Finally, less-than-one milligram samples were prepared for the comparison analysis. To obtain reasonably accurate estimates of the peak intensities of the mineral and standards, the time to accumulate a predetermined number of pulses (usually 32,000) was measured with the goniometer set in turn at the maximum intensity of each of the five lines. The values from the standards were used to plot working curves of the net (peak minus background) intensity ratios against the corresponding weight ratios.
**Fig. 4.** Part of spectrum from 0.7 mgr. of polybasite; 50 kv/40 ma, W, SF 8 × 0.8, TC 2, scan speed 1/4°/min.

**Fig. 5.** Same sample as in Fig. 4; 40 kv/30 ma, W, SF 32, TC 2, scan speed 1/4°/min.
SELENIAN POLYBASITE

The measured atomic ratios, and the empirical cell contents deduced from the measurements are listed in Table 1. Sulphur was obtained by

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<thead>
<tr>
<th>Measured atomic ratios</th>
<th>Empirical cell contents*</th>
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<tr>
<td>Cu/Ag</td>
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*Based on the premise that Cu + Ag = 32, Sb + As = 4 and Se + S = 22; S by difference.

difference. The results are admittedly only semi-quantitative, but they indicate that it is feasible to determine the nature of the chemical composition of a less-than-one milligram sample of a sulpho-salt mineral by x-ray spectroscopy. The results of this analysis show that Sb predominates over As and that therefore the mineral is not pearceite in the terminology of Peacock & Berry, that the Cu–Ag ratio is in general agreement with the ratio in all polybasite-pearceite minerals in that Ag predominates over Cu, and that Se accounts for a significant portion of the cell contents.

Classification of the polybasite-pearceite minerals

Polybasite and pearceite, with similar pseudo-hexagonal monoclinic form and similar compositions, 8(Ag,Cu)₂S.(Sb,As)₂S₃ and 8(Ag,Cu)₂S. (As,Sb)₂S₃, have been regarded as the Sb and As end-members respectively, of a single solid solution series.

Peacock & Berry (1947) first determined the unit cell of pearceite. They obtained values of:

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<th>a</th>
<th>b</th>
<th>c</th>
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<tr>
<td>Aspen, Colorado</td>
<td>12.64</td>
<td>7.29</td>
<td>11.90 Å</td>
<td>90°</td>
</tr>
<tr>
<td>Silver, Montana</td>
<td>12.80</td>
<td>7.39</td>
<td>11.94 Å</td>
<td>90°</td>
</tr>
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on rotation and Weissenberg films with [001] and [010] or [110] as the rotation axes on crystals from two localities. The difference in cell size is probably due to a difference in the Ag content of the (Ag,Cu) components; As and Sb account for a relatively small portion of the volume of the cell. The photographs showed hexagonal symmetry as regards the positions of reflection spots, but only monoclinic symmetry as regards their intensities. The systematically missing spectra conformed to the space group C2/m.
The unit cell of polybasite had previously been determined by Gossner & Kraus (1934) on unanalyzed material from the Guanajuato district in Mexico:

\[ a = 13.02, \ b = 7.52, \ c = 11.97 \ \text{Å}, \ \beta = 90^\circ \]

Peacock & Berry made rotation and Weissenberg studies of polybasite crystals from 5 additional localities, rotating as in pearceite, about [001] and [010] or [110]. The photographs showed the same hexagonal geometry and monoclinic symmetry as pearceite, and indicated that all the crystals have a pronounced pseudo-cell with roughly the same dimensions as the Gossner-Kraus polybasite cell (and the pearceite cell), but weak intermediate layer lines on the rotation photographs proved that all the crystals except one, have double these dimensions:

\[ a \sim 26, \ b \sim 15, \ c \sim 24 \ \text{Å}, \ \beta = 90^\circ \]

The exception was a specimen (UT - R 257) of massive crystallized polybasite from the Las Chispas mine, Sonora, Mexico on which they found that only the a and b dimensions are doubled

\[ a = 26.17, \ b = 15.11, \ c = 11.94 \ \text{Å}, \ \beta = 90^\circ \]

This represents a type that is intermediate in size between the Gossner-Kraus cell and the apparently more common, large polybasite cell with all dimensions doubled. Peacock & Berry regarded the Gossner-Kraus cell data as “partly unsatisfactory”, believing that indications of a double b-period had been wrongly attributed to twinning.

Arsenic ranged from zero to over one-half of the (Sb,As) component in the 17 analyses of polybasite available to Peacock & Berry. On the other hand, antimony comprised only a small fraction of the (As,Sb) component in the 6 available pearceite analyses and, although the analyses represented only 5 localities, the authors decided that the chemical data did not indicate a continuous chemical variation from arsenian polybasite to pearceite and concluded that it was proper to recognize the two minerals as distinct species rather than end-members of a series. The pearceite of Peacock & Berry, therefore, has the cell dimensions \( a \sim 13, \ b \sim 7.5, \ c \sim 12 \ \text{Å}, \ \beta = 90^\circ \) and the cell contents \( Z[8(\text{Ag},\text{Cu})_2\text{S}(\text{As},\text{Sb})_2\text{S}_3] \) in which \( Z = 2 \) and the (As,Sb) component is largely As. Their polybasite has cell dimensions \( a \sim 26, \ b \sim 15, \ c \sim 12 \) or 24 Å, \( \beta = 90^\circ \) (if the data of Gossner & Kraus are disregarded), but a

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\(^1\)There are two incorrect statements about the work of Peacock & Berry in a recent paper by Frondel (1963). He states: “More recently, Peacock and Berry (1947) have shown... that all of the cell dimensions of polybasite are doubled as compared to those of pearceite.” Also: “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.”
pronounced pseudo-cell has \( a \sim 13, b \sim 7.5, c \sim 12 \text{ Å}, \beta = 90^\circ \) like pearceite. The cell contents are \( Z[8(\text{Ag,Cu})_2\text{S}.(\text{Sb,As})_2\text{S}_8] \) in which \( Z = 2 \) in the pseudo-cell, and 8 or 16 in the true cells, and As varies from zero to more than one half of the (Sb,As) component. The polybasite pseudo-cells are generally somewhat larger than the pearceite cells, mainly because they usually contain more Ag relative to Cu.

In a study of pearceites and polybasites from 22 localities, Frondel (1963) confirmed the existence of the Gossner-Kraus polybasite cell (i.e. a cell with \( a \sim 13, b \sim 7.5, c \sim 12 \text{ Å} \) and Sb > As), found a pearceite with all dimensions doubled (i.e. with \( a \sim 26, b \sim 15, c \sim 24 \text{ Å} \) and Sb < As) and presented evidence to show that possibly complete mutual substitution of Sb and As occurs in both the small and the double cell (Fig. 6). This led Frondel to divide these minerals into two series. He re-defined the mineral pearceite as the end-member of one series characterized by the cell: \( a \sim 13, b \sim 7.4, c \sim 12 \text{ Å} \), and proposed the name antimonpearceite for the Sb analogue. Similarly he re-defined polybasite in terms of a second series with the double cell (\( a \sim 26, b \sim 15, c \sim 24 \text{ Å} \)), and called its As analogue arsenopolybasite. He stated that the proposed series were analogous to the enargite-stibioenargite and luzonite-famatinite series which are both \( \text{Cu}_3(\text{As,Sb})\text{S}_5-\text{Cu}_3(\text{Sb,As})\text{S}_5 \).

Frondel's classification makes no provision for species with cells which are intermediate in size, such as found by Peacock & Berry on polybasite from the Las Chispas mine, Sonora, Mexico. Frondel presumably doubted
the evidence for the intermediate cell—he tested crystals from the Las Chispas mine and obtained a value of 23.82 Å for $c[001]$, rather than the reported value near 12 Å. We had available to us a portion of the original specimen (UT — R 257) that had been studied by Peacock & Berry. It consisted of a $\frac{1}{4}$ inch aggregate of coarsely crystallized material. We confirmed the existence of the intermediate cell\(^3\) on this specimen, but we also discovered that while some areas give this cell, other seemingly identical areas are characterized by the small cell. The Las Chispas material therefore, crystallizes with the small, the double and an intermediate cell. This discovery points to a fundamental objection to Frondel's subdivision of these minerals into two series. Evidently doubled dimensions, which manifest themselves as weak intermediate layer lines on rotation photographs of the Las Chispas material, represent less-than-fundamental differences. One basis structural unit pervades the material and moreover is the dominant structural feature in all specimens of polybasite and pearceite. It has the dimensions $a \sim 13$, $b \sim 7.5$, $c \sim 12$ Å, and the cell contents $2[8(Ag,Cu)_2S.(As,Sb)_2S_3]$ with presumably complete substitution of As and Sb. In this respect Frondel's two series are not analogous to the enargite-stibioenargite and luzonite-famatinite series. Although the latter two series are identical chemically, they show no obvious similarity of structure—the enargite-stibioenargite series is orthorhombic while luzonite-famatinite is cubic or more probably tetragonal.

We believe it is desirable, in the description of these minerals, to recognize their basic similarity and return to the original classification in which pearceite and polybasite are regarded as the As and Sb end-members of one series with similar pseudo-hexagonal monoclinic form. The series is based on a structural unit with dimensions
\[
a \sim 13, \quad b \sim 7.5, \quad c \sim 12 \text{ Å}, \quad \beta = 90^\circ
\]
and composition
\[
(Ag,Cu)_{32}(Sb,As)_2S_{22}.
\]
Despite the basic similarity, small cells can be distinguished from doubled cells, and pearceites from polybasites by a close scrutiny of the powder patterns (Fig. 7). It is practical then to add to the name which signifies whether Sb or As predominates, a symbol that designates the type of cell—thus pearceite (1-1-1), where As $>$ Sb and the cell is identical with the basic structural unit, and polybasite (2-2-2), when Sb $>$ As and the cell has all dimensions doubled. The one intermediate cell which is presently known, has Sb $>$ As and only $a$ and $b$ doubled. It is practically

\(^3\)At our request, Professor L. G. Berry kindly re-examined several small fragments in his possession, with the same results.
Fig. 7. X-ray powder contact prints of low-angle reflections: Ni filtered Cu radiation; film radius = 180/\pi \text{ mm.} (2 \text{ mm. on film} = 1^\circ \theta).

1. Polybasite (2-2-2); Highland Bell mine, Beaverdell, B.C. (UT R 151).
2. Pearceite (2-2-2); Freiberg, Saxony.
3. Polybasite (2-2-1); Las Chispas mine, Sonora, Mexico (UT R 257).
4. Polybasite (1-1-1); Las Chispas mine, Sonora, Mexico (UT R 257).
5. Selenian polybasite (1-1-1); San Carlos mine, Guanajuato, Mexico (ROM M 3832).
6. Selenian polybasite (1-1-1); La Guadalupe Arcos mine, near Zacualpan, Mexico.
7. Pearceite (1-1-1); Aspen County, Colorado (UT R 451).
indistinguishable by powder pattern from a polybasite (2-2-2) from the Highland Bell mine, B.C. We propose to describe this material as polybasite (2-2-1). Under this scheme the selenian variety described in this paper would be designated as: selenian polybasite (1-1-1).

It is evident from Fig. 6, that when Sb comprises a significant fraction of the (Sb,As) component, the mineral is more commonly characterized by the double cell. When As is greatly in excess of Sb the cell is small—only one double cell in this composition range is known. This suggests that the doubling is a consequence of the presence of Sb in the structure and that the basic structure accommodates As more readily than Sb.

ACKNOWLEDGMENTS

We wish to express our thanks to Dr. J. A. Mandarino and Professor Clifford Frondel for the loan of specimens, to Mr. E. J. Brooker for doing several fire assays and advising on the x-ray spectrographic analysis, to Professor D. H. Gorman for assistance with the polished section study and to the National Research Council (of Canada) for generous financial assistance (to E.W.N.) to develop x-ray spectrographic analysis at the University of Toronto. Dr. Mandarino suggested the nomenclature used here to designate the type of cell of a member of the polybasite-pearceite series.

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