

# THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 48

JULY-AUGUST, 1963

Nos. 7 and 8

## PROUSTITE-PYRARGYRITE SOLID SOLUTIONS<sup>1</sup>

PRIESTLEY TOULMIN, 3D, *U. S. Geological Survey, Washington 25, D. C.*

### ABSTRACT

Proustite ( $\text{Ag}_3\text{AsS}_3$ ) and pyrargyrite ( $\text{Ag}_3\text{SbS}_3$ ) form a complete series of solid solutions at temperatures at least as low as  $300^\circ\text{C}$ . Evidence from natural occurrences suggests a miscibility gap at lower temperatures, but demonstration of such a gap has not been made in the field or in the laboratory.

As would be expected from the crystal structures, the  $c$ -axis length of the solid solutions is nearly constant, while the  $a$ -axis length is a function of the composition, increasing with increasing Sb content. Because of the resulting change in axial ratio, diffraction-angle separation between certain pairs of peaks in the diffraction pattern may be used directly as an indication of composition.

Study of specimens of natural ruby silvers has not revealed any examples of equilibrium two-ruby-silver assemblages. A specimen of pyrargyrite from Casapalca, Peru, has unit-cell dimensions corresponding to a composition of about 35 formula per cent  $\text{Ag}_3\text{AsS}_3$ , about twice the arsenic content of any pyrargyrite heretofore reported.

### INTRODUCTION

The extent of solid solution between the ruby silver minerals, proustite and pyrargyrite, has not previously been established satisfactorily. Miers (1888), in a very detailed study of the ruby silvers, concluded that the two minerals are "two species which may be always distinguished." He presents analyses of pyrargyrite containing up to 2.60 per cent As (17.2 formula per cent  $\text{Ag}_3\text{AsS}_3$ ) and of proustite with as much as 3.74 per cent Sb (16.2 formula per cent  $\text{Ag}_3\text{SbS}_3$ ), but states that the crystallographic elements of the minerals are not affected by composition (Miers, 1888, p. 99; Miers and Prior, 1887, p. 200).

Jaeger and van Klooster (1912) investigated the melting relations in the system  $\text{Ag}_3\text{AsS}_3$ - $\text{Ag}_3\text{SbS}_3$  by the method of cooling arrests and concluded from their thermal data and from microscopic examination of their charges that a complete series of solid solutions existed between proustite and pyrargyrite.

The system does not seem to have been studied since the introduction of  $x$ -ray diffraction methods, and the present study was undertaken in order to determine the extent of solid solution and to investigate the

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.

possibility of using the compositions of coexisting ruby silvers as a geothermometer.

Existing analyses, as well as spectrographic analyses made in connection with the present study, indicate that the ruby silver minerals are very nearly binary. Therefore the compositions of coexisting proustite and pyrargyrite, if this equilibrium assemblage is possible, should be determined by temperature and pressure alone.

#### EXPERIMENTAL METHODS

Charges were sealed in evacuated silica-glass tubes and heated in nichrome-wound muffle furnaces. Temperatures were measured potentiometrically by chromel-alumel thermocouples. The temperature uncertainty does not exceed 5° C.

X-ray diffraction studies were carried out on a Norelco diffraction spectrometer; precise cell-edge measurements were made with the Norelco counting-rate computer, using glass-slide smear mounts with NaCl as an internal standard. Ni-filtered Cu radiation was used, the wavelengths being taken as 1.54050 Å for  $\text{CuK}\alpha_1$ , 1.54434 Å for  $\text{CuK}\alpha_2$ , and 1.5418 Å for  $\text{CuK}\alpha$ . For NaCl,  $a$  was taken as 5.6399 Å at room temperature ( $26 \pm 3^\circ \text{C}$ .) by calibration against metallic silicon,  $a = 5.43062$  Å (Parrish, 1953, p. 14).

All materials were made up from the pure elements. Spectrographic analyses of the elements used show less than 0.01 per cent impurities in the silver, arsenic, and antimony, and less than 0.02 per cent in the sulfur. From the elements, crystalline  $\text{Ag}_2\text{S}$  and  $\text{Sb}_2\text{S}_3$  and vitreous  $\text{As}_2\text{S}_3$  were prepared by pyrosynthesis, and these in turn were fused together and crystallized to pure proustite and pyrargyrite. Intermediate ruby silvers were then made from the pure end-members. All syntheses were carried out in sealed, evacuated, silica-glass tubes.

#### EXISTENCE AND PROPERTIES OF SOLID SOLUTIONS BETWEEN PROUSTITE AND PYRARGYRITE

X-ray diffraction patterns of charges of composition  $\text{Ag}_3\text{AsS}_3$  and  $\text{Ag}_3\text{SbS}_3$ , quenched after having been annealed near 450° C. for several days, correspond to those of natural proustite and pyrargyrite (Table 1). The pattern for proustite agrees with that given by Wernick *et al.* (1958). After similar heat treatment, charges of intermediate composition give diffraction patterns intermediate between those of the end members. Since the character of the pattern changes continuously as a function of composition, it is concluded that a continuous solid solution series exists, at 450° C., between  $\text{Ag}_3\text{AsS}_3$  and  $\text{Ag}_3\text{SbS}_3$ . Microscopic examination confirms the homogeneity of charges of intermediate composition.

TABLE 1. POWDER PATTERNS OF SYNTHETIC PROUSTITE AND PYRARGYRITE  
Ni-filtered Cu radiation. Patterns prepared on Norelco diffractometer

Pyrargyrite				Proustite			
hkl	d <sub>calc.</sub> , Å	d <sub>obs.</sub> , Å	I/I <sub>1.0</sub>	hkl	d <sub>calc.</sub> , Å	d <sub>obs.</sub> , Å	I/I <sub>1.0</sub>
110	5.526			110	5.408	5.41	0.2
012	3.967	3.95	0.2	012	3.943	3.94	0.2
211	3.341	3.34	0.8	211	3.279	3.28	0.9
202	3.223	3.22	0.9	202	3.186	3.19	1.0
300	3.190	3.18	0.7	300	3.122	3.12	0.4
122	2.784	2.779	1.0	122	2.745	2.744	0.8
220	2.763			220	2.704		
113	2.572	2.566	0.97	113	2.555	2.557	0.7
131	2.539	2.532	0.9	131	2.489	2.490	0.7
312	2.267	2.260	0.3	312	2.230	2.230	0.2
321	2.129			104	2.117	2.111	0.02
104	2.125	2.121	0.2	321	2.086		
042	2.098			042	2.062		
410	2.089	2.085	0.1	410	2.044		
223	2.002			223	1.977		
024	1.983			024	1.972	1.971	0.1
232	1.961	1.957	0.5	232	1.926	1.925	0.3
214	1.867	1.864	0.3	214	1.852	1.854	0.1
330	1.842	1.838	0.1	330	1.803	1.800	0.07
241	1.771			241	1.735	1.734	0.09
502	1.753	1.751	0.2	502	1.720	1.720	0.07
413	1.696	1.704	0.1	413	1.670		
511	1.687			134	1.667	1.666	0.2
134	1.684	1.682	0.3	511	1.652		
422	1.671	1.669	0.2	422	1.639	1.638	0.1
404	1.611	1.609	0.2	404	1.593	1.593	0.09
152	1.599			152	1.569		
600	1.595	1.593	0.1	600	1.561	1.563	0.09
125	1.571			125	1.561		
333	1.556			333	1.531		
431	1.548			324	1.528		
324	1.547			431	1.516		
520	1.533	1.529	0.1	520	1.500	1.501	0.04
342	1.480			342	1.452		
315	1.457			006	1.450	1.448	0.07
006	1.453	1.453	0.1	315	1.445		
161	1.440			054	1.419		
054	1.438			161	1.410		
116	1.405			116	1.400	1.400	0.02
244	1.392			244	1.373		
612	1.384			612	1.357		
440	1.382			440	1.352		
235	1.365			235	1.352		
523	1.356			523	1.332	1.332	0.02
514	1.350	1.347	0.1	514	1.330		
306	1.322			306	1.315	1.314	0.02
621	1.312			621	1.285		
532	1.305			532	1.279		
226	1.286			226	1.277		
434	1.276			434	1.257		
262	1.270						
710	1.268						
425	1.255						

In order to refine the unit-cell edges of the ruby silvers, the six strongest lines in the diffraction pattern were chosen for measurement. These six lines ( (21\*1), (20\*2), (30\*0), (12\*2), (11\*3), and (13\*1) ) and the (111), (200), and (222) lines of the NaCl internal standard were determined by step-scanning over the intensity peaks at angular increments ( $2\theta$ ) of  $0.01^\circ$ , using a Norelco counting-rate computer. The positions of the ruby silver lines were corrected by comparison with the NaCl lines. The resulting six values for each sample were then used to calculate  $a$  and  $c$

TABLE 2. UNIT-CELL PARAMETERS OF SYNTHETIC RUBY SILVERS

Stated uncertainties for  $a$  and  $c$  are standard errors of estimate derived from least-squares treatment of diffraction data for six lines. Stated uncertainties for  $V_{UC}$  and  $c/a$  were calculated on the assumption that the uncertainties in  $a$  and  $c$  are independent of each other.

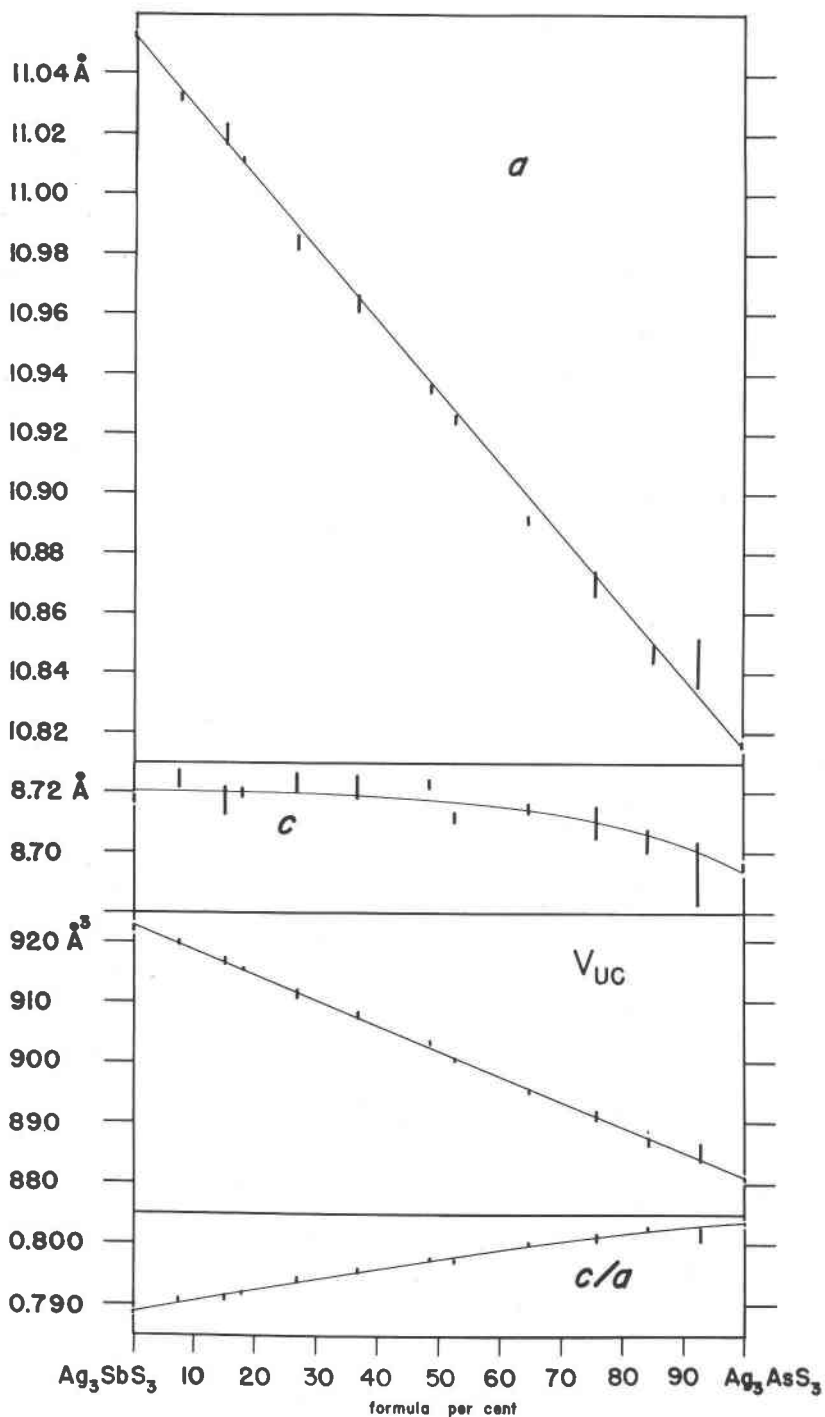
Formula per cent $\text{Ag}_3\text{AsS}_3$	$a$ , Å	$c$ , Å	$V_{UC}$ , Å <sup>3</sup>	$c/a$
0.00	$11.0520 \pm 0.0015$	$8.7177 \pm 0.0016$	$922.18 \pm 0.30$	$0.7888 \pm 0.0002$
7.50	$11.0329 \pm 0.0024$	$8.7247 \pm 0.0030$	$919.72 \pm 0.51$	$0.7908 \pm 0.0003$
15.00	$11.0198 \pm 0.0036$	$8.7170 \pm 0.0045$	$916.74 \pm 0.76$	$0.7910 \pm 0.0005$
17.93	$11.0110 \pm 0.0013$	$8.7197 \pm 0.0017$	$915.56 \pm 0.28$	$0.7919 \pm 0.0002$
26.94	$10.9840 \pm 0.0026$	$8.7234 \pm 0.0033$	$911.47 \pm 0.55$	$0.7942 \pm 0.0004$
36.88	$10.9632 \pm 0.0031$	$8.7218 \pm 0.0040$	$907.85 \pm 0.66$	$0.7956 \pm 0.0004$
48.55	$10.9351 \pm 0.0012$	$8.7320 \pm 0.0015$	$903.32 \pm 0.25$	$0.7977 \pm 0.0002$
56.62	$10.9247 \pm 0.0015$	$8.7119 \pm 0.0019$	$900.45 \pm 0.32$	$0.7974 \pm 0.0002$
64.70	$10.8914 \pm 0.0014$	$8.7149 \pm 0.0018$	$895.29 \pm 0.30$	$0.8002 \pm 0.0002$
75.88	$10.8701 \pm 0.0041$	$8.7103 \pm 0.0054$	$891.31 \pm 0.87$	$0.8013 \pm 0.0006$
84.26	$10.8466 \pm 0.0031$	$8.7039 \pm 0.0040$	$886.81 \pm 0.65$	$0.8025 \pm 0.0004$
92.76	$10.8434 \pm 0.0083$	$8.6932 \pm 0.0107$	$885.19 \pm 1.74$	$0.8017 \pm 0.0012$
100.00	$10.8160 \pm 0.0010$	$8.6948 \pm 0.0013$	$880.90 \pm 0.13$	$0.8006 \pm 0.0001$

by the method of least squares. The results are given in Table 2 and are plotted in Fig. 1.

It will be noted that the length of the  $c$ -axis remains nearly constant from one end of the series to the other, whereas the length of the  $a$ -axis changes rapidly with composition. The explanation of these relations is readily found in the ruby silver structure (Harker, 1936; Hocart, 1937),



FIG. 1. Unit cell parameters as functions of ruby-silver composition. Lengths of vertical bars represent twice the standard error of estimate for each point. The thin lines are meant only to represent reasonable fits to the sets of data points through which they are drawn.



which consists of two sets of spiral chains parallel to the  $c$ -axis. Each chain is built of alternating Ag and S atoms, and the chains of each set are interconnected by As (Sb) atoms, which are the apices of flat pyramidal  $\text{AsS}_3$  ( $\text{SbS}_3$ ) groups. Each S atom is part of a different Ag-S chain. Substituting a larger Sb atom for a smaller As atom tends to flatten

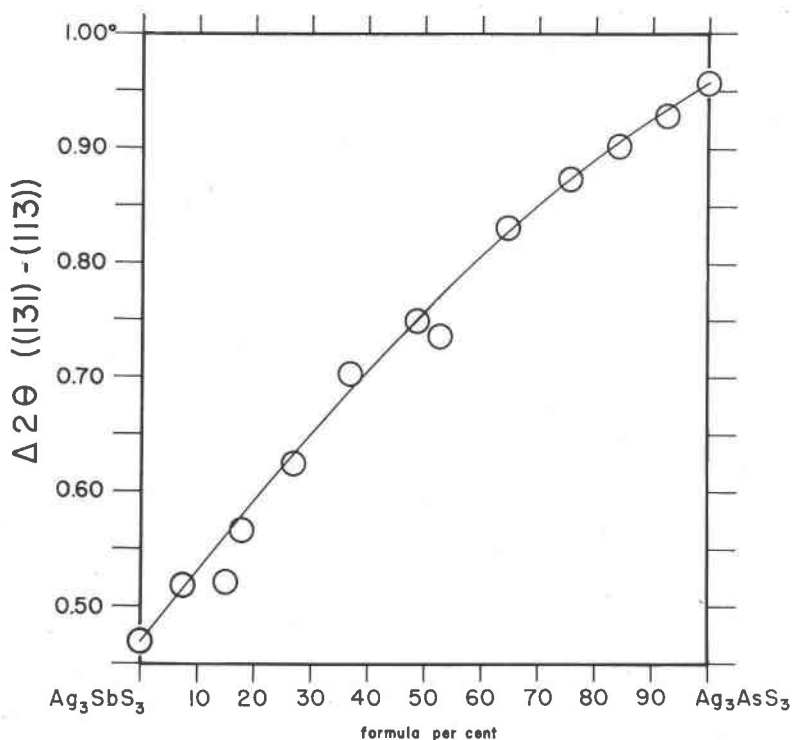


FIG. 2. Angular separation of the (13\*1) and (11\*3) diffraction peaks for  $\text{CuK}\alpha_1$  radiation as a function of ruby-silver composition.

still further the pyramidal groups, thereby increasing the separation of the chains from one another. The repeat distance parallel to the chains, on the other hand, is controlled principally by the bond angles and lengths of the Ag-S chain and so is much less affected by the Sb/As substitution. The slight decrease in the length of the  $c$ -axis at compositions more As-rich than about 1:1 seems to be real and presumably reflects deformation of the Ag-S bonds by the small As atoms.

Because of the anisotropy of change of dimension with composition, the axial ratio,  $c/a$ , changes rapidly, and different lines in the diffraction pattern change position at unequal rates. For this reason, the angular

separation of certain pairs of diffraction lines can be used directly as a measure of composition in the proustite-pyrargyrite series. The pair, (11\*3) and (13\*1), have proved especially useful, and a plot of angular separation versus composition (Fig. 2) permits approximate determination of the composition of a ruby silver. For more precise results, the cell-edge lengths may be determined from the d-spacings of several lines and compared with the data in Fig. 1 or Table 2.

The unit-cell volume is seen to be a linear function of mol fraction, within limits of error of measurement. An earlier incorrect statement to the contrary (Toulmin, 1958) resulted from fortuitous agreement of preliminary data with a calculated model.

#### PHASE RELATIONS

*Solvus.* The evidence suggesting a miscibility gap in the proustite-pyrargyrite system consists of 1) the supposed restriction of natural ruby silvers to compositions within 17 formula per cent of the end members, and 2) the supposed coexistence of two ruby silvers in nature. Particularly remarkable is the description of an intimate intergrowth of proustite and pyrargyrite from the San Antonio mine, Casapalca, Peru (Orcel and Plaza, 1928, p. 221 and Pl. VI A). The writer has not been able to obtain a specimen of the material illustrated by Orcel and Plaza, but has examined a specimen of pyrargyrite from the same mine, kindly furnished by the late Professor H. E. McKinstry of Harvard University. This material appears homogeneous in polished section under the microscope. Its x-ray diffraction pattern is that of a single-phase ruby silver, except for a broadening and incipient splitting of the (30\*0) peak. No other peak of the pattern is split, though some other peaks (*e.g.*, (13\*1)) are more sensitive than (30\*0) to variations in the ratio As/Sb. If (30\*0) is neglected, the pattern yields a value for *a* of 10.966 Å, indicating a composition of about 35 formula per cent  $\text{Ag}_3\text{AsS}_3$ , about twice the maximum arsenic content previously reported for pyrargyrite. Semiquantitative spectrographic analysis (Table 3) corroborates the high As content.

Examination of selected ruby-silver specimens in the collection of the U. S. National Museum has not brought to light any hand specimens containing more than a single ruby silver. Different specimens from the same mine or district commonly have different ruby silvers, however. Table 3 shows the results of semiquantitative spectrographic analyses of a number of natural ruby silvers. The content of elements other than Ag, As, Sb, and S is low except in sample 16991, which contained a little calcite. Elements characteristic of gangue minerals constitute a large part of the "impurity" in all the specimens. These analyses thus support

the inference that natural ruby silvers do not contain in solid solution large amounts of elements other than those represented by the components  $\text{Ag}_3\text{AsS}_3$  and  $\text{Ag}_3\text{SbS}_3$ . A consequence of this is that the  $x$ -ray data for the synthetic ruby silvers may safely be applied to the determination

TABLE 3. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES OF NATURAL RUBY SILVERS

Figures are in weight per cent and reported to the nearest number in the series 7, 3, 1.5, 0.7, 0.3, 0.15, etc. (geometric group midpoints). Comparisons of this type of semi-quantitative data with results of quantitative methods indicate an empirical probability of about 60 per cent that the analytical value will fall within the assigned group. Helen Worthing, analyst.

	A	B	C	D	E	F
Ag	>10	>10	>10	>10	>10	>10
As	0	0	7.	>10	>10	>10
Sb	>10	>10	>10	0.7	7.	>10
Be	0.003	0.00015	0	0.00015	0	0
Cr	0	0.0003	0.0003	0.0003	0.0003	0.0003
Cu	0.03	0.03	0.03	0.003	0.003	0.07
Ge	0.003	0.03	0	0	0	0
Mo	0	0	0	0	0.0007	0
Ni	0.003	0.007	0	0	0.003	0.007
Pb	0.007	0.07	0.00015	0	0.015	0.015
Sn	0	0.0007	0.0007	0	0	0.0007
Zn	0	0.03	0	0	0.03	0
G <sup>1</sup>	0.01	0.1	0.03	0.007	1	0.3

A. Pyrargyrite, Colquechaca, Bolivia. U. S. Natl. Museum, spec. no. C-779 Sample was a crystal from a vug.

B. Same specimen as A. Sample was from drusy coating.

C. Pyrargyrite, La Luz Mine, Guanajuato, Mexico. USNM no. R-1073.

D. Proustite, Chanarcillo, Chile, USNM no. R-1078.

E. Proustite, La Suz (*sic*) Mine, Guanajuato, Mexico. USNM no. 16991.

F. Pyrargyrite, San Antonio Mine, Casapalca, Peru. Specimen furnished by the late Prof. H. E. McKinstry, Harvard University.

The following elements were looked for but not detected: Na, K, P, Au, Bi, Cd, Ce, Co, Cs, Dy, Er, Eu, Ga, Ge, Hf, Hg, Ho, In, Ir, La, Li, Lu, Nb, Nd, Os, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sc, Sm, Ta, Tb, Te, Th, Tl, Tm, U, V, Y, Yb, Zr.

<sup>1</sup> G is the total of the following elements: Si, Al, Fe, Mg, Ca, Ti, Mn, B, Ba, Sr, W.

of natural ruby silvers. Table 4 shows the values of  $\Delta 2\theta_{13^*1-11^*3}$  found for a number of natural ruby silvers and the compositions implied by them.

The experimental results of the present study clearly confirm the conclusion of Jaeger and van Klooster (1912) that there is complete miscibility between proustite and pyrargyrite at solidus temperatures. Experiments in search of a miscibility gap at lower temperatures have been



made by heating both a homogeneous solid solution and a mechanical mixture of end members at 450°, 400°, 350°, 300° and 135° C. for periods up to 17 months. Both the solid solution and the mixture were approximately 50 formula per cent  $\text{Ag}_3\text{AsS}_3$ . The mechanical mixture homog-

TABLE 4. ANGULAR SEPARATIONS OF THE DIFFRACTION PEAKS (13\*1) AND (11\*3) OF NATURAL RUBY SILVERS FOR  $\text{CuK}\alpha$  RADIATION, AND THE COMPOSITIONS DERIVED THEREFROM

Specimen	$\Delta 2\theta$	Formula per cent $\text{Ag}_3\text{AsS}_3$
Pyrargyrite, Colquechaca, Bolivia, U. S. Natl. Mus., spec. no. C779	0.47°	$\frac{1}{2}$
Pyrargyrite, Colquechaca, Bolivia, USNM no. R-8051	0.47°	$\frac{1}{2}$
Pyrargyrite, Soracaya Mine, Bolivia, USNM no. C4996	0.49°	4
Pyrargyrite, La Luz Mine, Guanajuato, Mexico, USNM no. R1073	0.49 <sub>5</sub> °	5
Pyrargyrite, Little Emma Mine, Lump Gulch District, Jefferson County, Montana, USNM no. 11151	0.48°	2
Pyrargyrite, Montana, USNM no. 11926	0.47 <sub>5</sub> °	1 $\frac{1}{2}$
Pyrargyrite, Lander County, Nevada, USNM no. 13451	0.54 <sub>5</sub>	13
Proustite, La Suz [ <i>sic</i> ] Mine, Guanajuato, Mexico, USNM no. 16991	0.94 <sub>5</sub>	97
Proustite, Chañarcillo, Chile, USNM no. R1078	0.95	98

enized in one month at 450° and 400° C., and in 4 months at 350° C. After 14 months at 300° C., the solid solution showed no signs of exsolution, and the mixture had largely homogenized. Seventeen months at 135° C. produced little reaction in a mechanical mixture of pure proustite and pyrargyrite.

In this connection, it is interesting to note that homogenization of the mixture seems to be progressing in an unexpected fashion. The charge after 4 months at 300° consisted of two phases in unequal amounts, the less abundant having a composition of nearly pure pyrargyrite (about 1.5 formula per cent proustite component), and the more abundant having a composition of about 64 formula per cent proustite component. The overall composition of the batch is 50.0 formula per cent proustite component. After 14 months, still less pyrargyrite was present, and the major phase contained about 55 formula per cent  $\text{Ag}_3\text{AsS}_3$ . The inference seems inescapable that the pyrargyrite phase is dissolving directly in the proustite phase with practically no concomitant solution in the other direction. Thus the larger, heavier atoms of Sb seem to be more mobile than the smaller, lighter atoms of As. No satisfactory explanation for this phenomenon has yet come to mind.

*Melting.* Jaeger and van Klooster (1912) report sharp melting tempera-

tures for all compositions in the system  $\text{Ag}_3\text{SbS}_3\text{-Ag}_3\text{AsS}_3$ . Their data suggested a melting diagram of a binary system with complete miscibility in liquid and solid states and a minimum temperature of crystallization at an intermediate composition. They were unable, however, to detect any separation between liquidus and solidus, although such a separation must exist in such a system at all compositions except those of the end members and the minimum point.

Attempts to check Jaeger and van Klooster's diagram by the method of heating and cooling arrests had to be abandoned because of the severe difficulties presented by undercooling of the melt. The experiments were performed by heating and cooling the tube in an electric furnace and recording the emf and a chromel-alumel thermocouple whose bead was placed in a "dimple" in the sealed, evacuated silica-glass tube containing the charge. The emf was recorded every 5 seconds on a variable-range, variable-span recording potentiometer so adjusted that the entire chart width (11 inches) represented 10 mv. In a typical experiment, a charge consisting of pure proustite was heated until a very slight break in the curve of temperature vs. time indicated melting between  $490^\circ\text{C}$ . and  $497^\circ\text{C}$ . The charge was kept well above this temperature for several hours and then cooled slowly. Crystallization commenced only when the temperature had fallen to  $418^\circ\text{C}$ .; the latent heat released raised the temperature to  $430^\circ\text{C}$ . in about 15 seconds, where it remained for about 15 more seconds before dropping very rapidly to the temperature of the furnace. The supercooling could be reproduced quantitatively. Even vigorous agitation at  $440^\circ\text{C}$ . did not initiate crystallization of the melt, which was surprisingly nonviscous.

Jaeger and van Klooster (1912, pp. 267-268) obtained a crystallization temperature by the method of cooling arrests that agrees well with the temperature of *melting* found in the present study for proustite. No verified explanation for the apparent absence of supercooling in their experiments can be given, but the supercooling in the present work may be related to the high degree of purity of the reagents or to the fact that the present experiments were carried out in vacuo rather than under a nitrogen atmosphere, as was done by Jaeger and van Klooster.

Because of the very limited geologic interest of melting relations in this system, further investigation along these lines was temporarily abandoned.

*Inversions.* The rare minerals, pyrostitpnite and xanthoconite, are naturally occurring dimorphs of pyrargyrite and proustite and have been synthesized in aqueous and other media (Weil and Hocart, 1953; Béland, 1946; Peacock, 1947). They did not form in the experiments reported

in this paper. If these minerals are truly stable at all, their stability field(s) must lie at low temperature, for ruby silver solid solutions are stable at the solidus in the system,  $\text{Ag}_3\text{SbS}_3\text{-Ag}_3\text{AsS}_3$ . It is, of course, possible that other elements enter and stabilize pyrotilpnite and xanthoconite; existing analyses do not support such a view, but the data are old and few.

#### CONCLUSIONS

The following conclusions may be drawn from the present study:

1) The ruby silvers form a complete solid solution series from solidus temperatures down at least to 300° C.

2) The composition of synthetic ruby silvers can be determined with an accuracy of 2-3 per cent by *x*-ray measurements, if *a* is found by least-squares analysis of the six strongest lines. Measurement of the angular separation of (13\*1) and (11\*3) yields the composition with an accuracy of about 5 per cent.

3) Since natural ruby silvers are apparently nearly binary solid solutions of the components  $\text{Ag}_3\text{AsS}_3$  and  $\text{Ag}_3\text{SbS}_3$ , and since the end-member minerals, proustite and pyrargyrite, give *x*-ray diffraction patterns identical to those of the corresponding synthetic phases, the same *x*-ray methods should be applicable to the determination of the composition of natural ruby silver solid solutions.

4) The binary nature of the series also implies that if two ruby silvers can in fact coexist stably, their compositions will be fixed by the temperature and pressure alone. The temperature at which such an assemblage could form, however, would have to be considerably less than 300° C., and no conclusive evidence for it seems to be available.

#### ACKNOWLEDGMENTS

I am grateful to my colleagues Paul B. Barton, Jr., E-an Zen, and Philip M. Bethke for helpful and stimulating discussions. Mrs. Shirley K. Mosburg provided valuable assistance in making and measuring many diffraction charts. Barbara L. Hammond helped with some of the *x*-ray work, and D. E. Appleman devised the computer program and carried out the calculations on the Burroughs 220 digital computer. P. B. Barton, Jr., E. H. Roseboom, Jr., and D. E. Appleman read the manuscript and suggested notable improvements.

#### REFERENCES

- BÉLAND, RENÉ (1946) Synthesis of the silver sulpho-minerals in alkali sulphide solutions. Ph.D. thesis, Univ. of Toronto.
- HARKER, DAVID (1936) The application of the three-dimensional Patterson method and

- the crystal structures of proustite,  $\text{Ag}_3\text{AsS}_3$ , and pyrargyrite,  $\text{Ag}_3\text{SbS}_3$ . *Jour. Chem. Physics*, **4**, 381–390.
- HOCART, RAYMOND (1937) Schéma structural de la proustite et de la pyrargyrite. *Acad. Sci. (Paris) Comptes rendus*, **295**, 68–70.
- JAEGER, F. M. AND H. S. VAN KLOOSTER (1912) Studien über natürliche und künstliche Sulfoantimonite und Sulfoarsenite. *Zeit. anorg. Chemie*, **78**, 245–268.
- MIERS, H. S. (1888) Contributions to the study of pyrargyrite and proustite. *Mineral. Mag.* **8**, 37–102.
- AND G. T. PRIOR (1887) On a specimen of proustite containing antimony. *Mineral. Mag.* **7**, 196–200.
- ORCEL, J. AND G. R. PLAZA (1928) Étude microscopique de quelques minerais métalliques du Pérou. *Soc. franç. mineral. Bull.*, **51**, 213–246.
- PARRISH, WILLIAM (1933) X-ray reflection angle tables for several standards. *Philips Lab., Res. Lab. Tech. Rept.* **28**.
- PEACOCK, M. A. (1947) Artificial proustite and xanthoconite: *Univ. Toronto Studies, Geol. ser.*, **51**, *Contr. Canad. Mineralogy*, 1946, 85–87.
- TOULMIN, PRIESTLEY 3d (1958) Preliminary report on the system  $\text{Ag}_3\text{SbS}_3$ – $\text{Ag}_3\text{AsS}_3$  (abs). *Geol. Soc. Am. Bull.* **69**, 1769.
- WELL, RENÉ AND RAYMOND HOCART (1953) Recherches expérimentales sur la formation des minerais d'argent. *C. R. Congrès soc. savantes, Toulouse, sect. sci.* 183–188.
- WERNICK, J. H., S. GELLER AND K. E. BENSON (1958) Synthetic proustite,  $\text{Ag}_3\text{AsS}_3$  *Anal. Chem.* **30**, 303.

*Manuscript received, January 14, 1963; accepted for publication, February 16, 1963.*