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Phase Relations in the Systems $PbS–Ag_2S–Sb_2S_3$ and $PbS–Ag_2S–Bi_2S_3$

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Abstract

Phase relations in the systems $PbS–Ag_2S–Sb_2S_3$ and $PbS–Ag_2S–Bi_2S_3$ were studied in the temperature range 300°–500°C using evacuated glass capsule technique. The $PbS–AgSbS_2$ join shows a complete solid solution at 500°C, a miscibility gap between 65 and 90 mole percent PbS at 400°C, and at 300°C the presence of two small solid solutions between 50 and 52 mole percent PbS, and 25 and 40 mole percent PbS. Another solid solution includes the compositions of andorite ($PbAgSb_3S_6$), ramdohrite ($Pb_3Ag_2Sb_6S_{13}$), and fizelyite ($Pb_5Ag_2Sb_8S_{18}$).

An extensive solid solution exists along the lillianite-pavonite join, and has a miscibility gap between 25 and 46 mole percent PbS at 500°C. Pavonite also exhibits solid solution toward galenobismutite. Along the $PbS-AgBiS_2$ join, a complete solid solution exists between 400° and 500°C.

Correlations of experimental data obtained in this study with some natural mineral assemblages were made.

Introduction

Lead sulfosalt minerals are widespread in many hydrothermal ores, but rarely form a substantial portion thereof. In the systems under consideration, more than seventy-five sulfosalts have been reported; some of these are well established, others doubtful, and still others have been discredited. It was the purpose of this investigation to synthesize these sulfosalt minerals and to establish their phase relations. Because most sulfosalt minerals are deposited at low temperatures, late in the ore mineral sequence, this investigation was carried out in the temperature range 300°–500°C, the lower temperature dictated by the extreme sluggishness of the reaction.

Experimental Procedure

Elemental antimony (Baker analyzed reagent), bismuth (Baker analyzed reagent), lead (Mc/B reagent), sulfur (Fisher, U.S.P.), and chemically precipitated Ag_2S (A.D. Mackay, C.P.) were used as reactants. All have 99.99 percent or better purity. Reactants were prepared to a total weight of approximately one gram each. After thorough mixing by light grinding in an agate mortar, the reactants were sealed in evacuated quartz-glass capsules using the technique described by Kullerud and Yoder (1959). The lengths of capsules were as small as possible so that the vapor space above the charge was less than 20 percent of the volume. Samples were heated in horizontal muffle furnaces in which the temperature was regulated ±2°C. Temperatures were measured by means of calibrated chromel-alumel thermocouples and a Leeds and Northrup potentiometer. Charges were initially heated at 200°C for about twenty-four hours to react the sulfur slowly prior to heating at the desired temperature. When sulfur was no longer visible (one to two weeks), the mixtures were cooled, ground under acetone, re-sealed in new capsules, and annealed. Generally, 42 days were used for equilibration at 500°C, 52 days at 400°C, and 147 days at 300°C. Because reaction rates at 300°C were extremely sluggish, these samples were ground after about ten weeks, pelletized, and annealed for ten additional weeks.

At the end of the heat treatment, charges were quenched in air. Some duplicate runs quenched in ice water revealed no difference in phase assemblages. As a test of equilibrium, some samples were heated to complete melting, quenched in ice water, ground under acetone, and annealed at the desired temperatures for the same length of time as other experiments. The final assemblages of the same composition treated by the two techniques were identical.

X-ray powder diffraction using Ni-filtered copper radiation and reflected light microscopy were used

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for phase identification. The *d* values were measured using α-tungsten (a_o = 3.1648 Å; Swanson and Tatge, 1953) as an internal standard, and lattice parameters ±0.02 Å were computed by a program obtained from Dr. T. T. Chen, Carleton University, Ottawa, Canada.

The System $PbS–Ag_2S–Sb_2S_3$

The thirty-three phases, natural and synthetic, reported in this system (Fig. 1) have been summarized by Chang and Bever (1973). Phase relations in the binary systems $PbS–Ag_2S$, $Ag_2S–Sb_2S_3$, and $PbS–Sb_2S_3$ were studied by Van Hook (1960), Keighin and Honea (1969), and Craig, Chang, and Lees (1973), respectively.

Wernick (1960) and Godovikov and Nenasheva (1969a) found that continuous solid solution, with a disordered NaCl-type structure, existed along the $PbS–AgSbS_2$ join. Godovikov *et al* (1972) reported the synthesis of freieslebenite ($2PbS \cdot Ag_2S \cdot Sb_2S_3$) and brongniardite ($2PbS \cdot 3Ag_2S \cdot 3Sb_2S_3$).

The chemical compositions and lattice parameters of all the phases synthesized in the present study are listed in Table 1. Their phase relations are discussed below.

Phase Relations at 500°C

Phase relations in the system at 500°C are shown in Figure 2. The compositions of the two liquid fields existing on the $Ag_2S–AgSbS_2$ join were taken from Keighin and Honea (1969). Extension into the ternary region was visually estimated from the ratios of solid to liquid quenched product in polished sections. Pyrargyrite forms as fine dendrites in all silver-rich liquids on cooling. The liquid field on the antimony-rich side terminates in the $AgSbS_2–Sb_2S_3$ eutectic at 450°C (Keighin and Honea, 1969).

Solid phases stable at 500°C are boulangerite, robinsonite, zinkenite, andorite solid solution, and a solid solution which extends from α-miargyrite to galena. This solid solution, in which there is a disordered substitution of Ag^{1+} and Sb^{3+} ions for Pb^{2+} ions, is readily preserved on rapid cooling from 500°C. The tie lines between this solid solution and other phases (Fig. 2) were determined from the shift in d_{200} values of the solid solution.

The composition of the robinsonite synthesized in this study, $6PbS \cdot 5Sb_2S_3$, agrees well with the reported data of Craig *et al* (1973), but is at variance with the formula, $7PbS \cdot 6Sb_2S_3$, from other studies (Robinson, 1948; Berry, Fahey, and Bailey, 1952; Jambor, 1968; and Garvin, 1973). Electron probe analysis of robinsonite made by Jambor (1967) indicated a lead content (6 to 7 percent) consistently higher than appropriate for the formula $7PbS \cdot 6Sb_2S_3$. The solid solution range of robinsonite reported by Salanchi and Moh (1970) was not observed.

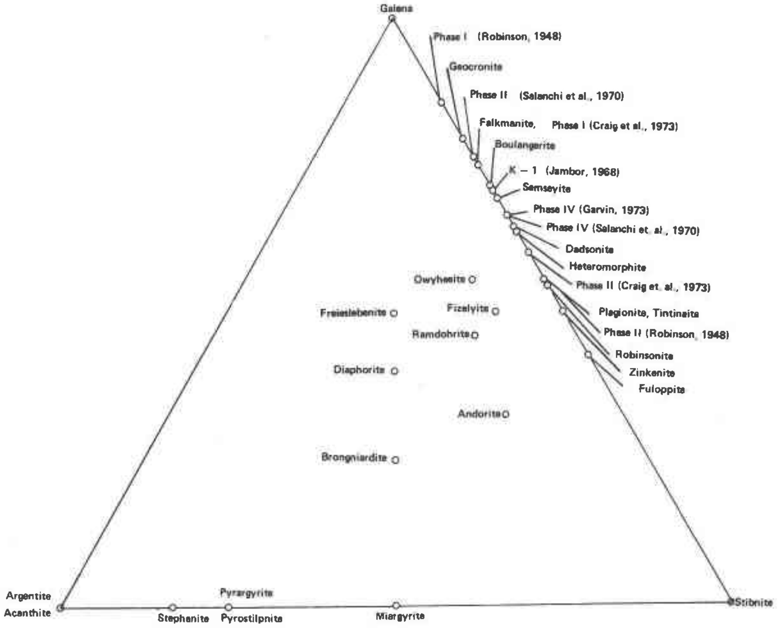

FIG. 1. Phases reported in the system PbS (galena)–Ag_2S (acanthite–argentite)–Sb_2S_3 (stibnite).

TABLE 1. Lattice Parameters and Compositions of Phases Synthesized in the System PbS-Ag_2S-Sb_2S_3

Name	Composition mole% PbS	Ag2S	Sb2S3	Crsyt. System	a	b	c	α	β	γ
Boulangerite	71.4	-	28.6	Monoclinic	21.50	23.47	8.05	-	99.26	-
Robinsonite	54.54	-	45.45	Triclinic	16.41	17.89	4.02	99.24	95.76	89.46
Zinkenite	50.0	-	50.0	Hexagonal	44.13	-	8.64	-	-	-
β -Miargyrite	-	50.0	50.0	Monoclinic	13.31	4.42	12.93	-	98.53	-
Pyrargyrite	-	75.0	25.0	Hexagonal	11.07	-	8.73	-	-	-
Freieslebenite	50.0	25.0	25.0	Monoclinic	7.66	12.69	5.83	-	90.75	-
Diaphorite	40.0	30.0	30.0	Orthorhombic	15.86	31.99	5.95	-	-	-
Brongniardite	25.0	37.5	37.5	Orthorhombic	15.86	31.54	5.90	-	-	-
Andorite s.s.	33.3	16.7	50.0	Orthorhombic	13.04	19.17	4.29	-	-	-
Andorite s.s.	26.0	19.8	54.2	Orthorhombic	13.00	19.26	4.27	-	-	-
Andorite s.s.	52.0	9.0	39.0	Orthorhombic	13.03	19.15	4.29	-	-	-
Galena - miargyrite s.s.	85.0	7.5	7.5	Cubic	5.883	-	-	-	-	-
Galena - miargyrite s.s.	70.0	15.0	15.0	Cubic	5.823	-	-	-	-	-
Galena - miargyrite s.s.	50.0	25.0	25.0	Cubic	5.787	-	-	-	-	-
Galena - miargyrite s.s.	40.0	30.0	30.0	Cubic	5.760	-	-	-	-	-
Galena - miargyrite s.s.	14.0	43.0	43.0	Cubic	5.690	-	-	-	-	-
α -Miargyrite	-	50.0	50.0	Cubic	5.603	-	-	-	-	-

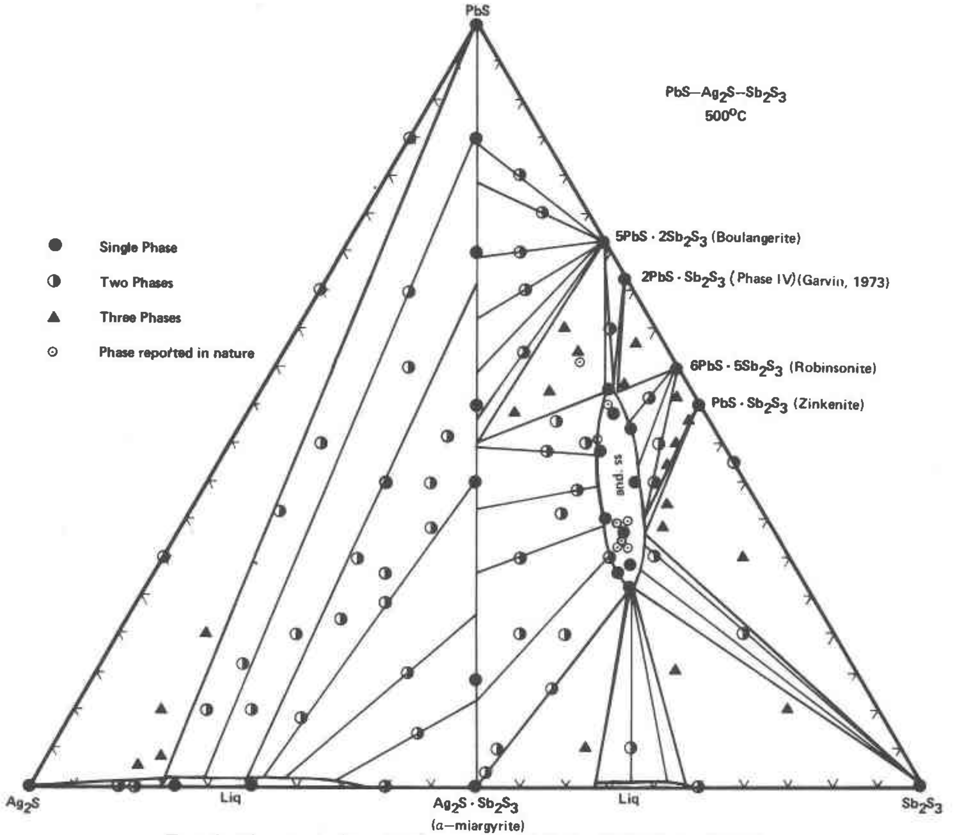

FIG. 2. Phase relations in the system PbS-Ag_2S-Sb_2S_3 at 500°C.

The composition of zinkenite, like that of robinsonite, has been a point of disagreement among previous investigators. Nuffield (1944) reported its composition as $PbS \cdot Sb_2S_3$, but from density measurements Harris (1968) proposed 6PbS $7Sb_2S_3$. Garvin (1973) and Salanchi and Moh (1970) supported this 6:7 composition, whereas Craig *et al* (1973) placed it at 1:1. The results of present investigation are in agreement with Craig *et al*'s ratio.

A run of composition 69.22 mole percent PbS and 30.78 mole percent Sb_2S_3 produced boulangerite plus a phase different from any known minerals. Its X-ray powder diffraction data agree well with Garvin's phase IV (Garvin, 1973). According to Garvin, phase IV has a composition between 57 and 66 mole percent PbS and is stable between 425° and 600°C. Salanchi and Moh (1970) also reported phase IV at 66 mole percent PbS, but the incongruent melting point and lower stability limit were stated as 597°C and 505°C, respectively. No X-ray data were provided so that a comparison could not be made. Craig *et al* (1973) reported phase II at 60 mole percent PbS melting incongruently at 603°C and with a lower stability limit undetermined. The three most intense peaks of phase II are at 3.72, **10**; 3.16, **6**; and 2.85, **5**.

Andorite displays extensive solid solution and forms equilibrium assemblages with all phases in the $PbS–AgSbS_2–Sb_2S_3$ half of the system except galena. Five reliable analyses of andorite, one of ramdohrite, and one of fizelyite (Nuffield, 1945) all fall in the andorite solid solution region (Fig. 2). It thus appears that at 500°C these minerals become parts of a solid solution.

Donnay and Donnay (1954) examined the density and unit cell parameters of museum specimens of andorite and ramdohrite ($6PbS \cdot 2Ag_2S \cdot 5Sb_2S_3$) and proposed that these names be replaced with andorite-IV and andorite-VI. These phases have identical a_0 and b_0 values, equal to 13.03 and 19.15 Å, respectively, but have c_0-axis dimensions which are multiples ($4c'$ and $6c'$) of a common pseudo-period c' = 4.29 Å. Kawada and Hellner (1971) determined the crystal structure of the sub-cell of andorite-VI (ramdohrite) and confirmed Donnay and Donnay's (1954) data.

Ramdohrite is the name applied by Ahlfeld (1930) to a lead-silver sulfantimonide of probable composition $Pb_3Ag_2Sb_6S_{13}$ or $Pb_6Ag_4Sb_{10}S_{23}$ from Potosi, Bolivia. Harcourt (1942) noted that its powder diffraction pattern is very similar to that of andorite. Nuffield (1945) deduced the cell content, $Pb_6Ag_4Sb_{10}S_{23}$ from analyses of impure material. Donnay and Donnay (1954), however, reported that cell volume and density consideration fit neither of the two formulae given by Ahlfeld. Obviously, more adequate analytical data are needed to establish its chemical formula.

Fizelyite was reported by Nuffield (1945) to be very similar to andorite and ramdohrite in X-ray powder diffraction patterns, polished sections, and specific gravity. The structure is orthorhombic with a_0 = 13.14, b_0 = 19.23, and c_0 = 8.72 Å. As for ramdohrite, available analyses of fizelyite are not consistent with a simple formula.

Calculations of lattice parameters (Table 1) failed to show any significant change with composition in the andorite solid solution. This was also reported by Nuffield (1945) and Donnay and Donnay (1954).

Phase Relations at 400°C

At 400°C (Fig. 3), the system shows (1) a miscibility gap along the $PbS–AgSbS_2$ join between 65 and 90 mole percent PbS, (2) the disappearance of liquid fields, (3) a slight shrinkage of the andorite field, (4) the disappearance of phase IV, and (5) the appearance of pyrargyrite.

Phase Relations at 300°C

At 300°C (Fig. 4) the $PbS–AgSbS_2$ join is marked by wide miscibility gaps, and by two solid solution series, one between 50 and 52 mole percent PbS and the other between 25 and 40 mole percent PbS, this latter spanning the compositional range from diaphorite to brongniardite.

Robinsonite has a lower stability limit of 318° ± 10°C on the $PbS–Sb_2S_3$ join. This lower stability limit may explain the rarity of robinsonite in nature. Semseyite ($9PbS \cdot 4Sb_2S_3$) was synthesized at 300°C from a composition of 69.22 mole percent PbS and 30.78 mole percent Sb_2S_3; it also appeared in assemblages with zinkenite and andorite in the ternary system. Semseyite has been synthesized only hydrothermally by Robinson (1948) and by Jambor (1968), and its stability along the join $PbS–Sb_2S_3$ has not been firmly established. Robinson reported an upper stability of hydrothermally synthesized semseyite at 415° ± 10°C, but the absence of this phase in the present study at 400°C suggests an upper limit below 400°C. Other members of the plagionite group, plagionite ($5PbS \cdot 4Sb_2S_3$), fuloppite ($3PbS \cdot 4Sb_2S_3$), and heteromorphite ($7PbS \cdot 4Sb_2S_3$), were not observed in the present investigation.

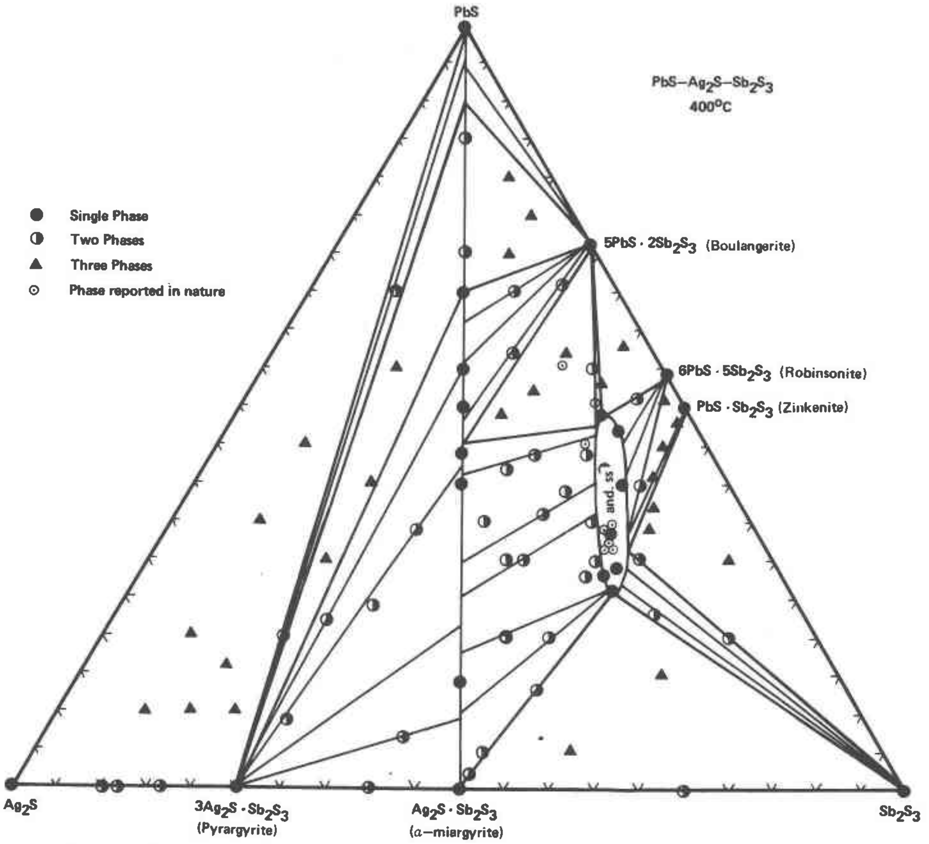

FIG. 3. Phase relations in the system PbS–Ag_2S–Sb_2S_3 at 400°C. The abbreviation "and. ss" = andorite solid solution.

Miargyrite is present at 300°C in its monoclinic form and has no detectable range of solid solution.

The andorite solid solution is considerably diminished in size at 300°C, and a two-phase assemblage of andorite and galena is present. The limits of andorite solid solution correspond with the reported compositions of andorite ($Pb_2Ag_2Sb_6S_{12}$) and fizelyite ($Pb_5Ag_2Sb_8S_{18}$), and include the composition of ramdohrite ($Pb_3Ag_2Sb_6S_{13}$).

Attainment of equilibrium along the join PbS–Sb_2S_3 at 300°C is questionable, as evidenced by the presence of galena in samples of boulangerite and semseyite compositions. Within the ternary region, however, experiments with samples of as little as 5 mole percent Ag_2S appeared to reach equilibrium in twenty-one weeks. Phase assemblages of semseyite + andorite and semseyite + zinkenite + andorite were obtained.

Phase Relations Along the PbS–$AgSbS_2$ Join

Phase relations along the PbS–$AgSbS_2$ join are shown in Figure 5; the liquidus and solidus curves are taken from Godovikov and Nenasheva (1969a). The cubic-monoclinic transition temperature of $AgSbS_2$ (380°C) determined is in agreement with Keighin and Honea (1969), but is 20°C higher than that determined by Wernick (1960). Lattice parameters of the NaCl-type solid solution along this join increase nonlinearly with increasing PbS-content (Table 1 and Fig. 6). Wide miscibility gaps exist between β-miargyrite and the brongniardite-diaphorite series, and between freieslebenite and galena, whereas a narrow gap exists between freieslebenite and the diaphorite–brongniardite series.

The structure of freieslebenite and diaphorite can be deduced from the galena structure as shown by Hellner (1958). Godovikov and Nenasheva (1969a) noticed that three of five analyses given for freieslebenite fit diaphorite ($Pb_2Ag_3Sb_3S_8$) and the remaining two can be calculated to $Pb_3Ag_4Sb_4S_{14}$ and $Pb_5Ag_3Sb_5S_{12}$. On the basis of new microprobe analysis from museum specimens of freieslebenite from Freiberg and Braunsdorf, Germany, and Hiendelencina, Spain, Sveshnikova and Borodaev (1972) obtained the formula $PbAgSbS_3$, which is in agreement with that obtained by Hellner (1958) and

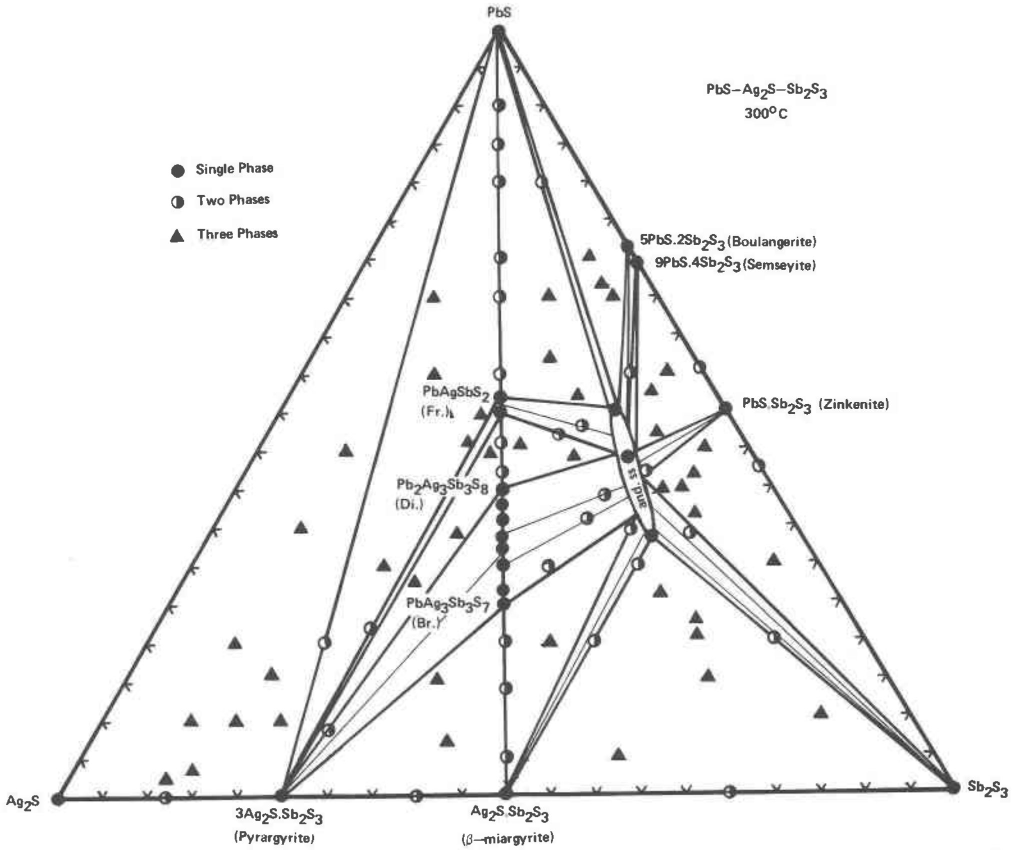

FIG. 4. Phase relations in the system PbS–Ag$_2$S–Sb$_2$S$_3$ at 300°C. Abbreviations are: Fr: freieslebenite, Di: diaphorite, Br: brongniardite, and. ss: andorite solid solution.

in the present study. As for the diaphorite–brongniardite series, the former is a well established phase and is regarded as the best authenticated of the intermediate phases along the PbS–AgSbS$_2$ join, whereas the latter is of questionable validity. Recently, Godovikov and Nenasheva (1969a) reported a new synthetic phase PbAg$_3$Sb$_3$S$_7$, which Godovikov *et al* (1972) called brongniardite. They gave the X-ray data and chemical and optical properties of this synthetic phase, but did not state whether their X-ray data were identical with those of natural brongniardite. The phase described by Godovikov and Nenasheva (1969b) has also been found in the present study.

The limits of diaphorite–brongniardite solid solution were established from runs at 2 mole percent PbS intervals between their stoichiometric compositions. Attempts were made to determine the phase relations along the join PbS–AgSbS$_2$ at lower temperatures by mixing the reactants with KCl-AlCl$_3$ flux (eutectic composition). The results were not conclusive. Phases obtained at 250°C were β-miargyrite, freieslebenite, galena, and unidentified phases.

Geological Significance

Andorite has a large field of stability and can occur with almost all other lead sulfantimonides. It is one of the major silver minerals of the ores at Oruro, Bolivia, where it occurs with zinkenite, boulangerite, plagionite, and small amounts of semseyite, freieslebenite, miargyrite, stibnite, and owyheeite. It is slightly older than or contemporaneous with other lead sulfosalts (Chace, 1948). With the exception of owyheeite the above association is compatible with the present data. If owyheeite (Fig. 1) forms at a temperature below 300°C, it could be one of the youngest members of the group, forming at the expense of freieslebenite, andorite, and galena. Its position in the paragenetic sequence could not established by Chace (1948). At Morey, Nevada, however, William (1968) reported owyheeite to be the youngest mineral and to have formed at the expense of andorite, fizelyite, freieslebenite, and other sulfosalts.

Two distinct species of andorite may occur in nature as syntaxic intergrowths (Donnay and Donnay, 1954). Recently, Borodaev *et al* (1971) reexamined ramdohrite from the type locality in Bolivia and reported an intergrowth of light and dark bands that yielded similar X-ray diffraction patterns. Chemical analyses gave the formula $Pb_2AgSb_3S_7$ to the light band and $PbAgSb_3S_6$ to the dark band. Natural occurrences, therefore, suggest the existence of miscibility gaps in the andorite solid solution series. There should perhaps be two solvi below 300°C, one between andorite and ramdohrite and the other between ramdohrite and fizelyite compositions.

The syntaxic intergrowths of members of the andorite series are particularly interesting as possible temperature indicators. The temperature at which natural samples homogenize on heating would be the minimum temperature of deposition. Brongniardite-miargyrite exsolution could similarly be used, but the rarity of brongniardite would greatly limit its application.

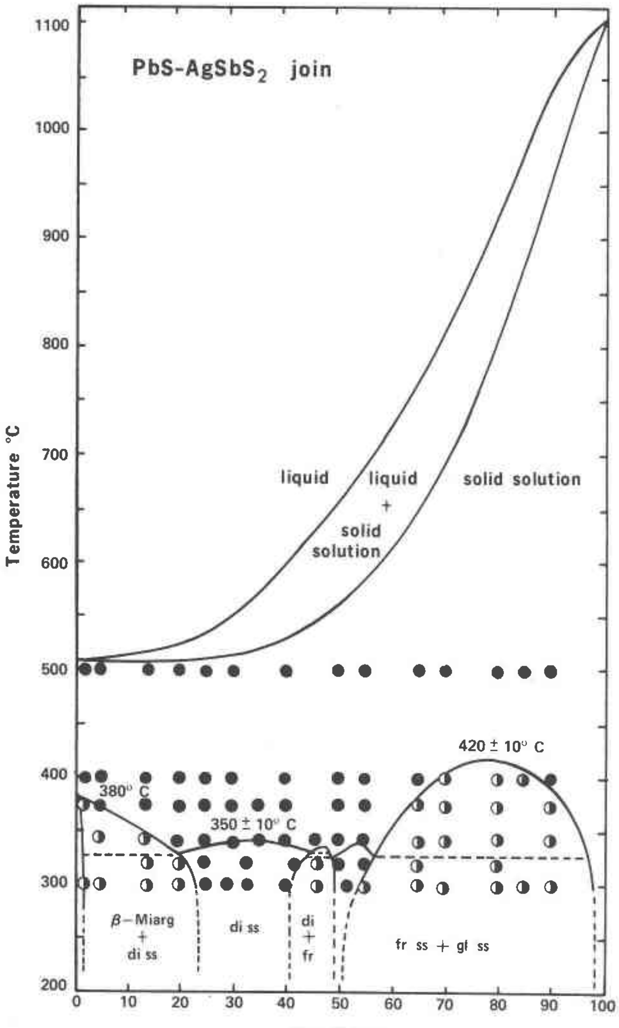

FIG. 5. Phase relations along the PbS–AgSbS$_2$ join. Symbols, solid circle: one phase; half-filled circle: two phases. Abbreviations are: miarg: miargyrite, di: diaphorite, fr: freieslebenite, gl: galena, ss: solid solution.

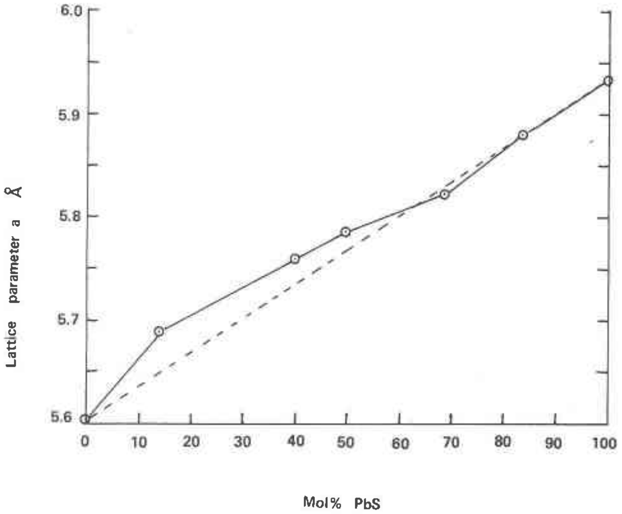

FIG. 6. Lattice parameters as a function of PbS mole percent along the PbS–AgSbS$_2$ join.

In a recent study of the Wood River lead silver deposits, Hall and Czamanske (1972) found diaphorite and Ag-boulangerite as inclusions in galena. The Ag-boulangerite has a composition $(Pb,Ag,Cu)_{5.4} \cdot Sb_{4.5}S_{11}$, intermediate between boulangerite and owyheeite. Neither Ag-boulangerite nor owyheeite is stable in the system PbS–Ag_2S–Sb_2S_3 in the temperature range of the present study.

The System PbS–Ag$_2$S–Bi$_2$S$_3$

Twenty phases reported to belong to this system are shown in Figure 7. Relevant data on these phases are summarized in a recent review by Chang and Bever (1973). Phase relations in the binary systems Ag_2S–Bi_2S_3 and PbS–Bi_2S_3 were studied by Van Hook (1960) and Craig (1967), respectively.

On the basis of natural intergrowths of galena and matildite, Ramdohr (1938) suggested an extensive solid solution along the PbS–$AgBiS_2$ join. The crest of the solvus was estimated by Ramdohr at about 350°C. Van Hook (1960) failed to determine the solvus but reported the unmixing of a sample of $AgBiS_2$ containing 3.9 mole percent PbS when held at 170°C in three months. Craig (1967) obtained complete homogenization of a natural sample containing 36 mole percent PbS at 225°C. Godovikov *et al* (1972) found that the series shows a miscibility gap below 220°C forming schirmerite (PbS · $2Ag_2S$ · $2Bi_2S_3$) and an unmixed cubic solid solution (60–90 mole percent) at 150°–220°C.

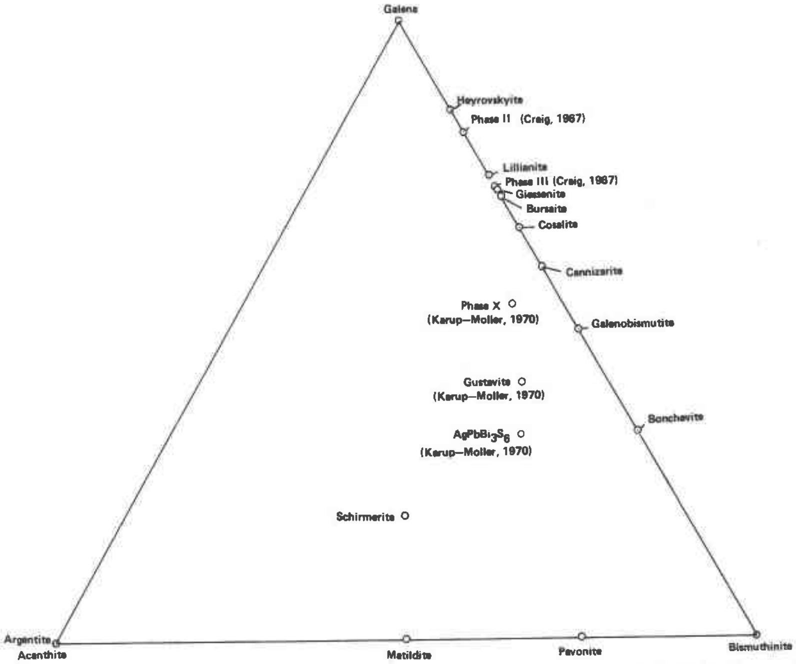

FIG. 7. Phases reported in the system PbS (galena)–Ag_2S (acanthite–argentite)–Bi_2S_3 (bismuthinite).

Investigations in the system PbS–Ag_2S–Bi_2S_3 were carried out by Van Hook (1960). Because his primary objective was to study the solubility of silver in galena, he established phase relations only in the galena–matildite solubility region. Craig (1967) showed the phase relations on the PbS–Ag_2S–Bi_2S_3 plane deduced from experiments conducted along the PbS–$AgBi_3S_5$ and PbS–$AgBiS_2$ joins in the system Pb–Ag–Bi–S.

All phases synthesized in the present study with their chemical compositions and lattice parameters are listed in Table 2, and their phase relations are discussed in the following isothermal sections.

Phase Relations at 500°C

At 500°C (Fig. 8) stable phases include heyrovskyite, lillianite, galenobismutite, pavonite, α-matildite, argentite, bismuthinite, and galena. Galena and α-matildite form a complete solid solution series with the disordered NaCl-type structure. α-matildite can accept Bi_2S_3 and Ag_2S in excess of its stoichiometric composition. The limits were determined as 5 mole percent Bi_2S_3 and 8 mole percent Ag_2S, by the appearance-of-phase method. Samples in which these limits are exceeded show pavonite and acanthite powder diffraction peaks, respectively. The a_0 cell edge here determined for α-matildite (5.64 Å) agrees well with that given by Van Hook (5.64 Å) and by Craig (5.648 Å). The variation in a_0 along the PbS–$AgBiS_2$ join and the effect of excess Ag_2S and Bi_2S_3 on a_0 also agree well with Van Hook's results. The substitution of Ag^{1+} and Bi^{3+} for $2Pb^{2+}$ is not so easily explainable when the Ag:Bi ratio departs from 1:1. Such solid solutions can arise from cationic or anionic vacancies, or interstitial occupancy to balance the charge. If it is assumed that the large S^{2-} ions form rigid frameworks within which the relatively mobile metallic ions normally occupy the octahedral sites, it is possible that some tetrahedral occupancy takes place on the silver-rich side and vacant cationic structural positions are present on the bismuth-rich side of the solid solution.

Tie lines between galena–matildite solid solution series and other phases in the system were constructed on the basis of the shift of d_{200} values of the NaCl-type phases.

At 500°C, an extensive solid solution exists along the lillianite–pavonite join with a miscibility gap between 25 and 46 mole percent PbS. The pavonite series also has a solid solution range toward galenobismutite. Experiments conducted at temperatures above 500°C (Fig. 9) show that melting near 670°C precludes complete solid solution between lillianite and pavonite.

Lillianite was here synthesized from a composition of 73 mole percent PbS and 27 mole percent Bi_2S_3. The X-ray diffraction data agree very well with those given by Craig (1967) for his phase III. Corresponding phases synthesized by Otto and Strunz (1968), Klyakhiv and Dimitriyeva (1968), and Salanchi and Moh (1969) have been shown to be similar to Craig's phase III, as well as to natural lillianite (Klyakhiv and Dimitriyeva, 1968; Takagi and Takeuchi, 1972). The lattice parameters determined in this study for silver-free lillianite (Table 2) are in fair agreement with those given by Takagi and Takeuchi (1972) for a natural sample of lillianite from Tsubakihara mine, Japan (a_0 = 13.535, b_0 = 20.451, c_0 = 4.104 Å). Chemical analysis of their specimen is not given, but the specimen is stated to contain a small amount of silver.

Pavonite was readily formed at all temperatures within the range of the present investigation. Lattice parameters (Table 2) are in fair agreement with those given by Nuffield (1954) for a natural sample from Porvenir mine, Bolivia (a_0 = 13.35, b_0 = 4.03, c_0 = 16.34 Å, β = 94.50°). The presence of small amounts of Pb, Cu, and Fe, as indicated by the chemical analysis of this specimen, may account for the difference.

A phase synthesized from a composition of 82 mole percent PbS and 18 mole percent Bi_2S_3 gave X-ray diffraction data which correspond well with those of heyrovskyite (Klominsky *et al,* 1971), and phase II (Craig, 1967). Experiments to check its lower stability limit showed no sign of breakdown at 325°C in 3000 hours (Craig, 1967). Some natural samples, however, show cosalite-galena aggregates pseudomorphous after heyrovskyite (Klominsky *et al,* 1971). The lattice parameters determined for this phase (heyrovskyite in Table 2) agree well with those given by Klominsky *et al* (1971) for a natural sample containing more than 1 percent Ag in solid solution (a_0 = 13.705, b_0 = 31.19, c_0 = 4.121 Å).

Galenobismutite was synthesized from a PbS Bi_2S_3 composition. Phase IV, reported by Craig (1967), has identical X-ray diffraction data though its composition is stated to be 48.7 mole percent PbS and 51.3 mole percent Bi_2S_3. Lattice parameters determined in this study (Table 2) are in good agreement with those given by Berry (1940) for a natural sample from Nordmark, Sweden (a_0 = 11.74, b_0 = 14.55, c_0 = 4.08 Å).

Phase Relations at 400°C

At 400°C (Fig. 10) the α-matildite solid solution is limited along the Ag_2S–Bi_2S_3 join to between 45 and

TABLE 2. Lattice Parameters and Compositions of Phases Synthesized in the System PbS–Ag_2S–Bi_2S_3

Name	Composition mole% PbS	Ag_2S	Bi_2S_3	Cryst. System	a	b	c	α	β	γ
Heyrovskyite	82.0	-	18.0	Orthorhombic	13.71	31.46	4.13	-	-	-
Galenobismutite	50.0	-	50.0	Orthorhombic	11.61	13.57	4.08	-	-	-
Bismuthinite	-	-	100.0	Orthorhombic	11.17	11.30	3.99	-	-	-
Lillianite	73.0	-	27.0	Orthorhombic	13.47	20.75	4.13	-	-	-
Lillianite s.s.	65.0	2.9	32.1	Orthorhombic	13.44	20.66	4.15	-	-	-
Lillianite s.s.	60.0	5.0	35.0	Orthorhombic	13.37	20.43	4.13	-	-	-
Lillianite s.s.	53.0	7.0	40.0	Orthorhombic	13.41	20.29	4.12	-	-	-
Lillianite s.s.	48.0	8.7	43.3	Orthorhombic	13.40	20.12	4.11	-	-	-
Pavonite	-	25.0	75.0	Monoclinic	13.30	4.04	16.43	-	94.10	-
Pavonite s.s.	4.0	23.0	73.0	Monoclinic	13.31	4.05	16.41	-	93.73	-
Pavonite s.s.	12.0	21.0	67.0	Monoclinic	13.35	4.06	16.47	-	94.68	-
Pavonite s.s.	15.0	20.0	65.0	Monoclinic	13.36	4.06	16.49	-	94.07	-
Pavonite s.s.	20.0	18.0	62.0	Monoclinic	13.35	4.07	16.50	-	93.60	-
Galena - matildite s.s.	10.0	45.0	45.0	Cubic	5.68	-	-	-	-	-
Galena - matildite s.s.	20.0	40.0	40.0	Cubic	5.70	-	-	-	-	-
Galena - matildite s.s.	30.0	33.8	36.2	Cubic	5.71	-	-	-	-	-
Galena - matildite s.s.	50.0	25.0	25.0	Cubic	5.77	-	-	-	-	-
Galena - matildite s.s.	70.0	15.0	15.0	Cubic	5.82	-	-	-	-	-
Galena - matildite s.s.	80.0	10.0	10.0	Cubic	5.86	-	-	-	-	-
α -Matildite	-	50.0	50.0	Cubic	5.65	-	-	-	-	-

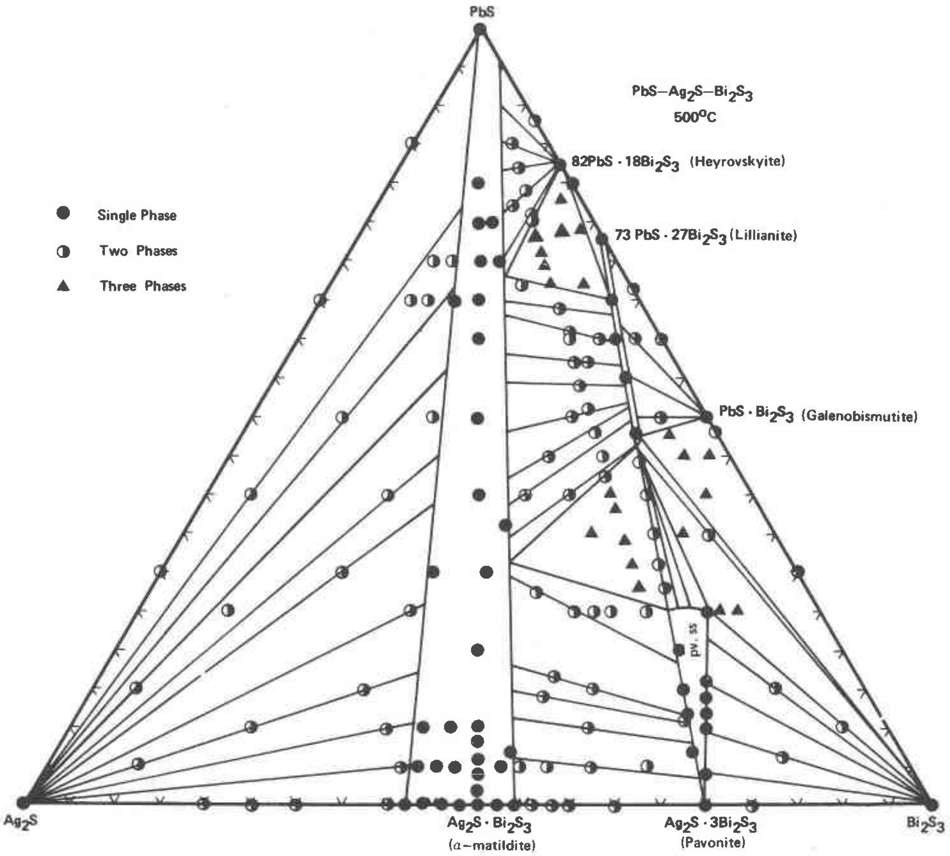

FIG. 8. Phase relations in the system PbS–Ag_2S–Bi_2S_3 at 500°C.

55 mole percent Bi_2S_3, whereas galena can take only 2 mole percent Bi_2S_3 in solid solution. The composition of galena–matildite solid solution in equilibrium with heyrovskyite and lillianite solid solution has shifted from 68 mole percent PbS at 500°C to 85 mole percent PbS at 400°C, thus narrowing the regions of two- and three-phase assemblages containing heyrovskyite. The lillianite-pavonite miscibility gap has widened to between 10 and 48 mole percent PbS.

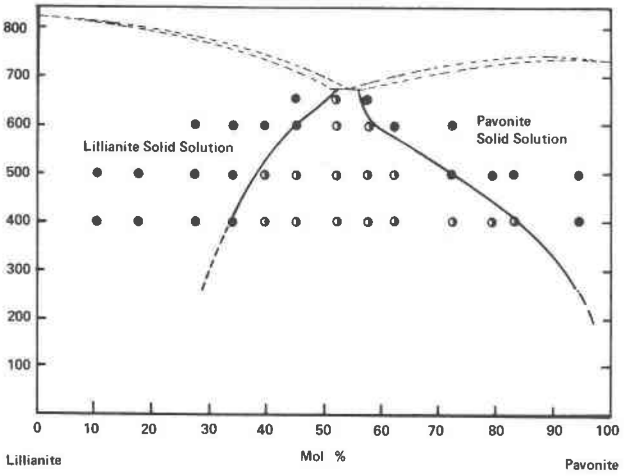

FIG. 9. Phase relations between pavonite and lillianite.

The most striking feature at 400°C is the disappearance of galenobismutite. Runs conforming to its composition and those adjacent to it in the binary and ternary regions consistently showed lillianite and bismuthinite instead of galenobismutite. Several repeated attempts gave identical results at 400°C for a period of 8 weeks, although Craig (1967) and Salanchi and Moh (1969) have reported its synthesis at 400°C or lower. At 420°C for the same length of time galenobismutite was synthesized as a single phase from the composition PbS · Bi_2S_3. We do not understand the discrepancy between our data and those of Craig (1967) and Salanchi and Moh (1969); nevertheless, we believe galenobismutite to be unstable below 400°C and support this further with evidence from natural occurrences.

Phase Relations at 300°C

Experimental runs at 300°C failed to reach equilibrium in a period up to thirty weeks. Attempts

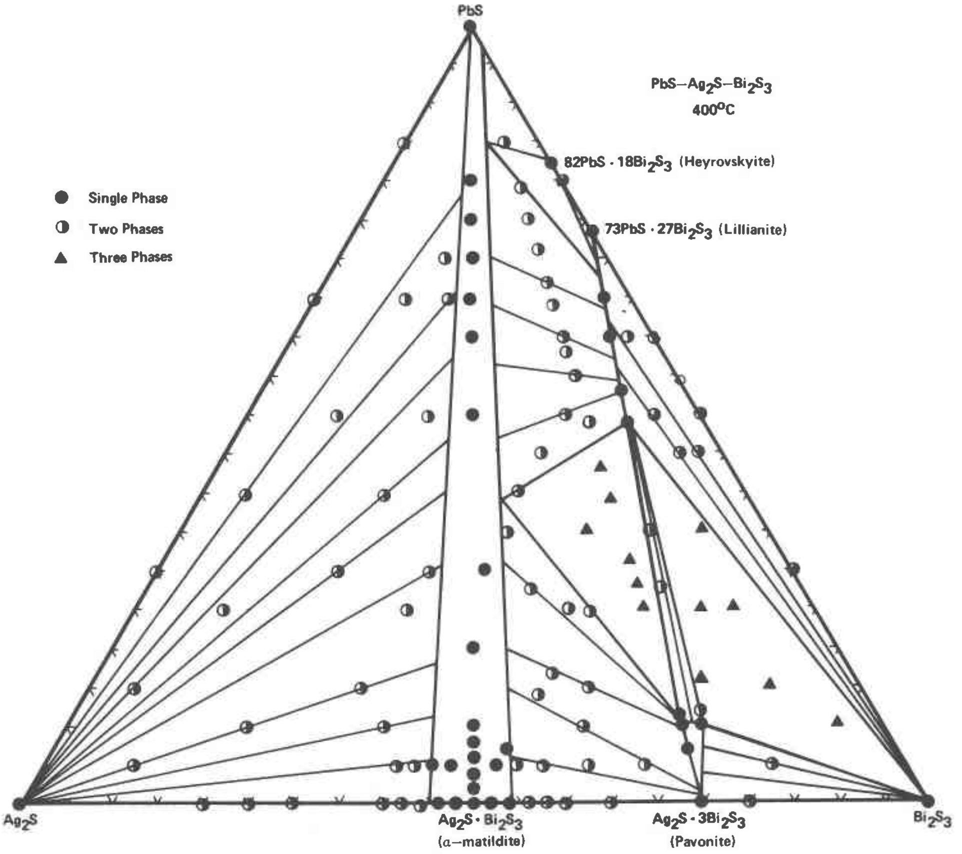

FIG. 10. Phase relations in the system PbS–Ag_2S–Bi_2S_3 at 400°C.

to construct a possible phase diagram on the basis of reaction trends at 300°C were unsuccessful because of the existence of multiple possible interpretations.

Geological Significance

The lillianite–pavonite solid solution found in this study suggests the possible occurrence of minerals having compositions along this join. The presence of a miscibility gap which increases in size with decreasing temperature further suggests that such minerals should commonly exhibit exsolution phenomena. Remarkably, both suggestions have been met by Karup-Moller (1970), who reported the new mineral gustavite ($Pb_6Ag_3Bi_{11}S_{24}$) and its associated phases, $PbAgBi_3S_6$ and $Pg_8Ag_2Bi_{10}S_{24}$ (phase X), in an assemblage from Greenland (Fig. 7). Based on close similarity in crystallographic and chemical data, he suggested a continuous solid solution between lillianite and $PbAgBi_3S_6$ and its possible extension to the Ag_2S–Bi_2S_3 join at $Ag_3Bi_7S_{12}$ composition. The compositions of each of the phases, as suggested by Karup-Moller, can be derived from that of lillianite by double substitution of $Ag^{1+} + Bi^{3+}$ for $2Pb^{2+}$. The series would therefore be similar to the PbS–$AgBiS_2$ series. However, two points need consideration in this regard: (1) an inspection of chemical compositions of phases analyzed by Karup-Moller (Fig. 18, Karup-Moller, 1970) clearly shows that the natural samples do not fall exactly on the line connecting lillianite and $Ag_3Bi_7S_{12}$ proposed by Karup-Moller, but coincide well with the lillianite–pavonite join, and (2) no phase having composition $Ag_3Bi_7S_{12}$ has been synthesized or reported in nature.

The coexistence of pavonite and gustavite in the synthetic study corresponds to several occurrences described by Karup-Moller (1972). Gustavite commonly shows exsolution of phase X, and pavonite exhibits exsolved pavonite of anomalous chemical composition (Karup-Moller, 1970). Such occurrences are in accordance with what would be expected from the present investigation.

Regions of binary and ternary phase assemblages containing heyrovskyite shrink with decreasing temperature (Fig. 10). Klominsky *et al* (1971) reported the replacement of heyrovskyite by galena and cosalite without any change in the bulk composition. This suggests that heyrovskyite may have a lower stability limit, below 300°C, which would restrict its occurrence.

The lower stability limit of galenobismutite found in the present investigation indicates that the occurrence of this mineral should be restricted to those deposits formed above 400°C. Ramdohr (1969) stated that the main occurrence of galenobismutite is in the Bi-rich high-temperature replacement deposits and in gold quartz veins. This correlates with the experimental results obtained in the present study.

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