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Mineralogy and Trace Element Content of the Wood River Lead-Silver Deposits, Blaine County, Idaho [1]

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Abstract

The Wood River lead-silver deposits, near Bellevue in south-central Idaho, occur in veins in sheared zones in contact metamorphosed siliceous and limy argillites of ~~Missis~~ *Devonian* ~~sippian~~ age near contacts with quartz diorite. Galena and sphalerite are the principal ore minerals, siderite the principal gangue mineral; the ore averages 1.25 ounces silver for each percent lead.

Seven purified mineral separates of galena contain 2,100 to 5,000 ppm silver and 3,100 to 4,700 ppm antimony; antimony and silver are in an atomic proportion of approximately 1:1. Electron microprobe analyses show that slightly less than one half of the antimony and silver is in solid solution in the galena. The rest is present in minute, high Ag-Sb inclusions of five distinct compostions, though principally as diaphorite $(Pb_2Sb_3Ag_3S_8)$. Precise analyses of these inclusions were obtained by electron microprobe using a series of synthesized complex sulfosalts as standards. Some limitations on thermal stability of the mineral assemblages were obtained by these syntheses and by annealing natural materials at temperatures between 251° and 399° C.

Introduction

THE Wood River lead-silver deposits are in Blaine County in the Mineral Hill district, south-central Idaho, in the vicinity of Hailey and Bellevue (Fig. 1). (Hailey is 5 miles northwest of Bellevue.) Deposits lie on the west side of the Wood River between Deer Creek and Galena Gulch and on the East Fork of the Wood River 9 miles north of Hailey. They have produced an estimated $26 million in gold, lead, silver, and zinc—mostly from extensive operations in argillitic rocks during the latter part of the nineteenth century. Gold-pyrite veins are present, principally in granitic rocks west of the lead-silver deposits. Only the lead-silver deposits are considered in this paper.

The earliest description of the Wood River lead-silver deposits was by Lindgren (1900). Westgate, Umpleby, and Ross (1930) mapped the geology and ore deposits of the Hailey 30-minute quadrangle during 1912–1914 and 1923–1929. Hewett examined the Minnie Moore and neighboring mines (Fig. 1) in 1908 and 1910 and described these deposits in Westgate, Umpleby, and Ross (1930). In 1949 the Idaho Bureau of Mines and Geology mapped the Mineral Hill district under the supervision of A. L. Anderson (1950).

Ore samples collected for this investigation were restricted to three deposits that were in operation in 1969—the Silver Star Queen, Eureka, and Dennison. Polished sections were studied microscopically to

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determine the mineralogy and paragenetic sequence and to aid in selection of samples to study by electron microprobe and by X-ray diffraction. Purified mineral separates were analyzed by emission spectrography.

Geology of the Mine Area.—Rocks in the Bellevue-Hailey area are predominantly black siliceous argillite, siltstone, and limestone of ~~Mississippian~~ *Devonian* Pennsylvanian, and Permian age intruded by quartz diorite and quartz monzonite masses (probably outliers of the Idaho batholith) and by lamprophyre dikes (Fig. 1). The Milligen Formation of ~~Missis~~ *Devonian* sippian age is the oldest formation exposed in the area. This formation is apparently at least 3,000 feet thick, but the base is not exposed. The Milligen is overlain by the Wood River Formation of Pennsylvanian and Permian age (Bostwick, 1955). In most places the contact is a thrust fault. The Paleozoic rocks have been folded, extensively faulted, and contact-metamorphosed to hornfels and calchornfels near intrusive rocks.

Ore-Deposits.—The lead-silver deposits are predominantly in contact metamorphosed, siliceous and limy argillite of the Milligen Formation near contacts with quartz diorite (Fig. 1). The deposits are in a band of Milligen Formation west of the Wood River that extends from Galena Gulch to Croy Creek, and north of Croy Creek in Red Elephant, Bullion, and Kelly Gulches. A few deposits extend into the quartz diorite.

The lead-silver deposits occur as veins in strongly brecciated and sheared zones. The sheared zones
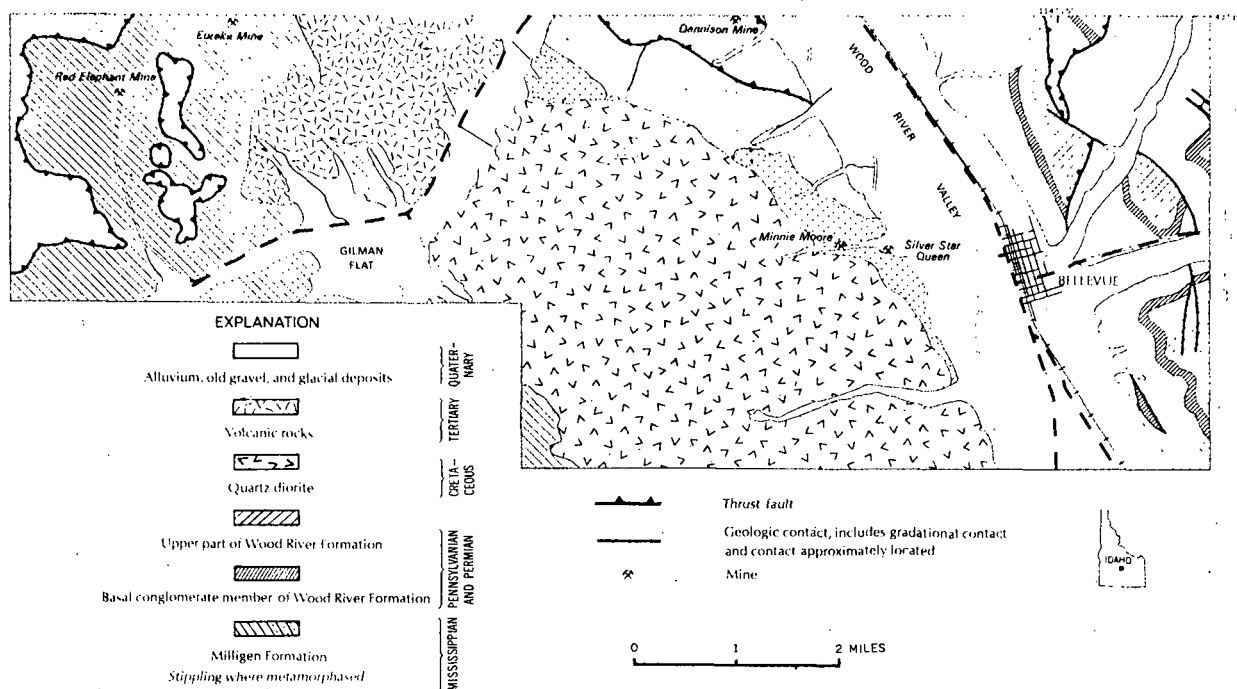
FIG. 1. Location and geological map of the Wood River district, Blaine County, Idaho.

are thicker and more extensive than the veins, and the veins have sharp contacts within the sheared zones. The veins strike northwestward and dip moderately to steeply to the southwest. Individual veins may be as much as several thousand feet long. The lead-silver ore, however, is localized in small high-grade shoots within the veins. The largest shoots were at the Bullion mine, where one had a pitch length of 1,200 feet, a thickness of a few inches to more than 15 feet, and a breadth of about 100 feet (Umpleby, Westgate and Ross, 1930, p. 101), and at the Minnie Moore mine, where ore extended 1,400 feet down dip. Beyond the limits of ore shoots, the veins may be completely barren and difficult to follow. Most of the ore shoots have continued to depths of only a few hundred feet.

Analytical Methods

Spectrographic Analyses.—Quantitative spectrographic analyses were made of purified mineral separates of galena and sphalerite. Mineral separates were made on a minus 60–plus 150 mesh fraction that was purified using a magnetic separator, heavy liquids, and a micropanner. Final cleaning of the sphalerite separate was done by the chemical method described by Czamanske and Ingamells (1970). Quantitative spectrographic analyses were made using a series of synthetic sulfide standards prepared by G. K. Czamanske to contain known amounts of selected minor elements found in natural sulfide minerals. Quantitative analyses are reported to two significant figures and have an accuracy of plus or minus 15 percent, except near limits of detection, where they are less accurate and only one digit is significant.

Selenium Analyses.—Selenium was determined quantitatively by distillation of the volatile tetrabromide from a perchloric acid solution containing a mixture of bromine and hydrobromic acid. Excess bromine and selenium tetrabromide were reduced with sulfur dioxide and hydroxylamine. The color of the hydrosol of elemental selenium was matched against selenium standards.

Electron Microprobe Analyses.—Electron microprobe analyses reported in this paper were obtained by G. K. Czamanske with an ARL EMX-SM microprobe using an accelerating voltage of 15KV and a specimen current of 2 or 3 × 10⁻⁸ amperes on benitoite. Lines analyzed and crystals used for each element are as follows: Pb, $M\alpha_1$, ADP; Sb, $L\alpha_1$, LiF; Ag, $L\alpha_1$, ADP; S, $K\alpha_1$, ADP; Cu, $K\alpha_1$, LiF; Fe, $K\alpha_1$, LiF; and Zn, $K\alpha_1$, LiF. All values reported are based on direct comparison of counting rates for unknowns and chemically similar synthetic sulfide standards, with appropriate hand corrections for background and instrument drift. Standards employed were PbS, Sb_2S_3, Cu_2S, FeS, ZnS,

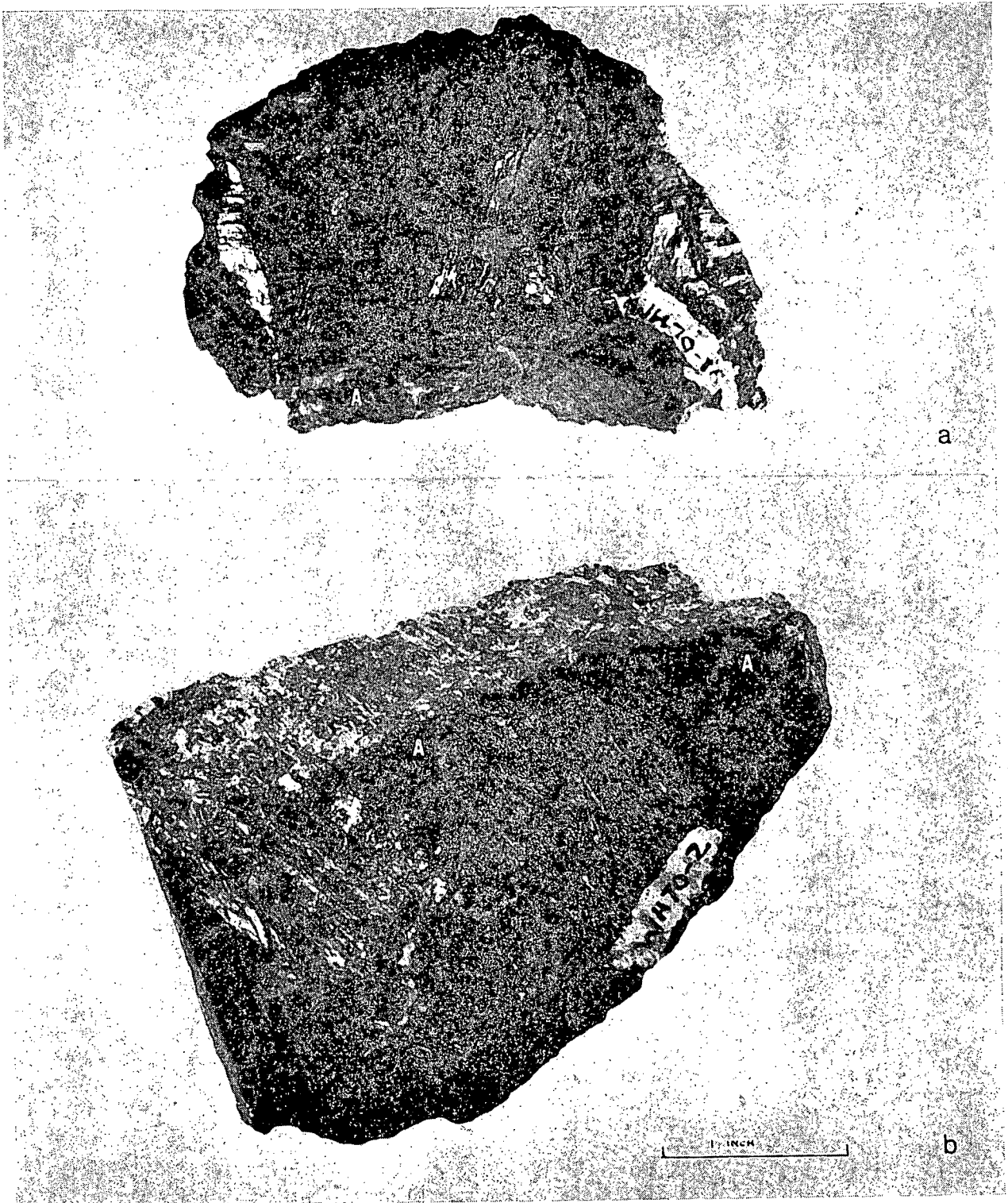FIG. 2. a. Unsheared coarse-grained galena and sphalerite ore. b. Foliated galena
with unsheared coarse-grained sphalerite (A).

$CuFeS_2$, $Pb_2Cu_2Sb_2S_6$, $Pb_5Sb_4S_{11}$, $Cu_7Fe_2Ag_3Sb_4S_{13}$, and $Pb_2Ag_3Sb_3S_8$. It is our experience that accurate analyses of complex heavy-metal sulfides cannot be obtained using a simple comparative procedure with end-member sulfides, e.g., PbS, Sb_2S_3, Cu_2S, or FeS.

Mineralogy

Nature of ore.—The lead-silver deposits contain heavy, massive sulfide ore. Vugs or crystal-lined cavities are rare, although some have been described by Umpleby, Westgate, and Ross (1930, p. 98) from the North Star Mine. Some of the ore is banded as a result of multiple reopening of veins during the period of mineralization.

Galena is the principal sulfide mineral in the primary ore, and some shoots consist almost wholly of it. The galena is argentiferous; for each percent of lead, the ore averages 1.25 ounces silver per ton. Arsenopyrite, boulangerite, silver-bearing boulangerite(?), bournonite, chalcopyrite, diaphorite, freibergite, gudmundite, marcasite, pyrargyrite, pyrite, pyrrhotite, and sphalerite are present in lesser amounts. Siderite is the principal gangue mineral; calcite and quartz are present but less abundant. Gangue minerals extend beyond the limits of the ore shoots. In most places both ore and gangue minerals are strongly sheared. Near the surface, galena is altered to cerrusite and siderite to iron oxides, but the depths of oxidation are shallow.

Galena.—Galena ranges in texture from extremely fine grained to coarsely crystalline. Where the ore is not foliated, cleavage faces of galena and carbonate gangue are commonly 3/8 to 1/2 inch across (Fig. 2A). However, most of the ore is strongly foliated and fine grained (Fig. 2B). As other sulfide minerals have not been broken up and coarse euhedral sphalerite or siderite of habit identical to the coarse-grained ore may be completely enclosed in the foliated galena, recrystallization of the galena cannot reflect intense movement. Rather, the reduction in grain size and the pronounced foliation are interpreted to result from gliding within the galena structure under pressure and elevated temperature, but with little actual displacement.

The galena contains abundant antimony and silver and small amounts of bismuth, cadmium, copper, iron, manganese, selenium, and tin (Table 1). The zinc is present is sphalerite occluded in galena and serves as an indicator of sample purity.

Seven purified mineral separates of galena contain 2,100 to 5,000 ppm silver and 3,100–4,700 ppm antimony; the ratio of silver to antimony ranges from 0.53 to 1.2. Only one sample (70–16), from the 900-foot level of the Silver Star Queen mine, is coarse-grained, unfoliated galena. It contains 3,400 ppm silver and 3,700 ppm antimony—an atomic ratio of 1 to 1. This galena was scanned on the electron microprobe to determine the distribution of silver and antimony. The predominant galena phase is nearly uniform in composition and contains, on the average, 0.11 percent silver and 0.16 percent antimony. This coarse-grained galena contains inclusions of diaphorite, less than one micron in maximum dimension, amounting to about 1.0 percent by volume. The inclusions are generally uniform in size, at approximately $1/2 \times 3/4$ micron, and are irregularly distributed. As quantitative spectrographic analysis (Table 1) indicates that the bulk galena separate averages 0.34 percent silver, roughly 70 percent of this silver is in the diaphorite inclusions. (The compositions of all known minerals in the PbS-Ag_2S-Sb_2S_3 system are given in Figure 3. Points plotted are from Wernick, 1960; Barstad, 1959; Craig, written commun., 1971; and this study).

Most of the galena that was mined from the Eureka and Silver Star Queen mines in 1969 was strongly foliated and fine grained. This foliated galena has the same abundance of minor elements as the coarse-grained galena (Table 1). Foliated galena contains principally antimony and silver as minor elements in an atomic ratio approximately 1:1; bismuth, cadmium, copper, and iron are present in smaller amounts. The distribution and abundance of

TABLE 1. Minor Element Content of Galena, Mineral Hill District, Wood River Area, Idaho (Parts per Million)

Field No.	Mine	Texture	Level	Ag	Bi	Cd	Co	Cu	Fe	Mn	Sb	Se*	Sn	Zn
WH70-5A	Silver Star Queen	Foliated galena	450	2100	<10	<20	<4	450	500	55	4000		<20	550
WH70-11A	Silver Star Queen	Foliated galena	900	5000	41	50	<4	350	70	<2	4700		<20	1000
WH70-12A	Dennison	Foliated galena	Lower adit 3700	<10	95	<4	260	500	<2	3500		200	<200
WH70-13A	Eureka	Foliated galena	250	3700	33	35	<4	230	500	120	3100		<20	<200
WH70-16A	Silver Star Queen	Coarse-grained	900	3400	<10	28	<4	500	100	2	3700		<20	<200
WH70-19A	Silver Star Queen	Foliated galena	450	3700	<10	<20	<4	160	50	<2	3100	65	20	480
WH70-20A	Silver Star Queen	Foliated galena	450	3900	<10	<20	<4	80	N	2	4300	8	<20	<200

Quantitative spectrographic analyses by R. E. Mays.
* Analyzed by Joseph Budinsky by colorimetric method.
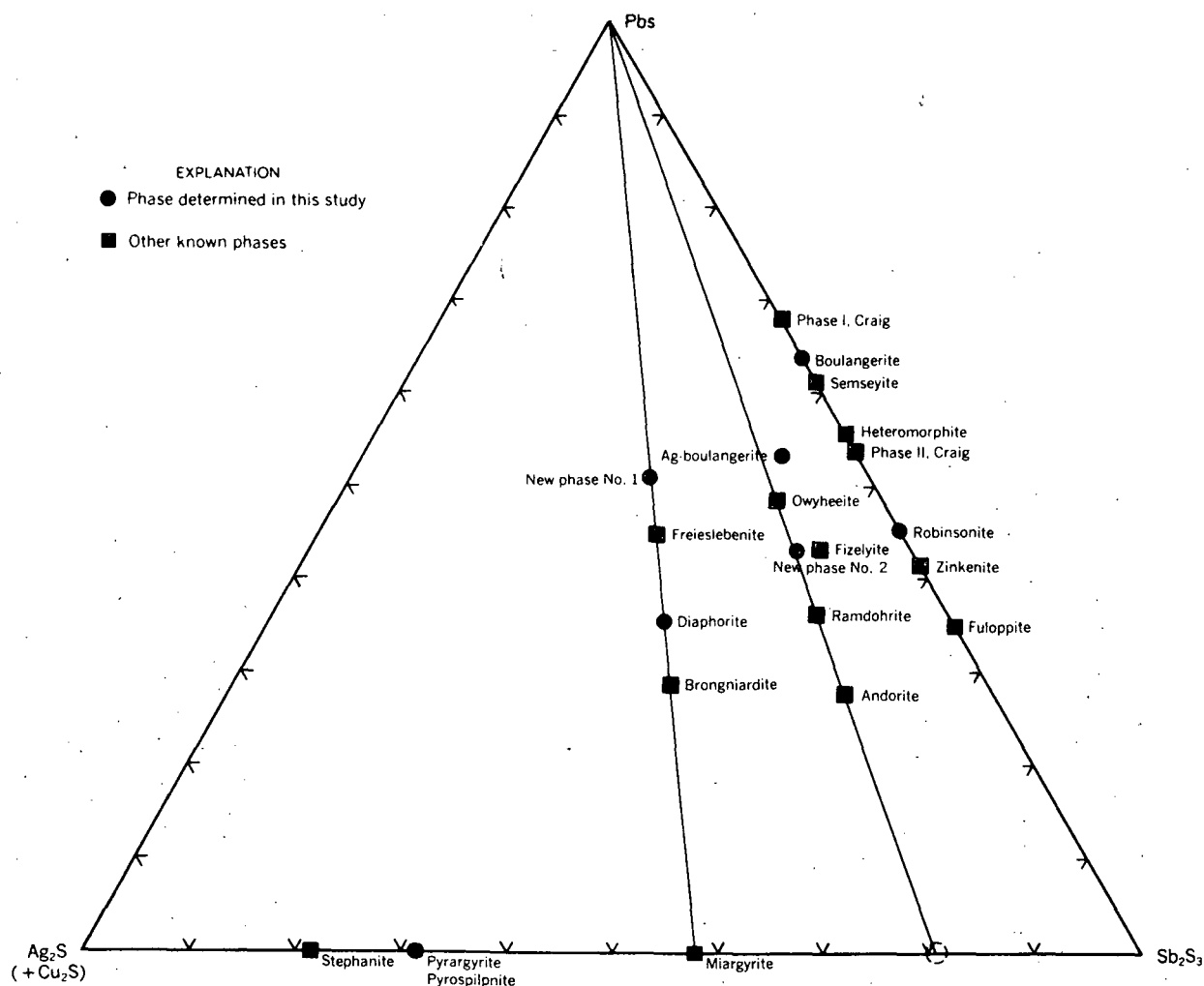N Not detected.

EXPLANATION
● Phase determined in this study
■ Other known phases

Pbs

Phase I, Craig
● Boulangerite
■ Semseyite
■ Heteromorphite
■ Phase II, Craig
Ag-boulangerite ●
New phase No. 1 ●
■ Owyheeite
■ Freieslebenite
● Robinsonite
● ■ Fizelyite
New phase No. 2
■ Zinkenite
● Diaphorite
■ Ramdohrite
■ Fuloppite
■ Brongniardite
■ Andorite

Ag₂S
(+Cu₂S)
■ Stephanite ● Pyrargyrite
Pyrospilpnite
■ Miargyrite
Sb₂S₃

FIG. 3. Mineralogy of the PbS-Ag₂S-Sb₂S₃ system (weight percent).

antimony, copper, iron, and silver in the foliated galena was examined by election microprobe. The electron microprobe examination showed that the antimony and silver, as in the coarse-grained galena, are not uniformly distributed, but are concentrated in minute inclusions that have an irregular distribution. Hence, the abundance of antimony and silver in the lattice of the foliated galena is less than that determined by emission spectrographic analysis of galena separates. Electron microprobe determinations of antimony and silver contents of galenas exclusive of the inclusions are given in Table 2. Because of low concentration levels and the lack of ideal standards, the reported values have a probable accuracy of only ±20 percent. Antimony contents range from 300 to 2,500 ppm and silver contents from 200 to 2,500 ppm. Coupled substitution of Sb and Ag is clearly indicated. Typically, slightly less than one half of the antimony and silver is in solid

solution in the galena; the rest is present in minute inclusions, predominantly as diaphorite (Pb_2Sb_3-Ag_3S_8). The unit cell edge of all this galena is $5.928\text{Å} \pm 0.001$ (Table 2). Galena peaks were measured against those of CaF_2 as an internal standard; precision, using an oscillating technique, was $2\theta \pm 0.01°$. The CaF_2 peaks were calibrated against Matthey silicon (laboratory number S3354); a cell edge of $a_0 = 5.4307\text{Å}$ was used for silicon. The unit cell edge measured is smaller than would be expected for the cubic β phase of the $AgSbS_2$-$(PbS)_2$ solid solution system. From the data of Wernick (1960, p. 594) the unit cell should be $a_0 = 5.9359 - (0.00289)$ (mol percent $AgSbS_2$) if the substitution followed Vegard's law. The average unit cell edge for steel galena of 5.928Å should correspond to composition $97.5(PbS)_2 - 2.5\ AgSbS_2$. However, the galena contains only 0.6 molecular percent $AgSbS_2$, and the unit cell edges for these natural $(PbS)_2 -$

TABLE 2. Semiquantitative Abundances of Antimony and Silver in Galena Exclusive of Micro-Inclusions [Samples 70-14 and 70-15 are from Eureka mine; all others from Silver Star Queen mine]

Field No.	Level	Ag (ppm)	Sb (ppm)	Ag:Sb Atomic Proportions	Unit Cell Edge a_0
	Steel galena				
70-1	450	1,700	1,900	1:1	5.928±0.001
70-5	450	800	900	1:1	5.928±0.001
70-6	900	1,600	1,800	1:1	5.929±0.001
70-7	900	1,700	2,500	0.8:1	5.928±0.001
70-11	900	1,700	1,700	1.1:1	—
70-14	4th	400	500	0.9:1	—
70-15	4th	200	300	0.8:1	—
70-19	450	2,100	2,400	1:1	—
70-20	450	2,500	2,300	1.2:1	—
Average		1,400	1,600	1:1	—
	Coarse-grained galena				
70-16	900	1,100	1,600	0.8:1	5.928±0.001

$AgSbS_2$ solid solutions apparently have negative departures from Vegard's law.

Inclusions in the foliated, steel galena are larger than those in the coarse-grained galena. In addition to diaphorite, found as inclusions in the coarse-grained galena, four types of inclusions were detected in the steel galena (Table 3, Fig. 3). All types have oval to irregular shapes and range from approximately 2 by 3 microns to as large as 20 by 30 microns in cross section. All five types of inclusion contain 27 ± 2 percent antimony and 19 ± 1 percent sulfur. Several types are present in most sections, but only freibergite inclusions were found in the two specimens analyzed from the Eureka mine (Table 4).

Diaphorite inclusions in the foliated galena are typically larger than those found in the coarse-grained galena, ranging from 2×3 to 4×7 microns. Apparently during disruption of the coarse galena by gliding, and aided by concomitant annealing, the minute diaphorite inclusions of the coarse-grained galena were mobilized and recrystallized to a coarser grain size in the foliated galena.

All trace elements but antimony and silver are present in small quantities. Some chalcopyrite inclusions are present in galena, especially where bournonite is present. The iron values reported for galena mainly reflect chalcopyrite inclusions; the copper values both chalcopyrite and bournonite.

Bismuth, cadmium, manganese, selenium, and tin apparently are in the galena structure, as no inclusions have been recognized that contain these elements.

Because of the high reflectivity of galena, small

TABLE 3. Compositions of Inclusions in Argentiferous Galena, Wood River Area

Type No.	Composition (weight percent)			Atomic Proportions	Mineral Name and Formula
I	Pb =	29.5		0.142	Diaphorite
	Sb =	27.0		0.218	$Pb_2Ag_3Sb_3S_8$
	Ag =	23.3		0.216	
	S =	19.6		0.613	
		99.4			
II	Pb =	55.2		0.266	Boulangerite
	Sb =	26.0		0.213	$Pb_5Sb_4S_{11}$
	S =	19.0		0.591	
		100.2			
III	Pb =	45.6		0.223	Silver-bearing
	Sb =	28.4		0.236	boulangerite(?)
	Ag =	6.3		0.059	$(Pb,Ag,Cu)_{5.4}Sb_{4.6}S_{11}$
	Cu =	0.1		0.002	
	S =	18.5		0.583	
		98.9			
IV	Pb =	42.9		0.204	Bournonite
	Cu =	12.3		0.208	$PbCuSbS_3$
	Sb =	25.3		0.194	
	S =	19.6		0.634	
		100.1			
V	Cu = 19.8	16.7	14.1	0.265	Freibergite
	Ag = 25.5	30.6	33.8	0.286	$(Cu,Ag,Fe)_{12.2}Sb_{4.2}S_{13}$
	Fe = 4.6	4.4	5.4	0.080	
	Sb = 26.1	26.1	24.8	0.216	
	S = 22.9	21.4	20.6	0.673	
	98.9	99.2	98.7		

inclusions of phases with distinct but also high reflectivity are easy to overlook. We first became aware of the abundance of micro-inclusions while using sample-current image displays both to accurately locate the microprobe beam on small obvious inclusions and to carefully avoid inclusions while analyzing the galena phase. Nearly all of our searching of polished surfaces was done by viewing hundreds of oscilloscope displays of sample-current.

TABLE 4. Types of Inclusions in Argentiferous Galena [Samples 70-14 and 70-15 from Eureka mine; all others from Silver Star Queen. √ present, 0 not present]

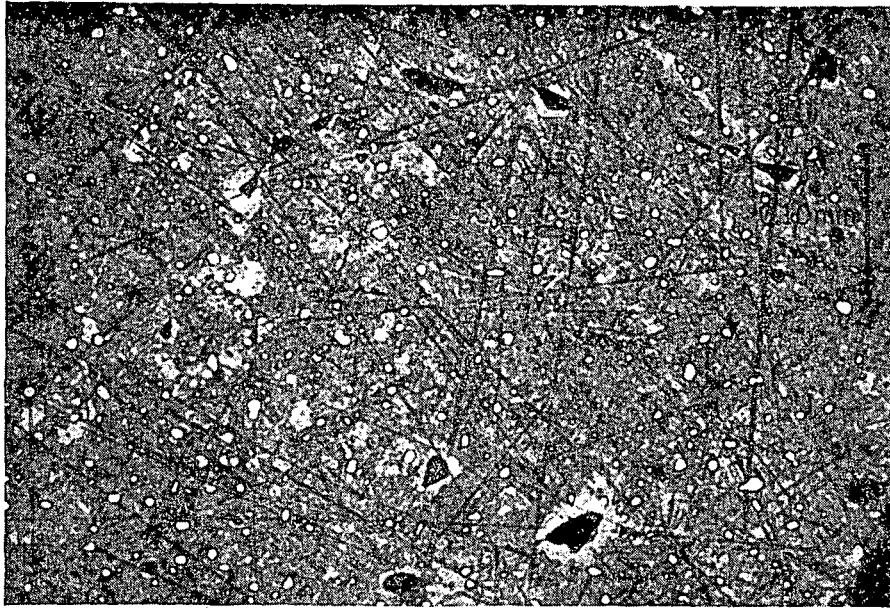| Sample No.	I Diaphorite	II Boulangerite	III Ag-boulangerite(?)	IV Bournonite	V Freibergite
70-1	√	0	√	√	0
70-5	√	√	0	0	√
70-6	0	√	0	√	√
70-7	√	0	0	√	0
70-11	√	√	√	√	0
70-14	0	0	0	0	√
70-15	0	0	0	0	√
70-19	√	0	0	0	0
70-20	√	0	0	0	0

Fig. 4. Foliated galena (dark) etched with hydrobromic acid to show the distribution of bournonite inclusions (light).

Etching with hydrobromic acid proved useful for investigating the overall distribution of the largest inclusions, especially bournonite (Fig. 4). However, the micron-size inclusions of diaphorite can not readily be detected by etching.

Annealing of Steel Galena.—Splits of a 60–100 mesh separate of foliated galena from specimen 70–11, collected on the 900 level of the Silver Star Queen mine, were annealed in evacuated silica tubes for 30 days at 251°, 292°, 350°, and 399° C to determine whether or not the inclusions would go into solid solution in the galena. Inclusions detected in the unheated foliated galena were bournonite, diaphorite, and silver-bearing boulangerite(?) (Table

5). (Boulangerite, detected in a polished section of this specimen, was not detected in any grains of the galena separate). The silver-bearing boulangerite(?) has a composition intermediate between boulangerite and owyheeite ($Pb_5Ag_6Sb_{15}$) (Fig. 3). Whether such a join exists has not been determined by experimental phase studies. Galena heated for 30 days at 251° and 292° C contains the same inclusions, of identical size, as the unheated galena. The only changes are a slight increase in the copper content and corresponding decrease in the silver content of the silver-bearing boulangerite(?) (Table 5). Galena heated for 30 days at 350° C retains bournonite inclusions of the same composition as the unheated

TABLE 5. Compositions and Molecular Proportions of Variable and "New" Phases in Annealed, Sheared Galena

Temp. Annealed (°C)	Composition (wt percent)						Atomic Proportions					Mineral name and Formula
	Pb	Sb	Ag	Cu	S	Sum	Pb	Sb	Ag	Cu	S	
Unheated	45.6	28.4	6.3	0.1	18.5	98.9	0.223	0.236	0.059	0.002	0.583	$(Pb,Ag,Cu)_{5.4}Sb_4S_{11}$ Ag-boulangerite(?)
251°	45.5	28.4	5.5	0.6	18.7	98.7	0.223	0.237	0.052	0.010	0.591	$(Pb,Ag,Cu)_{5.3}Sb_{4.4}S_{11}$ Ag-boulangerite(?)
292°	45.4	28.4	5.0	0.7	19.6	99.1	0.221	0.235	0.047	0.011	0.611	$(Pb,Ag,Cu)_{5.0}Sb_{4.2}S_{11}$ Ag-boulangerite(?)
350°	45.4	29.3	3.7	1.5	20.4	100.3	0.218	0.240	0.034	0.024	0.636	$(Pb,Ag,Cu)_{4.8}Sb_{4.2}S_{11}$ Ag-boulangerite(?)
350°	43.1	20.3	17.5	0.4	18.0	99.3	0.209	0.168	0.163	0.006	0.561	Type 1 inclusion $(PbS)_{56}(AgSbS_2)_{44}$
350°	36.6	32.0	7.7	1.9	20.3	98.7	0.179	0.266	0.072	0.030	0.642	Type 2 inclusion (Fizelyite?)

galena. But at this temperature the diaphorite inclusions disappear, the Ag-boulangerite(?) becomes still richer in copper and poorer in silver, and two new types of inclusions appear (Table 5 and Fig. 3). Type 1 inclusion has the composition $(PbS)_{56}$-$(AgSbS_2)_{44}$. No mineral of this composition has been described, and Wernick (1960) did not synthesize this compound in his studies of the $(PbS)_2$-$AgSbS_2$ system. The other new inclusion (type 2) has a composition very near fizelyite $(Pb_5Ag_2$-$Sb_8S_{18})$. It has similar atomic proportions of lead, silver, and sulfur but is deficient in antimony by the amount of copper it contains (Table 5, Fig. 3).

The split heated for 30 days at 399° C contained no detectable inclusions. Based on 25 points from 10 grains, this heated galena has an indicated silver content of 0.34 percent and an antimony content of 0.48 percent. No fully satisfactory explanation can be offered for the fact that this Sb value agrees well with that reported in Table 1 (0.47), whereas the Ag value is distinctly lower than the value reported there (0.50). However, the "homogenized" galena grains show greater than two-fold variations in Sb and Ag content (a reflection of original heterogeneous distribution of inclusions). Because Sb is of about equal concentration in all accessory phases and Ag content ranges from 0 to 23 weight percent, a small sampling would be expected to give a better value for Sb.

In an effort to further understand the breakdown of the high temperature, chemically complex galena to form exsolution phases, the galena that had been homogenized at 399° C was reannealed at two lower temperatures, 250° and 300° C, for 14 weeks. In this reannealed galena exsolution phases as much as 6 by 8 microns in size were detected that contained up to 24 weight percent Sb and 2 weight percent Cu. In no case was Ag concentrated in these inclusions, and in some cases the Pb concentration dropped to 20 weight percent. No exsolved body approached the composition of any of the naturally exsolved phases. While searching this reannealed galena for exsolution bodies, the original material that had been heated at 399° C, 6 months previously, was again carefully searched. Contrary to our earlier finding that it was homogeneous, we now detected rare, minute (1 × 2 micron) inclusions similar to those described above for the reannealed material. While it cannot be stated unequivocally that these inclusions exsolved at room temperature, that is our interpretation.

Other Ore Minerals

Arsenopyrite (FeAsS).—Arsenopyrite is an early mineral, present in small amounts with iron sulfide minerals, generally where siderite is the predominant gangue mineral. Arsenopyrite is disseminated as diamond-shaped crystals 1–2 mm in maximum dimension in samples collected from the 450-foot level of the Silver Star Queen mine and from the dump of the Liberty Gem mine, and it is reported by Umpleby, Westgate, and Ross (1930, p. 100) from the North Star mine on the north side of the East Fork of the Wood River.

Boulangerite $(Pb_5Sb_4S_{11})$.—Boulangerite was identified by electron microprobe analyses of micronsize inclusions and veinlets in foliated galena from the Silver Star Queen mine. All polished sections of galena that contain minute boulangerite inclusions contain at least two other of the group of five types of inclusions. Boulangerite inclusions are too minute to resolve under the microscope, but the electron microprobe analysis establishes the identification (Table 3).

Boulangerite was identified previously in the Wood River district, from the North Star and Independence mines on the north side of the East Fork of the Wood River, by Shannon (1921, p. 594; 1921, p. 423–426). The boulangerite there occurred as fibrous masses and needles lining cavities in a quartz gangue and as a late mineral veining galena, sphalerite, pyrite, and arsenopyrite.

Argentiferous Boulangerite(?) $(Pb,Ag,Cu)_{5.4}$ $Sb_{4.5}S_{11}$.—Two specimens from the Silver Star Queen mine contain minute inclusions of the general composition of boulangerite, but with one atomic equivalent of lead replaced by Silver (Table 3). Their composition is intermediate between boulangerite and owyheeite (Fig. 3). The inclusions are too small to obtain the physical or optical properties of the mineral. No silver is indicated in boulangerite analyses listed in Palache, Berman, and Frondel (1944, p. 421). Inclusions of this type were also present in galena 70–11 from the Silver Star Queen mine that was annealed at 251°, 292°, and 350° C. The annealing experiments showed an apparently systematic change in the Ag content of this phase, as Ag was in turn replaced by Cu (Table 5). Values obtained on unheated grains for Pb, Ag, and Cu were 45.6, 6.3, and 0.1 wt percent respectively; and on grains heated at 350° C, 45.4, 3.7, and 1.5 wt percent.

Bournonite $(PbCuSbS_3)$.—Bournonite is a common ore mineral in the Wood River ores, and much that was identified as tetrahedrite by earlier workers undoubtedly was bournonite. The identification of bournonite is based on X-ray diffraction pattern and electron microprobe analyses. The analyses are given in Table 3. The pattern is similar to that given in Berry and Thompson (1962, p. 133), except for two extra peaks at d = 3.43 and 3.83. The former is from galena impurity, the latter not identified. The X-ray diffraction data are:

dÅ	Intensity	dÅ	Intensity
4.34	3	2.81	2
4.08	4	2.73	10
3.90	3	2.68	4
3.83	6	2.59	3
3.68	4	2.36	1
3.43	5	2.30	1
3.25	2	2.10	5
2.97	10	1.98	4
2.90	2	1.85	3

Bournonite occurs as fine-grained irregular masses and veinlets in, or closely associated with, galena and as the previously discussed micron-size inclusions in galena (Fig. 4). It contains abundant veinlets and inclusions of chalcopyrite. In polished section, bournonite shows a conchoidal fracture and, in places, polysynthetic twinning. Silver was not detected in any electron microprobe analyses of bournonite, and galena ore containing bournonite is lower in total silver than ore where it is absent. The bournonite has mutual borders with galena. During the annealing experiments, bournonite disappeared between 350° and 399° C.

Chalcopyrite ($CuFeS_2$).—Chalcopyrite is present in small quantities generally closely associated with bournonite. It occurs as thin rims at the contact between galena and bournonite; in veinlets and disseminated, irregular, rounded grains replacing bournonite; and as tiny blebs in sphalerite. Chalcopyrite is a late mineral; it replaces bournonite but is veined and cut by galena.

Ore at the Liberty Gem mine contains abundant chalcopyrite. The chalcopyrite is associated with an early pyrite phase of mineralization in which the pyrite was shattered and invaded by a network of chalcopyrite.

Diaphorite ($Pb_2Ag_3Sb_3S_8$).—Minute inclusions of the composition of diaphorite have been identified by electron microprobe analysis in all but one sample of foliated galena from the Silver Star Queen mine from the 450 and deeper levels and in coarse-grained galena from that mine. The diaphorite contains 23.3 percent silver and is one of the principal sources of silver in the deeper levels of the Silver Star Queen mine. Two samples of foliated galena from the 450-level contain only diaphorite inclusions. All samples from the deeper levels contain two or three types of inclusions (Table 4). The diaphorite inclusions are too small to obtain X-ray diffraction or optical data.

Freibergite ($(Cu,Ag,Fe)_{12.2}Sb_{4.2}S_{13}$).—Freibergite, the silver-bearing tetrahedrite, was identified in small inclusions in galena and in inclusions in thin chalcopyrite rims around bournonite. Typical compositions, as determined by electron microprobe for specimens 70–5, 70–6, and 70–15, are given in Table

3. The first two analyses represent different compositions within a single grain in specimen 70–5. The most Ag-rich analysis presented is for freigergite in specimen 70–14 and is the highest Ag content reported in the literature. The atomic proportions in Table 3 and the chemical formula above correspond to the freibergite of intermediate composition. The freibergite generally contains approximately 0.8 percent zinc.

Six silver-rich tetrahedrites listed in Palache, Berman, and Frondel (1944, p. 377) contain silver in amounts up to 18 percent, but usually less than 5 percent. Staples and Warren (1946) describe a freibergite from the Highland-Bell mine that contains 25.25 to 26.40 weight percent silver, and Timofeyevskiy (1967) one from Ust' Teremki ore field, Darasun district, that contains 23.86 weight percent silver.

There was not sufficient freibergite in our samples to obtain an X-ray diffraction pattern for positive identification; but atomic ratios obtained are closest to, but do not exactly fit, those for freibergite. There is considerably more silver and less sulfur in our freibergite analyses than in the published analyses of that mineral.

Gudmundite (FeSbS).—Gudmundite is present in small amounts associated with pyrrhotite and siderite. It occurs as small, hard, silver-white prismatic forms in pyrrhotite and siderite on the 250-foot level of the Eureka mine. The mineral was identified by electron microprobe analysis and has the following composition by weight percent: Fe, 29 ± 1; Sb, 58.5 ± 0.5; S, 15.8 ± 0.5. The gudmundite occurs in late-stage siderite veinlets containing pyrite, marcasite, and pyrrhotite.

Marcasite (FeS_2).—Bladed crystals 1/2 to 2 mm long, composed of both marcasite and pyrite, occur at the Liberty Gem and Silver Star Queen mines in late-stage siderite veinlets that cut the main galena

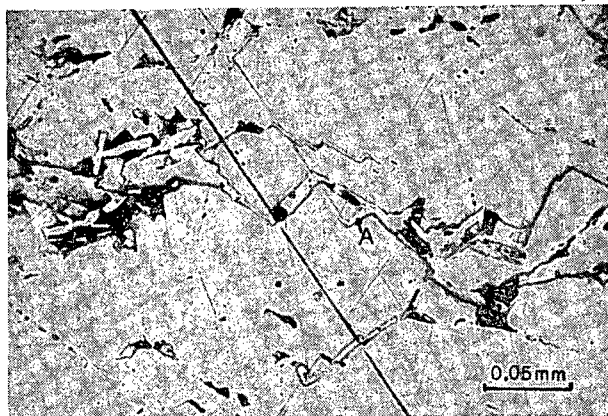Fig. 5. Sulfide blades comprised of marcasite (gray) and pyrite remnants (bright).

FIG. 6. Pyrrhotite (A) veining galena along
a cleavage parting.

stage of mineralization. The marcasite is porous
and takes a poor polish, the pyrite takes a good
polish. In general, marcasite is the dominant con-
stituent of the bladed crystals and pyrite occurs as
irregular remnant patches within grains (Fig. 5).
These bladed marcasite-pyrite crystals are similar in
appearance to those described by Kelly and Turne-
aure (1970, p. 619).

Electron microprobe analyses on a 3-micron grid
of selected areas of marcasite from the Liberty Gem
and Silver Star Queen mines show antimony to
range from 0.5 to 1.8 and silver from a trace to 0.54
weight percent. Coarse pyrite adjacent to the marca-
site contains no detectable antimony or silver.

Pyrargyrite (Ag_3SbS_3).—One grain of pyrargy-
rite associated with galena was identified by electron
microprobe analysis of specimen 70–11 from the 900-
foot level of the Silver Star Queen mine.

Pyrite (FeS_2).—Pyrite, an early mineral, is pres-
ent in only small quantities in the lead-silver deposits.
It occurs as tiny cubes and pyritohedrons dissemi-
nated in siderite and host rock near ore and as cor-
roded relics in galena, marcasite, and pyrrhotite.

Pyrrhotite ($Fe_{1-x}S$).—Monoclinic pyrrhotite is
present in small quantities as a late-stage mineral
with pyrite, marcasite, and gudmundite in a siderite
gangue. The pyrrhotite forms slender crystals,
commonly along the grain boundaries of galena or
veining galena (Fig. 6).

Sphalerite (ZnS).—Sphalerite is an abundant ore
mineral, but it was not economic to recover in the
early history of the district. However, large amounts
of sphalerite have been recovered from ore mined
during the past 20 years. The compositions of two
sphalerite mineral separates from the Silver Star
Queen mine and one from the Eureka mine are given
in Table 6. The sphalerite contains only 2 to 3 per-
cent iron. Cadmium, the principal minor element,
ranges from 4,500–5,700 ppm. The sphalerite con-
tains some chalcopyrite blebs and veinlets that un-
doubtedly account for most of the copper reported.

Two of the analyzed sphalerites contain substantial
amounts of silver: 600 ppm (20 ounces per ton) in
one, 725 ppm (24 ounces per ton) in the other. Both
these samples contain antimony, and it is probable
that the copper and antimony occur as a coupled
substitution for zinc in the sphalerite. Attempts to
determine Ag distribution in the sphalerite with the
microprobe were unsuccessful because silver was not
detectable. No tin mineral was recognized in the
sphalerite, but two samples contain more than 200
ppm (Table 5).

Paragenesis

The paragenesis of the ore and gangue minerals,
given in Table 7, is somewhat speculative because it
is patched together from numerous observations that
could not always be unequivocally related to one
another. It is based upon a modest number of sam-
ples from, and brief observation of, the three deposits
being worked in 1969; older workings were
inaccessible.

Siderite is the most common gangue mineral, and
some veins or parts of veins are composed entirely
of it. Most of the siderite is early and was shattered
prior to introduction of the early pyrite and arseno-
pyrite, which are disseminated widely through the
siderite gangue. Early pyrite is in the form of cubes
and pyritohedrons. It takes a smooth polish, one of
the features that distinguishes early pyrite from the
porous, late marcasite-pyrite crystals. Both pyrite
and arsenopyrite were shattered before the main
period of lead-silver mineralization, and before the
introduction of chalcopyrite.

Argentiferous galena-sphalerite ore is restricted to
well-defined shoots within the more extensive areas

TABLE 6. Minor Element Content of Sphalerite, Wood River District, Idaho (parts per million)

Field No.	Mine	Level	Ag	Ba	Bi	Cd	Co	Cu	Fe	Mn	Sb	Sn	Pb
WH70-11B*	Silver Star Queen	900	600	5	<10	4,500	<4	300	20,000	60	365	250	1,100
WH70-13B*	Eureka	250	725	3	<10	4,800	<4	1,800	30,000	60	500	24	900
WH70-16B*	Silver Star Queen	900	38	5	<10	5,700	<4	270	20,000	65	<100	225	200

* Quantitative spectrographic analysis. Analyst Christ Heropoulos.
N Not detected.

TABLE 7. Mineral Sequence, Wood River

	Early ±400° C Shattering	+370° C Shattering	Late −280° C Shattering
Siderite	———			
Quartz	———		
Arsenopyrite		——	
Pyrite		——	
Sphalerite			——
Galena			——
Chalcopyrite		——	—
Diaphorite		—	———
Bournonite		—	———
Ag-bournonite (?)			——
Freibergite			—
Boulangerite			——
Gudmundite			——
Marcasite			——
Pyrrhotite			——
Calcite			—

of siderite-pyrite-arsenopyrite mineralization. Where ore is banded, sphalerite forms an outer band, suggesting that reopening of veins permitted introduction of galena, which was deposited upon the sphalerite (specimens 70–16, 70–8A). Bournonite was deposited during the late stages of galena mineralization. The galena apparently was deposited above 350° C as a homogeneous phase in the 2PbS-βAgSbS₂ system, containing as much as 1.3 mol percent $AgSbS_2$. Upon cooling below 350° C, diaphorite exsolved and formed disseminated inclusions less than 1 micron in size. The galena subsequently was subjected to elevated temperature and pressure and a foliated galena formed. Concomitant with this recrystallization, the galena exsolved additional diaphorite and the minerals boulangerite, Ag-boulangerite(?), bournonite, and freibergite, prior to the late-stage iron mineralization.

A late stage of pyrite-marcasite-pyrrhotite-siderite mineralization cuts across the earlier sulfide mineral stages. The pyrite-marcasite is in porous prismatic forms (Fig. 5) that encompass earlier euhedral pyrite. Very late pyrrhotite is generally found along the margins of the late-stage pyrite-marcasite veinlets, and also occurs along galena cleavages (Fig. 6). Milky, white calcite veinlets cut all the above minerals.

Thermal Considerations

The Wood River ores deposited over a temperature range from above 350° C during the early stage of mineralization to less than 280° C during the last stages. Close spatial association between the ores and black siliceous argillite near the borders of the Idaho batholith suggests a genetic association. The argillite was metamorphosed to hornfels, and limy parts to calc-hornfels, prior to ore mineralization. Micron-size fluid inclusions in quartz in the hornfels indicate that the metamorphism was accompanied by

highly concentrated, NaCl-rich brines poor in CO_2. The inclusions contain NaCl and hematite daughter minerals. The inclusions are too small to permit determination of homogenization temperatures on a heating stage, but the large size of the bubbles in the fluid inclusions suggests a temperature for the alteration of more than 350° C. Observed uniformity in bubble size indicates that the fluid was not boiling.

Some approximations of deposition temperatures can be made from individual minerals and mineral assemblages to indicate the ores were deposited over a range from above 350° C to less than 280° C. Galena is interpreted to have been deposited as a single phase in the system (PbS)₂-βAgSbS₂. All silver and antimony-rich microinclusions went into solid solution in the galena in the annealing experiments at temperatures between 350° and 400° C.

Monoclinic pyrrhotite has a maximum temperature of 315° ± 10° C (Desborough and Carpenter, 1965). Gudmundite is not stable above 280° C (Barton, written commun., 1971). Marcasite also generally indicates a low temperature of deposition, although it is stable to a temperature of 430° C at a pressure of 1,000 bars (Kullerud, 1967, p. 353). The stability of gudmundite thus places an upper limit of 280° C on the temperature of deposition of the late-stage marcasite-pyrite-pyrrhotite-chalcopyrite-gudmundite-siderite veinlets.

Acknowledgments

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