

110M
637

THESIS

Subject AN INVESTIGATION OF ARGENTIFEROUS GALENA.

Name ARVID E. NISSEN.

UNIVERSITY OF
MINNESOTA
LIBRARY

"AN INVESTIGATION OF ARGENTIFEROUS GALENA ORES".

A Thesis Submitted to the Faculty of the
Graduate School of the University of Minnesota

by
Arvid E. Nissen

In partial fulfillment of the requirements
for the degree of Master of Science.

1914

REPORT
of
COMMITTEE ON THESIS

THE undersigned, acting as a committee of
the Graduate School, have read the accompanying
thesis submitted by Arold E. Nissen
for the degree of Master of Science
They approve it as a thesis meeting the require-
ments of the Graduate School of the University of
Minnesota, and recommend that it be accepted in
partial fulfillment of the requirements for the
degree of _____

Samuel H. Hoyt
Chairman

W. H. Emerson

a. w. Johnston

191

UNIVERSITY OF
MINNESOTA
LIBRARY

169591

Nov 23 1914 A. 72

An Investigation of Argentiferous
Galena Ores.

Preface

- A. Review of Literature
- B. Present Work

I. Methods Employed

- a. Preparation of Melts
- b. Thermal analysis
- c. Micrographical analysis
- d. Chemical analysis
- e. Microscopical examination

II. Results Obtained

- a. Synthetic Melts
- b. Natural ores

C. Conclusions.

The object of this investigation is to study the manner of the occurrence of silver in argentiferous galena.

Finlayson¹ states that "a considerable number of specimens of galena were examined from deep workings but in none of these could any silver or silver bearing mineral be identified by any etching reagent."

¹Finlayson, Ec. Geol. Vol. 5, p. 727

A question here suggests itself as to what mineral of silver may be expected to occur in galenas. If the silver ore is primary, and considering the genesis of galena deposits as being a precipitation of Pb, Ag, Cu and Fe from hot ascending magmatic waters, it seems that the sulphide, argentite, is the mineral that could be most reasonable expected to occur. Friedrich² has partially worked out the constitution diagram galena - argentite and found the compositions between 2% galena and 8% argentite to consist of heterogeneous mixtures of practically pure galena and argentite. He gives the melting point of Pbs as 1114°C, Ag₂S as 835°C and the eutectic composition as 77% Ag₂S at 630°C. An evolution of heat, which becomes very weak toward the galena end of the diagram, was recorded at 175°C. There is no entectic structure under 5% Ag₂S. No limits of solid solution are given.

For the purpose of comparing argentite in the ores with a mineral that was definitely known to be argentite, artificial melts were made of lead sulphide and silver sulphide. The lead sulphide was Wisconsin galena free from silver and other impurities and galena concentrates from tables. The latter had some silicious impurities as well as silver. The argentite was produced synthetically by boiling chemically pure silver foil in flower sulphur. The silver was first weighed and boiled directly in a No.0 graphite crucible for about 20 minutes. Then 40 gm. of galena was poured in on top, the excess S being allowed to remain. The crucible was covered with a tight fitting silica cover and placed in an air-gas furnace of the G. Meker and Cie type, which had been previously heated to about 1200°C. About 15 minutes were required for melting. Then the hot crucible and melt was transferred rapidly without pouring to a silica crucible, which had been heated previously on top of the furnace. A cover was put on and in this manner the melts cooled slowly to room temperature in about 40 minutes. Some of the melts were chill cast in order to note the effect on the texture of the galena.

² Friedrich, Metallurgie, Vol 4, p 479, 1907

During the fusion of the ores, the excess sulphur came off as heavy fumes of SO_2 , but the atmosphere in the crucible was plainly reducing. Small dots of S were discernable on the polished sections. These disappeared when the specimen was heated in a gas flame.

A thermal analysis was commenced in order to study the constitution and to construct at least the lead rich end of the constitution diagram, when the work of Friedrich¹ was discovered. The air-gas furnace was used to make the melts and the cooling curves were obtained with a platinum - platinum rhodium thermal couple and a Siemens and Halske millivoltmeter. The couple was cased in a silica tube closed at one end. Difficulties were experienced due to the breaking of the quartz casing which allowed the gases to attack the elements. A base metal element of nickel and constantan was substituted. With the latter couple, an external resistance was needed on account of the high electromotive force of this element. However this couple was also unsatisfactory as it could not withstand the high temperatures of the galena rich melts.

Heat treatment for micrographical analysis was employed on a series of the artificial melts. An electric tube furnace of the Herous type with variable resistance was used. A temperature range of $1200^{\circ}C$ was possible and the furnace could easily be kept constant, within 10° , at lower temperatures for two hours. The temperature readings were obtained with a platinum-platinum rhodium thermal couple and a Siemens and Halske millivoltmeter. The annealing was carried on for periods of 45 to 85 minutes. The specimen was in a thin layer of asbestos and bound with a wire, one end of which protruded from the furnace. To guard against oxidation, the specimen was placed in a graphite crucible and large pieces of charcoal placed in the furnace on both sides. On quenching, the charcoal was removed, the specimen quickly pulled out by means of the wire and plunged into ice water at $0^{\circ}C$. The quenching from

I. loc. cit. p. 2

900°C was complete in about 4 seconds.

All of the ores were assayed for silver by the crucible method and checked by the scorification method. The results checked very closely and in each case the average was taken. The composition of the synthetic melts was calculated from the known weight of silver, calculated to argentite (87.06Ag), and from the known weight of galena taken.

For microscopical examination, the specimen was ground down to a flat surface on a piece of coarse emery paper on a glass plate. This surface was further ground on successive grades of Hubert paper, starting with the coarsest, No.2, and turning the specimen thru 90° for each succeeding paper finishing with No.000. During the polishing, the rouge was lightly applied, otherwise it completely filled the cracks, leaving considerable iron oxide which was attacked by the acid on etching. The oxide marred the etch and required a long wash to remove. After washing, the specimens were rinsed in alcohol and wiped dry. After trying iodine, hydrochloric acid, picric acid and nitric acid, the latter was found to be the only etching reagent that could be used successfully to develop the structure. Cold concentrated acid was used for the natural ores and warm 50% acid for the melts. This distinction was necessary as the melts etched very slowly in cold concentrated acid. The acid oxidized the galena surface dark, leaving the argentite light.

Two microscopes were used, a small Campbell-Leitz and a Guertler-Leitz of the LeChatelier type. The first was used for preliminary examination at low magnifications (52 to 282) with both oblique and vertical illumination. The second was used for final examination at high magnification (64 to 1500) using oil immersion lenses.

Microphotographs were taken with the Guertler-Leitz microscope camera. Seed's Process plates were used with the ordinary Eastman Pyro developer and hypo fixing bath. A blue glass light filter was used which fixed the proper time of exposure as 15 and 20 seconds for high and low power respectively.

The results obtained from this investigation are listed below. Fig. I gives the melts and their composition, together with the numbers of the microphotographs, illustrating the structure and appearance of galena and argentite.

| Melts | Composition | Illustration |
|-------|----------------------------------|----------------------|
| 1 | PbS 99.38, Ag ₂ S .62 | Plate A Fig. 1 and 2 |
| 2 | " 98.86 " 1.14 | " A " 3 and 4 |
| 3 | " 98.30 " 1.70 | " B " 5 and 6 |
| 4 | " 97.21 " 2.79 | " B " 7 and 8 |

Fig. I

The argentite is the white constituent and appears as a circular or irregular mass and generally has a hollow center. Argentite may be easily distinguished from the other white sulphides and galena, by determining the relative hardness by means of a fine cambric needle. Evidence of a eutectic for these compositions was not found. The argentite may be coated dark on long deep etching when it is necessary to repolish slightly on a chamois skin before it can again be readily differentiated. However, the latter is not very satisfactory, it being better to repolish on the rouge wheel and re-etch to the proper depth. The dark areas in the pictures are pits. The galena, which is silvery and brightly metallic before etching, takes on a dark gray or brown film, which, if the etch is light, can readily be removed by polishing on a chamois skin. A polyganal structure of galena was obtained from three of the ores on etching (Figs. 17, 18 and 19, plate E). In Figs. 17 and 18, the lenses did not allow sufficiently sharp definition to distinguish any inter grain filling. However, in Fig. 19, the argentite, while not appearing as a continuous filling, outlines the galena very suggestively into polyganal areas and the filling can be very plainly traced to the large argentite segregate in the center of the figure.

Plate A

Figure 1. x 140 Remelted galena containing
 .62% Ag_2S 99.38% Pbs.

Figure 2. x 1000 Same as Figure 1

Figure 3. x 78 Remelted galena containing
 1.14% Ag_2S , 98.86% Pbs.

Figure 4 x 580 Same as Figure 3

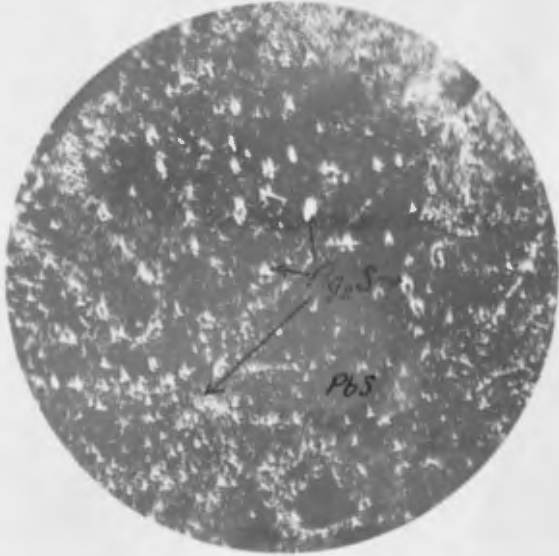


Figure 1

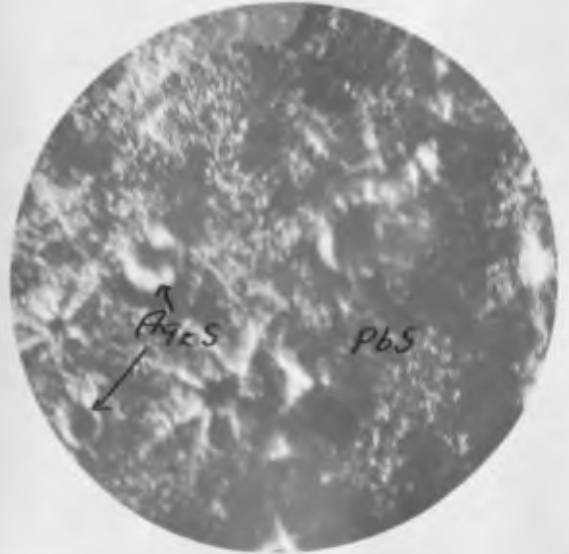


Figure 2

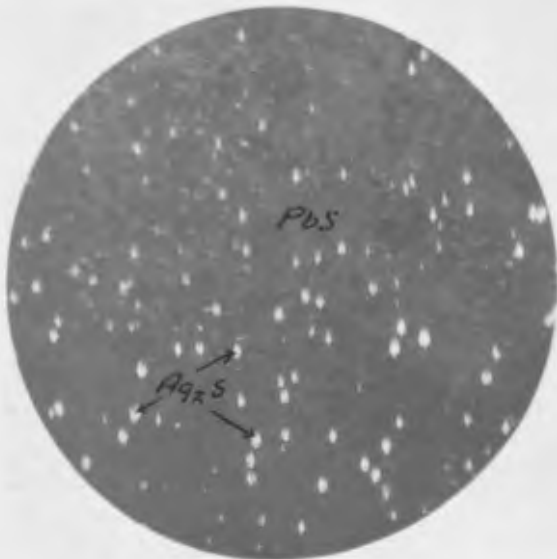


Figure 3

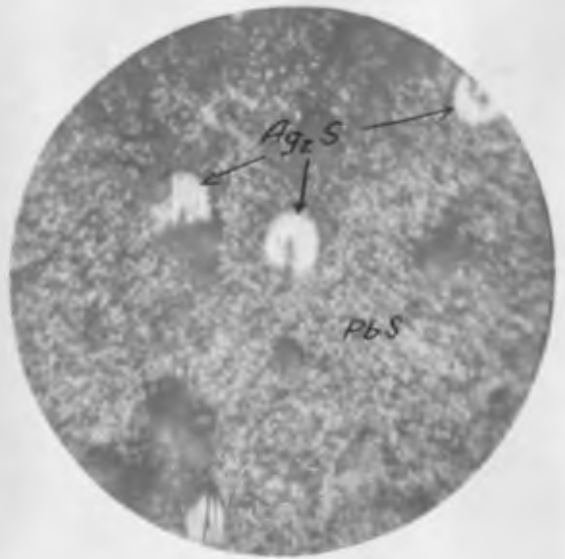


Figure 4

Plate B

Figure 5 x 78 Remelted galena
containing 1.70% Ag_2S , 98.30% PbS .

Figure 6 x 580 Same as Figure 5

Figure 7 x 78 Remelted galena
containing 2.79% Ag_2S , 97.21% PbS .

Figure 8 x 580 Same as Figure 7

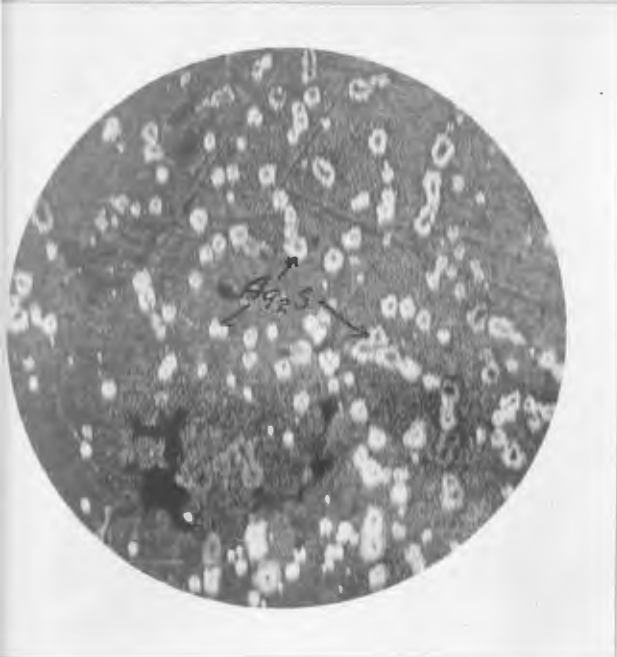


Figure 5

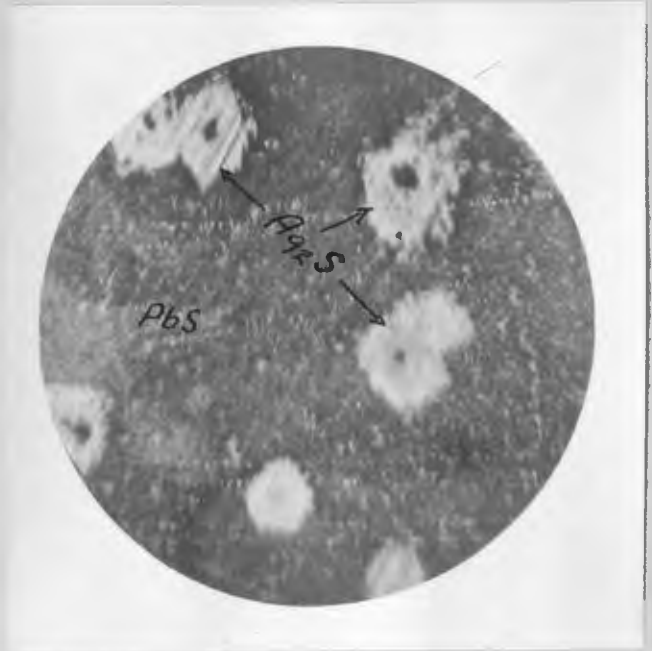


Figure 6



Figure 7

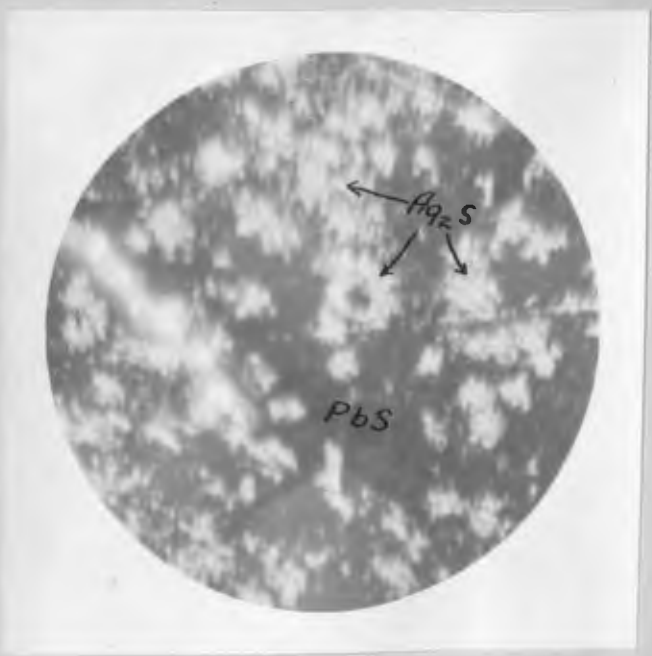


Figure 8

From the argentite segregations it would seem that the limit of solid solution at ordinary temperatures is inside of .6%. Later, in the discussion of the natural ores, it is shown that this runs to at least .2% Ag_2S . To ascertain the limits of solid solution and the structure of the argentite at higher temperature melts 1, 2 and 3 were annealed and quenched from temperatures as indicated in Fig. 2. In no case was

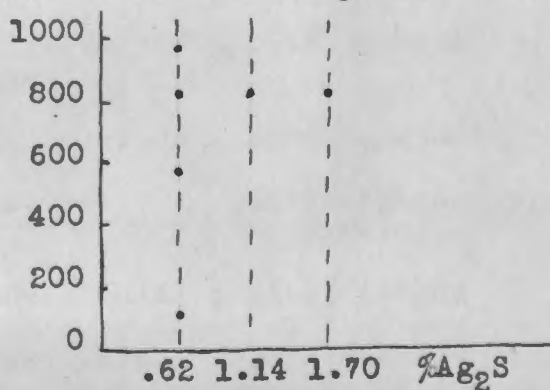


Fig. 2

there any evidence of solid solutions and all above 800°C showed evidences of having been in the partly liquid zone. In no case did the melt take any impurity from the graphite crucible. The quenched galena was, as a whole, coarsely crystalline with small areas of a finer texture. The argentite showed a prevailing ring or doughnut structure, which was in many cases elongated as in the slowly cooled specimens. Plate D, Fig. 16 shows the eutectic structure of a slowly cooled remelted galena concentrate. The round grey mineral in the eutectic is a silicate impurity in the concentrate.

The natural ores examined are represented in

Fig. 3

| No. | Place | Impurities | oz. Ag | %Ag ₂ S |
|-----|-----------------------------------------|---------------------------------------------|--------|--------------------|
| 100 | Inyo Co. California | pyrite, sphalerite, gangue, chalcopyrite | 176.80 | .69 |
| 101 | Eureka Dist., Nev. | pyrite, gangue | 200.40 | .78 |
| 102 | Mendota Mine, George- town, Colorado | sphalerite, quartz pyrite | 95.20 | .367 |
| 103 | Comet Mine, Jefferson Co., Montana | pyrite, gangue | 51.80 | .195 |
| 104 | Cleer Creek, Colorado | pyrite, quartz | 22.40 | .08 |
| 105 | Ten Mile District, Montana | quartz, sphalerite, pyrite | 63.94 | .253 |
| 106 | Cuevas Alemaña, Spain | pyrite, gangue | 101.04 | .392 |
| 107 | Idaho Springs, Colo. | sphalerite, quartz, pyrite | 31.72 | .12 |

Figure 3

Plates C and D, figs. 9, 10, 11, 12, 13, 14 and 15, and plate E, fig. 19, illustrate the occurrence of argentite in native ores. In figs. 9 and 10, the argentite occurs in and near the fissures in the ore and is therefore believed to be secondary where the galena has been replaced by a secondary mineral. This replacement or oxidation appears to have been preceded by an intense shattering of the ore. The argentite occurs at the contact of the alteration and in the fissures and has evidently been introduced at a later period. Some argentite also occurs in the galena away from fissures and may be primary. However, a section at 90° to the one shown may disclose the Ag₂S as connected to a fissure, and thus show an entire secondary origin. Fig. 12 shows argentite. Compared with the synthetic

Plate C

Figure 9 x 78 Ore from Eureka, Nevada.

Shows galena replaced by secondary mineral and secondary and possibly primary argentite. .78% Ag_2S

Figure 10 x 78 Same as Figure 9

Figure 11 x 78 Ore from Mendota Mine,

Georgetown, Colo. .367% Ag_2S

Figure 12 x 1000 Ore from Ten Mile District,

Montana. .253% Ag_2S

Plate C.

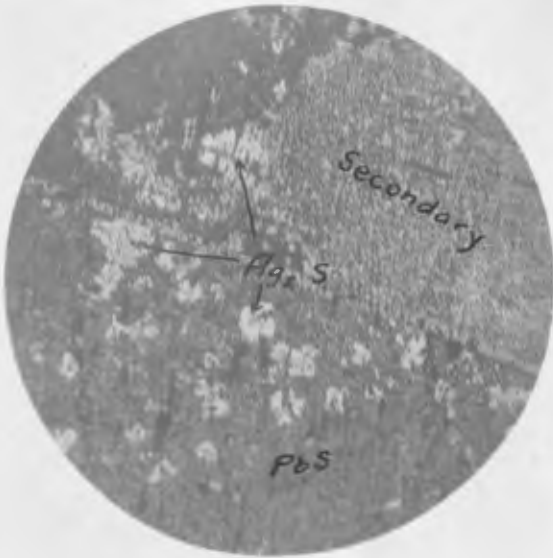


Figure 9

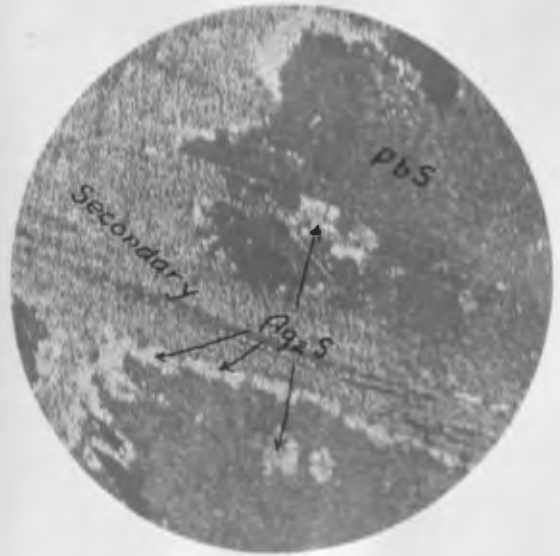


Figure 10

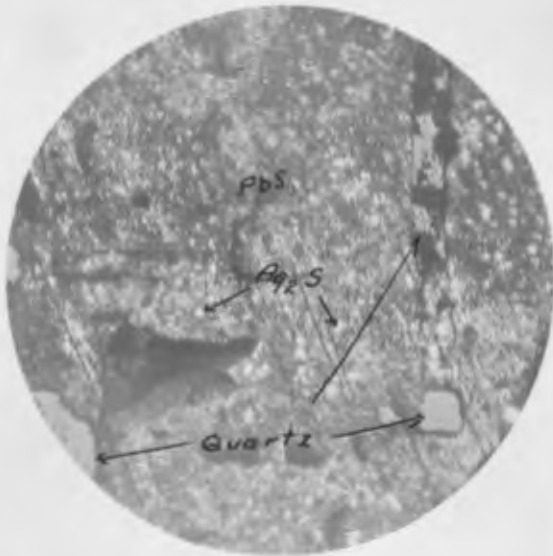


Figure 11

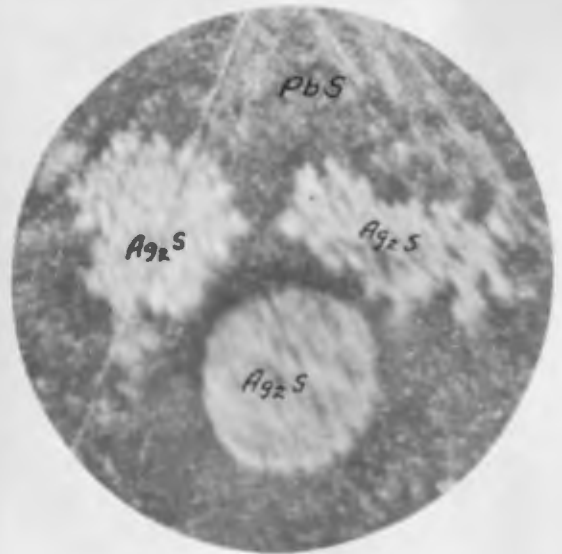


Figure 12

Plate D

Figure 13 x 140 Ore from the Comet Mine,
Jefferson Co., Montana. .195% Ag_2S .

Figure 14 x 1000 Same as Figure 13

Figure 15 x 78 Ore from Idaho Springs, Colo.
Shows a probable secondary occurrence of Ag_2S
.12% Ag_2S

Figure 16 x 130 Galena concentrate melt.
Shows the eutectic structure. The gangue is
an impurity in the concentrate.

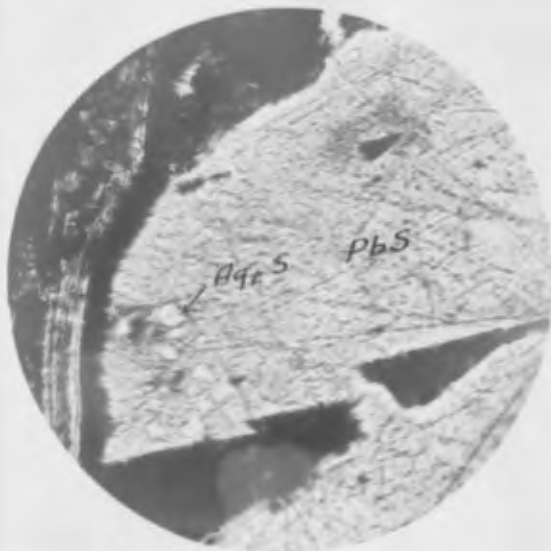


Figure 13

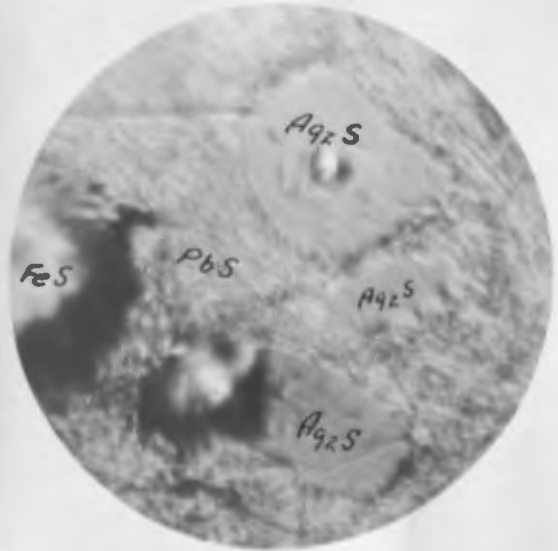


Figure 14

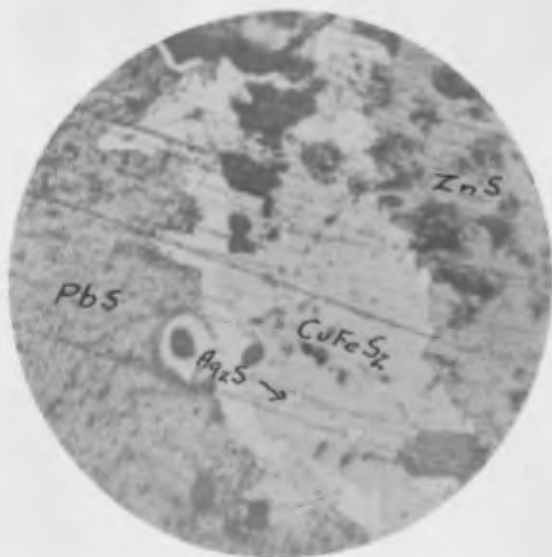


Figure 15

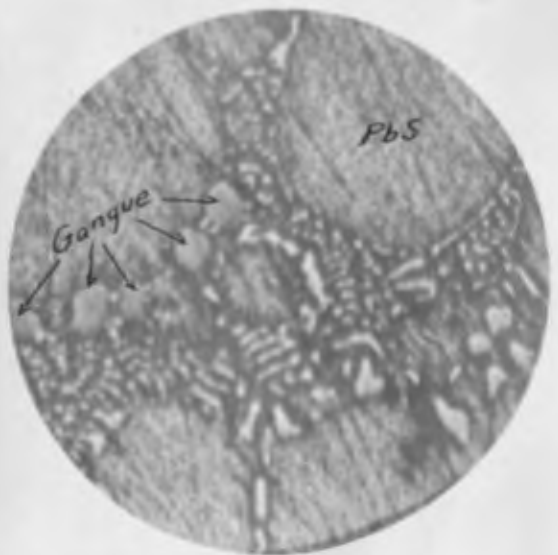


Figure 16

Plate E

Figure 17 x 1000 Ore from Mendota Mine,
Georgetown, Colorado . Shows a possible
argentite filling between galena grains.
.367% Ag_2S .

Figure 18 x 140 Ore from Comet Mine
Jefferson Co., Montana.
Same as Figure 17 .195 % Ag_2S

Figure 19 x 1000 Ore from Cuevas Almeria
Spain. The argentite discernable in this ore
is plainly a polyganal grain filling emanating
from an argentite segregation. .392 % Argentite



Figure 17



Figure 18

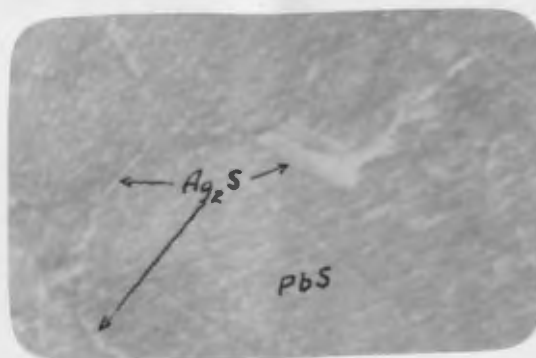


Figure 19

melts (Plate B, Fig.6) a similarity is readily noted. The rounded form of argentite is very characteristic of all the melts, altho the irregular structure is not at all uncommon. (Fig.8, Plate B) Fig.11, Plate C, shows the occurrence of argentite in a medium grade ore. The picture does not give an idea of the average silver content of this ore as it represents a segregated area. The dark areas show the cubic cleavage of galena. They are pits, gauged out in the polishing. Fig.13 shows a small group of argentite in a coarsely crystalline galena. The same, under higher magnification, is seen in Fig.14. No definite forms of argentite are found, due to hindered crystal growth, in any of these ores. The pyrite on the left shows cubic crystallization. A pit is noted in the center of one of the argentite masses, which corresponds to the structure of the melts. Fig.15 illustrates a probable secondary or later occurrence of argentite. This also represents a segregation of argentite. The galena and sphalerite are here apparently of contemporaneous origin. They have been shattered and a solution carrying Cu, Fe and Ag has entered, depositing argentite and chalcopyrite. The occurrence of argentite in the chalcopyrite and the sharp boundaries are noteworthy as is the doughnut structure of the argentite in the galena. No argentite was found in the examination of the sections of ore, No. 104, altho the assays show silver. As ore No.104 contains only 22.4 oz per ton (.08% Ag_2S) of silver, it may be inferred that Ag_2S and Pbs are here in solid solution or that the surface polished is one free from any argentite.

From this investigation, the following conclusions may be drawn:

1. That silver occurs as argentite in some primary and in some secondary argentiferous galena ores.
2. That the limit of solid solutions at atmospheric temperatures is below .2% Ag_2S and below .6% Ag_2S at 600°

to 800°C.

3. That the entectic is not recognized in concentrations as low as 2.70% Ag_2S .

This problem was outlined by Messrs. Hoyt and Emmons and the material for the investigation was obtained thru the courtesy of Mr. G. P. Merrill of the Smithsonian Institution. The laboratory work was done under the direction of Mr. Hoyt in the metallographic laboratory of the Minnesota School of Mines.