

## The Ag-Au-S System

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### Abstract

Determination of phase relations in the Ag-Au-S system between 100° and 850°C by silica tube, differential thermal analysis, and high-temperature X-ray experiments reveals that the condensed system consists of three basic parts: the Ag-Au complete solid solution, the Ag<sub>2</sub>S-Au<sub>2</sub>S partial solid solution, and sulfur. At low temperatures, two ordered silver-gold sulfides exist, Ag<sub>3</sub>AuS<sub>2</sub> and AgAuS; they invert at 185° and 310°C, respectively, to a simple, cubic solid solution. Above 310°C a complete solid solution exists from Ag<sub>2</sub>S to approximately Ag<sub>0.9</sub>Au<sub>1.1</sub>S. This solid solution has a body-centered cubic structure for silver-rich compositions, which changes via a second-order transition to a simple, cubic structure between Ag<sub>2</sub>S and Ag<sub>1.5</sub>Au<sub>0.5</sub>S. The silver-rich end of the solid solution inverts to a face-centered modification at high temperatures. The sulfides melt in the interval 680° to 838°C with a minimum in the liquidus at Ag<sub>1.3</sub>Au<sub>0.7</sub>S.

Enthalpies of transition for the Ag<sub>2</sub>S III-II, Ag<sub>3</sub>AuS<sub>2</sub> low-high, and AgAuS low-high transitions were measured by differential scanning calorimetry and found to be, respectively: 950; 2,270(min)-2,760(max); and 1,570(min)-1,920(max) calories/mole. Within experimental error, the sulfide solid can be modeled as a regular solution with components AgS<sub>0.5</sub> and AuS<sub>0.5</sub> and with  $W_G \cong -1,000$  calories. Estimated temperature-dependent standard free energies of formation are (T = K and units of calories): -43,880 + 20.8T (acanthite, Ag<sub>2</sub>S III), -40,410 + 20.8T (uytenbogaardtite, low Ag<sub>3</sub>AuS<sub>2</sub>), -37,910 + 15.3T (high Ag<sub>3</sub>AuS<sub>2</sub>), -36,740 + 23.4T (low AgAuS), -33,340 + 17.6T (high AgAuS), and -22,700 + 29.6T (Au<sub>2</sub>S).

### Introduction

THE condensed Ag-Au-S system consists of three parts: the Ag-Au complete solid solution, the Ag<sub>2</sub>S-Au<sub>2</sub>S partial solid solution, and sulfur. Previous studies have investigated parts of this system, but the system as a whole is of interest. Assemblages from this system occur in many gold-silver deposits. Acanthite (Ag<sub>2</sub>S), electrum (Ag-Au alloy), and sulfur are moderately common; uytenbogaardtite (Ag<sub>3</sub>AuS<sub>2</sub>) has only recently been described (Barton et al., 1978) and AgAuS has not yet been found in nature. Although the high-temperature phase relations are not of direct geologic interest due to rapid reaction rates, the phase relations do suggest a need for refinement of the electrum-tarnish method (Barton and Toulmin, 1964) and offer insight into the chemistry of noble metal sulfides. Further, determined phase relations and thermodynamic data can be recast in terms of variables of use in ore petrology, thus allowing an improved description of the behavior of gold and silver in gold-silver deposits.

MacLaurin (1896) first examined the sulfidation of electrum and determined that at elevated temperatures a substantial amount of gold can be taken into a silver sulfide. The low-temperature, stoichiometric sulfides Ag<sub>3</sub>AuS<sub>2</sub> and AgAuS were first produced by reaction of Ag<sub>2</sub>S with thiogold

(I) solutions (Tavernier, 1966). Graf (1968) studied the sulfide binary between Ag<sub>2</sub>S and Ag<sub>1.5</sub>Au<sub>0.5</sub>S by resistivity and differential thermal analysis methods and established the presence of a eutectoid in the high-temperature sulfide solid solution between these compositions. Folmer et al., (1976) extended the work of Graf using differential thermal analysis, differential scanning calorimetry, and high-temperature X-ray methods to cover the binary from Ag<sub>2</sub>S to AgAuS to temperatures above 300°C, indicating another eutectoid between Ag<sub>1.5</sub>Au<sub>0.5</sub>S and AgAuS and the presence of a second-order transition in the solid solution. Others, including Messien et al. (1966), Tavernier et al. (1967), and Llabres and Messien (1968) examined the crystallography and thermal behavior of the ternary sulfides. Smit et al. (1970) measured heats of transition and Barton and Toulmin (1964) determined the temperature and compositional dependence of sulfur pressure over equilibrium electrum + sulfide assemblages.

### Experimental Methods and Results

The experimental portion of this study consisted of two parts. First, experiments with various bulk compositions were carried out at selected temperatures to determine the tie lines between the phases. Second, the sulfide phase relations

TABLE 1. Electrum- + Sulfide-Bearing Runs

T°C	Run	X <sub>Ag</sub> <sup>el</sup>	X <sub>Ag<sub>2</sub>S</sub> <sup>ss</sup>	log f <sub>S<sub>2</sub></sub> <sup>1</sup>	log f <sub>S<sub>2</sub></sub> <sup>2</sup>	S <sub>liq</sub>	Starting materials	Run time (weeks)
100	T36	0.15	0.81	-11.74		no	(Ag, Au) + S	8
100	T45	0.37	0.995	-15.43		no	"	8
200	T62	0.33	0.96	-10.67		no	"	8
200	T65	0.35	0.98	-10.91		no	"	8
300	T78	0.14	0.77	-5.59		no	"	7
500	T85	0.05	0.44	-1.70	-1.05	yes	"	7
500	T86	0.21	0.84	-3.53		no	"	7
500	T89	0.30	0.91	-4.42	-4.06	no	"	7
500	T91	0.68	0.995	-7.12	-7.26	no	"	7
500	T161	0.12	0.66	-2.64		no	AgAuS (+Ag)	7
500	T162	0.17	0.81	-3.05		no	"	7
500	T163	0.03	0.39	-0.99	-1.05	yes	Au + S + AgAuS	7
700	T94	0.06	0.46	-0.31	0.45	yes	(Ag, Au) + S	6
700	T96	0.12	0.69	-0.85	-0.78	no	"	6
700	T98	0.35	0.92	-2.90	-2.72	no	"	6
700	T100	0.73	0.995	-5.03	-4.99	no	"	6
700	T166	0.04	0.38	0.05	0.45	yes	Au + S + AgAuS	7
700	T167	0.37	0.92	-3.06		no	AgAuS (+Ag)	7
700	T168	0.18	0.76	-1.56		no	"	7
700	T169	0.16	0.71	-1.42		no	"	7
850	T104	0.08	0.62	0.62	1.30	yes	(Ag, Au) + S	6
850	T106	0.54	0.97	-2.99	-2.83	no	"	6
850	T108	0.78	0.99	-4.00	-3.50	no	"	6

<sup>1</sup> Calculated after the method of Barton and Toulmin (1964), but using the thermodynamic model from this study.

<sup>2</sup> Measured values, pyrrhotite indicator or sulfur vapor pressure.

were investigated using differential thermal analysis (DTA), differential scanning calorimetry (DSC), and high-temperature X-ray methods.

Synthesis experiments were done using standard silica tube techniques (see, for example, Scott, 1974). The reagents used were ASARCO 99.999 + percent pure Ag, Au, Fe, and S. Several electrum compositions were prepared by reacting gold and silver filings well above liquidus temperatures and then annealing for 1 day at 950°C. AgAuS was synthesized at 700°C (1 week) from a stoichiometric mixture of electrum (Ag<sub>0.5</sub>Au<sub>0.5</sub>) and sulfur. Electrum filings plus sulfur, or AgAuS plus silver, comprised the starting materials for most of the runs, allowing equilibrium to be approached from two directions: by sulfidation of a silver-rich electrum or by desulfidation (using physically separated Ag-metal as a "getter" for sulfur) of a gold-rich sulfide. Standard one-atmosphere, nichrome-wound furnaces with automatic temperature controllers were used. Temperatures were constant within 5°C of the desired value. Run times varied from 6 to 8 weeks at all temperatures. On removal from the furnaces, the runs were quenched by dropping into cool water and examined through the tubes for leakage and for phases present (sulfide, metal, condensed sulfur). The morphology of the electrum and the sulfide varied uniformly as a function of composi-

tion: silver-rich compositions produced electrum "wires" and anhedral masses of sulfide whereas the gold-rich compositions produced euhedral crystals of both electrum and sulfide. Polished sections of most runs were prepared; some run products were examined by X-ray diffraction.

After initial reaction, a small amount of synthetic pyrrhotite was inserted in some sulfur-deficient runs at 500°, 700°, and 850°C. The pyrrhotite indicator of Toulmin and Barton (1964) allowed determination of sulfur fugacity,  $f_{S_2}$ , by measurement of the  $d_{(102)}$  spacing of the pyrrhotite (a silicon internal standard was used,  $a = 5.4305 \text{ \AA}$ ). In this study, when using the pyrrhotite indicator, the estimated error in  $\log f_{S_2}$  is  $\pm 0.4$ . Table 1 lists the useful runs.

Polished sections were examined in reflected light and analyzed by means of electron microprobes at the U. S. Geological Survey (Reston, Virginia) and the University of Chicago. For the sulfides the Ziebold-Ogilvie and MAGIC correction schemes were used, with synthetic AgAuS as a standard. Determination of the electrum compositions involved an empirical method utilizing a series of 10 standards. Instability, particularly for the sulfide, under the electron beam often led to poor reproducibility of the analyses. Similar problems with stability have been observed by Rucklidge and Stumpfl (1968) and Barton et al.

(1978). To minimize this problem a variety of operating conditions were used so as to maximize the reproducibility and accuracy (as measured by analyses of the standards). Overall, the best analyses resulted when an expanded electron beam was used with beam currents of  $0.15 \mu\text{A}$  or less at 20 kV. The estimated error in the mole fraction of silver sulfide is three percent. Negligible amounts of gold and silver were detected in the sulfur ( $0.0 \pm 0.1 \text{ wt } \%$ ). With the sulfide only a qualitative measure of the minor departures from  $\text{M}_2\text{S}$  stoichiometry could be made (in  $\text{Ag}_2\text{S}$  the maximum variation is  $\text{Ag}_{2.015}\text{S}$  to  $\text{Ag}_{1.978}\text{S}$ ; Rau, 1974). Analyses, however, were sufficient to rule out compounds significantly different from  $\text{M}_2\text{S}$  (e.g.,  $\text{MS}$ ,  $\text{M}_4\text{S}$ ). The difficulty of grinding the run products, relatively small variation in cell dimensions, and inability to quench the high-temperature polymorphs of the silver-rich compositions made X-ray diffraction determination of composition impractical.

Equilibrium has not specifically been demonstrated in the determination of individual tie lines; however, several lines of evidence suggest that equilibrium was reached in a number of runs. 1. Sulfidation and desulfidation runs which approach equilibrium from different directions are consistent with each other. 2. Convergence of all the high-temperature and some of the low-temperature data to consistent relationships indicates that the determined tie lines are controlled by a common factor—presumably approach to equilibrium. Several runs made below  $500^\circ\text{C}$  are included because they are consistent with the higher temperature results. 3. Agreement within error between sulfur fugacities in the runs measured by the pyrrhotite indicator method and those calculated from the electrom-tarnish method supports the probability of equilibration. 4. Reaction rates for the silver-rich end of the solid solution are extremely rapid and, while there is a marked decrease in reaction rates with increasing gold content (also found by Lichter and Wagner, 1960), all reactions appeared to go to completion within one or two days at temperatures of  $500^\circ\text{C}$  or above. 5. At elevated temperatures pronounced recrystallization of the sulfide and electrum took place with the electrum tending to migrate to the outside of the sulfide. 6. When analyzed, all phases were homogeneous.

Differential thermal analysis was performed with approximately 50 mg of sample enclosed in a silica glass capsule. A three-lead, two thermocouple arrangement was used with one thermocouple placed in an indentation in the capsule next to the sample and the other held about 1 mm away from the capsule. The capsule and thermocouples

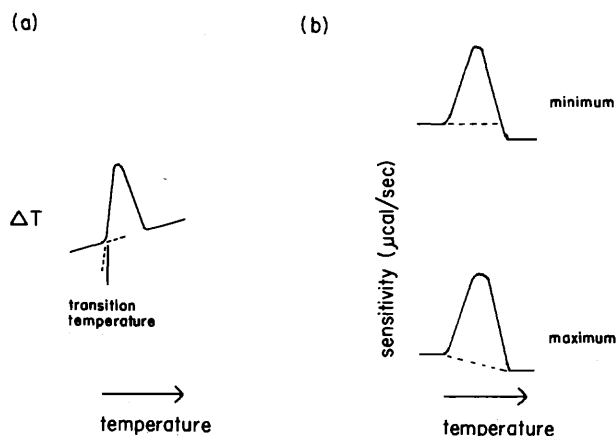


FIG. 1. Differential thermal analysis and differential scanning calorimetry measurement methods; (a) the transition temperatures measured by differential thermal analysis are defined by the intersections of the extensions of the base lines and the leading edges of the peaks, (b) the minimum and maximum areas on differential scanning calorimetry patterns used to obtain the enthalpies of transition.

were inserted in a hole drilled in a ceramic block which was then placed in a split furnace. A Leeds and Northrop two-pen recorder simultaneously recorded the temperature and the differential temperature. Heating rates were commonly on the order of  $10^\circ\text{C}/\text{min}$ , while cooling rates varied from  $40^\circ$  to less than  $1^\circ\text{C}/\text{min}$ . Nearly all measurements were made using heating and cooling rates between  $5^\circ$  and  $15^\circ\text{C}/\text{min}$ . The heating rate was controlled manually by a variable transformer to within 20 percent of the desired value. Air cooling was used exclusively, thus the cooling rate varied as a function of the temperature, although some control could be maintained. All the transition temperatures were determined by taking the intersection of the extensions of the base lines before the peaks and the leading edges of the peaks (Fig. 1a). The chromel-alumel thermocouples were calibrated against the freezing and boiling points of water and the melting point of bismuth. Measurements are precise to within  $2^\circ\text{C}$ ; for solid-solid transitions reproducibility is  $\pm 3^\circ\text{C}$ , for the melting (freezing) transitions reproducibility is  $\pm 5^\circ\text{C}$ . All differential thermal analysis transition observed were reversible, even though undercooling of several tens of degrees took place in some cases; Table 2 summarizes these results.

In compositions between  $\text{Ag}_2\text{S}$  and  $\text{Ag}_{1.5}\text{Au}_{0.5}\text{S}$  unexpected thermal behavior occurred for some runs at temperatures below  $200^\circ\text{C}$ . Similar behavior was observed by Tavernier et al. (1967). Instead of differential thermal analysis signals consistent with eutectoidal behavior, three distinct thermal effects were observed on heating, corresponding roughly to the temperatures of the

TABLE 2. Differential Thermal Analysis Results

Run	Composition	Transition temperatures (°C) (those for cooling in parentheses)
T111	Ag <sub>1.8</sub> Au <sub>0.2</sub> S	115, 782 (785)
T112	Ag <sub>1.6</sub> Au <sub>0.4</sub> S	183, 740
T113	Ag <sub>1.5</sub> Au <sub>0.5</sub> S	185, 739
T114	Ag <sub>1.4</sub> Au <sub>0.6</sub> S	182-236, 730 (732)
T115	Ag <sub>1.2</sub> Au <sub>0.8</sub> S	182-289, 726
T116	AgAuS	310, 747
T131	Ag <sub>1.65</sub> Au <sub>0.35</sub> S	115-158, 760
T124	Ag <sub>1.99</sub> Au <sub>0.01</sub> S + (Ag, Au)	807
T127	Ag <sub>1.90</sub> Au <sub>0.10</sub> S + (Ag, Au)	784
T134	Ag <sub>1.8</sub> Au <sub>0.2</sub> S + S	709
T135	Ag <sub>1.5</sub> Au <sub>0.5</sub> S + S	680 (682)
T136	Ag <sub>1.2</sub> Au <sub>0.8</sub> S + S	701 (712)
T129/118	Ag <sub>0.94</sub> Au <sub>1.06</sub> S + (Au, Ag)	756

eutectoid (113°C), the Ag<sub>2</sub>S III-II transition (177°C), and the Ag<sub>3</sub>AuS<sub>2</sub> low-high transition (185°C). The signal for each thermal effect varies as a function of composition and is most intense (per unit mass) at the composition of the substance involved in the effect. For instance, the silver sulfide transition is most intense at  $X_{Ag_2S}^{90} = 1$  and decreases monotonically as gold is added. In this study this behavior was observed only in sulfides that had been synthesized at 500°C from electrum and sulfur. An explanation for this behavior is that segregation of the gold and silver components resulted in independent regions of Ag<sub>2</sub>S, Ag<sub>3</sub>AuS<sub>2</sub>, and a mixture of the eutectoid composition; such a mixture would produce the observed pattern of transitions. Physical mixtures of Ag<sub>2</sub>S and Ag<sub>3</sub>AuS<sub>2</sub>, when equilibrated, did not show the unusual thermal response in either this study or that of Graf (1968). Folmer et al. (1976) prepared their material from gold and silver filings and sulfur; but, although they noted the occurrence of metastable transitions, they did not observe similar transitions.

High-temperature X-ray work was done on Guinier-Lenne (Nonius) cameras at the U. S. Geological Survey (Reston, Virginia) and the Uni-

versity of Chicago. Because of their tendency to decompose and/or oxidize, sulfides were mixed with ground glass (to reduce absorption) and sealed in glass capillaries. Heating rates were approximately 5°C/hr over the range 25° to 700°C. X-ray patterns for three compositions (Ag<sub>1.65</sub>Au<sub>0.35</sub>S, Ag<sub>1.5</sub>Au<sub>0.5</sub>S, AgAuS) confirmed the number of phase transitions and the temperatures found by differential thermal analysis.

Differential scanning calorimetry was performed on a Perkin-Elmer DSC-2 at the U. S. Geological Survey (Reston, Virginia). Sealed aluminum pans enclosed synthetic Ag<sub>2</sub>S, Ag<sub>3</sub>AuS<sub>2</sub>, and AgAuS. After calibration of the instrument, several measurements of the heats of transition for each of these materials were made with heating rates of 10°C/min and 5 mc/sec sensitivity. Charges weighed about 10 mg. No evidence of decomposition of the sulfides could be detected on opening the sample pans after the measurements. Minimum and maximum values for the heats of transition were obtained by measuring the areas under the peaks with a planimeter. The minimum area is that between the peak and the straight line extension of the low-temperature base line; a line joining the high- and low-temperature base lines delimits the maximum area (see Fig. 1b). Heats of transition were normalized to indium metal for which enthalpy of melting was taken as 780 ± 10 cal/mole (Hultgren et al., 1973a). Values are given in Table 3 for the transitions: Ag<sub>3</sub>AuS<sub>2</sub> low-high and AgAuS low-high. Smit et al. (1970) report different values for these transitions and, although their estimated accuracy was only 20 percent (measurements by differential thermal analysis), there does not appear to be a simple numerical origin for the discrepancy between their values and mine.

### Phase Relations

At temperatures of interest the phase relations in the bounding binary systems are well known

TABLE 3. Measured and Calculated Enthalpies of Transition (Calories/Mole)

	This study <sup>1</sup>		Smit et al. (1970) <sup>2</sup>	Mills (1974)	Calculated <sup>3</sup>
	min	max			
Ag <sub>2</sub> S III-II		950 <sup>4</sup>	1,200	950 <sup>5</sup>	
Ag <sub>3</sub> AuS <sub>2</sub> low-high	2,270	2,760	4,000		2,050
AgAuS low-high	1,570	1,920	3,500		1,600

<sup>1</sup> Estimated accuracy of each value is 4 percent.

<sup>2</sup> Estimated accuracy is 20 percent.

<sup>3</sup>  $\Delta H_{tr} = T_{tr}\Delta S_{tr}$ ; these numbers assume an ideal entropy of mixing of the gold and silver, and that the low form is ordered and the high form disordered.

<sup>4</sup> The maximum and minimum are the same because the high and low temperature baselines were at the same level.

<sup>5</sup> Mills' preferred value.

(e.g., Kracek, 1946; White et al., 1957; Hansen and Anderko, 1958; Elliot, 1965; Hultgren et al., 1973b). A brief discussion follows based on the literature data for each of these binary systems.

### Ag-S

The silver-sulfur system has been studied by several investigators, most definitively by Kracek (1946) and Rau (1974) whose data on the phase relations are summarized in Figure 2. Between 25°C and the liquidus there are three polymorphs of  $\text{Ag}_2\text{S}$  (crystallographic data for all phases are given in Table 4).  $\text{Ag}_2\text{S}$  III, acanthite, shows little deviation from stoichiometric  $\text{Ag}_2\text{S}$ ; from 176.3° (Ag-saturated) to 177.8°C (S-saturated)  $\text{Ag}_2\text{S}$  III inverts to  $\text{Ag}_2\text{S}$  II, argentite (Kracek, 1946), which is body-centered cubic (phases denoted as in Kracek, 1946). A structure for  $\text{Ag}_2\text{S}$  II proposed by Rahlfs (1935) has the sulfur at the origin and center of the cell and the silver statistically distributed over 42 sites (positions b, d, and h in space group  $\text{Im}\bar{3}\text{m}$  which are 6-, 12-, and 24-fold degenerate, respectively, see the *International Tables for X-ray Crystallography*, vol. 1, space group # 229). A modification of this model proposed by Folmer et al. (1976) has the 6(b) and 12(d) sites with slightly higher occupancies than the 24(h). Between 586° (Ag-saturated) and 622°C (S-saturated)  $\text{Ag}_2\text{S}$  II inverts to  $\text{Ag}_2\text{S}$  I (Kracek, 1946), which is thought to be face-centered cubic (Djurle, 1958; Frueh, 1961).

Jeannot et al. (1969) and Jeannot and Perrot (1970) present thermodynamic evidence for the existence of  $\text{Ag}_4\text{S}$  below 450°C. However, this finding conflicts with all other reported phase relations and with electrochemical cell measure-

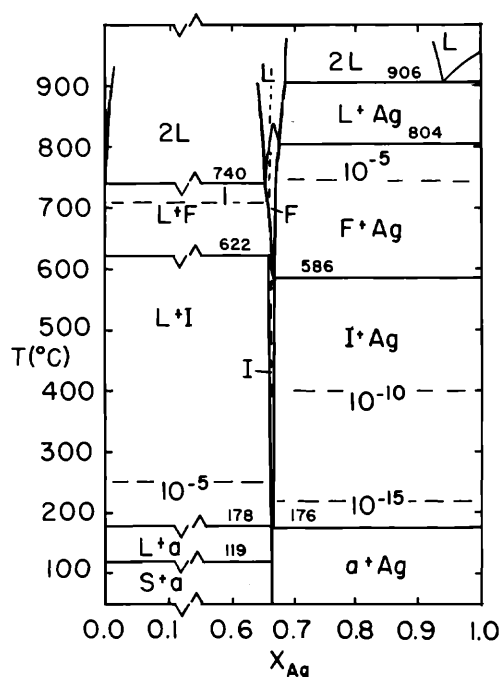


FIG. 2. Temperature-composition diagram for the Ag-S system. The dashed lines are isopleths of the fugacity of sulfur (atm). The phases are: S = solid sulfur, a = acanthite ( $\text{Ag}_2\text{S}$  III), I = argentite ( $\text{Ag}_2\text{S}$  II), F =  $\text{Ag}_2\text{S}$  I, and L = liquids (Ag, S,  $\text{Ag}_{2+x}\text{S}$ ).

ments made by Wagner (1953), hence  $\text{Ag}_4\text{S}$  will not be discussed.

Throughout the temperature range of interest silver is solid and sulfur is present as vapor plus either solid or liquid (melting point—119.3°C).

### Ag-Au

Silver and gold form a complete solid solution

TABLE 4. Crystallographic Data for Phases in the Ag-Au-S System

Phase	Cell parameters				$\beta$	Space group(s)	Reference(s)
	Z	a	b	c			
Ag	4	4.0862 Å	—	—	—	Fm3m	(1)
Au	4	4.0786	—	—	—	Fm3m	(1)
$\text{Ag}_2\text{S}$ III	4	4.229	6.931	7.862	99.61°	$\text{P}2_1/\text{n}$	(2)
$\text{Ag}_2\text{S}$ II	2	4.88	—	—	—	$\text{Im}\bar{3}\text{m}$	(3)
$\text{Ag}_2\text{S}$ I	4	6.3	—	—	—	F — (?)	(4)
$\text{Ag}_3\text{AuS}_2$ low	8	9.75	—	9.85	—	$\text{P}4_122, \text{P}4_1$	(5)
$\text{Ag}_3\text{AuS}_2$ high	1	4.94	—	—	—	$\text{Pn}\bar{3}\text{m}$	(3), (6)
$\text{AgAuS}$ low	16	8.38	13.42	9.09	111.4	I2, Im, I2/m	(6)
$\text{AgAuS}$ high	2	5.10	—	—	—	$\text{Pn}\bar{3}\text{m}$	(3), (6)
$\text{Au}_2\text{S}$	2	5.020	—	—	—	$\text{Pn}\bar{3}\text{m}$	(7)

- (1) PDF card 14-72.
- (2) PDF card 14-73.
- (3) Folmer et al. (1976).
- (4) Djurle (1958).
- (5) Graf (1968).
- (6) Smit et al. (1970).
- (7) Hirsch et al. (1966).

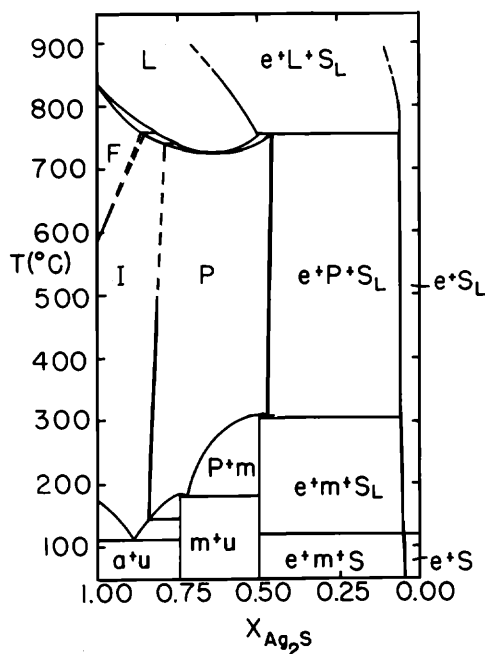


FIG. 3. Temperature-composition diagram for the  $\text{Ag}_2\text{S}$ - $\text{Au}_2\text{S}$  join, dashed where uncertain. The phases are: S = solid sulfur,  $S_L$  = liquid sulfur, e = electron, a = acanthite ( $\text{Ag}_2\text{S}$  III), u = uytenbogaardite (low  $\text{Ag}_3\text{AuS}_2$ ), m = low  $\text{AgAuS}$ , I = body-centered cubic solid solution, P = primitive cubic solid solution, F = face-centered cubic solid solution, L = sulfide liquid. Vapor is present throughout.

(face-centered cubic) over the temperature range of interest (Hultgren et al., 1973b). At high temperatures the solid solution is completely disordered, whereas below  $350^\circ\text{C}$  there is some tendency for short range order (Syncek et al., 1969).

#### *Au-S*

Although several gold sulfides may be precipitated from solution (Laist, 1954; Cugnac-Pailliotet and Pourdier, 1972), none appear to be stable under conditions of interest. Barton and Toulmin (1964) observed no tarnish on gold kept in contact with sulfur for periods up to one year at temperatures from  $-15^\circ$  to  $500^\circ\text{C}$ . Kullerud and Yoder (1959) and R. C. Newton (pers. commun., 1978) did not observe any sulfide to form on gold in the presence of liquid sulfur at temperature between  $700^\circ$  and  $900^\circ\text{C}$  and pressures to 10 kb. In this study no sulfide was observed to form on gold in a 24-hour experiment conducted at 10 kb and  $300^\circ\text{C}$ . Hirsch et al. (1966) state that metastable  $\text{Au}_2\text{S}$  precipitated from solution has a  $\text{Cu}_2\text{O}$  structure (a structure type unknown for  $\text{Ag}_2\text{S}$ ).

#### *Ag-Au-S*

The ternary solids lie along the  $\text{Ag}_2\text{S}$ - $\text{Au}_2\text{S}$  join, extending from  $\text{Ag}_2\text{S}$  to slightly beyond  $\text{AgAuS}$ ;

phase relations along this join are summarized in Figure 3.

At low temperature there are two stoichiometric ternary compounds— $\text{Ag}_3\text{AuS}_2$  (uytenbogaardite) and  $\text{AgAuS}$ . Messien et al. (1966) reported low temperature  $\text{Ag}_3\text{AuS}_2$  to be cubic ( $a = 9.72 \text{ \AA}$ ) with space group  $P4_13$ . Graf (1968) later demonstrated that the symmetry is actually tetragonal (see Table 4). Graf's observed powder reflections show that the space group is primitive and the only possible nonunit translational symmetry elements are a  $4_1$  or a  $4_3$ . Possible space groups are  $P4_122$ ,  $P4_1$ ,  $P4_322$ , and  $P4_3$ .

At intermediate temperatures on the  $\text{Ag}_2\text{S}$ - $\text{Au}_2\text{S}$  join there are two solid solutions ranging from  $\text{Ag}_2\text{S}$  to about  $\text{Ag}_{0.9}\text{Au}_{1.1}\text{S}$ . The silver-rich end of the solid solution is body-centered cubic ( $\text{Im}3m$ ) with a modified  $\text{Ag}_2\text{S}$  II structure. Because  $\text{Ag}_2\text{S}$  and  $\text{Ag}_3\text{AuS}_2$  there is a transition from the body-centered to the primitive cell (Folmer et al., 1976). With increasing temperature this transition shifts to more gold-rich compositions. The primitive structure is continuous to the gold-rich limit of the solid solution. These solid solutions have two eutectoids between the low-temperature ordered compounds. Between  $\text{Ag}_2\text{S}$  and  $\text{Ag}_3\text{AuS}_2$  there is a eutectoid at  $\text{Ag}_{1.78}\text{Au}_{0.32}\text{S}$  and  $113^\circ\text{C}$  (Graf, 1968; confirmed in this study and by Folmer et al., 1976). Between  $\text{Ag}_3\text{AuS}_2$  and  $\text{AgAuS}$  and close to  $\text{Ag}_3\text{AuS}_2$  Folmer et al. (1976) indicated a eutectoid at  $181^\circ\text{C}$ . Low-temperature  $\text{Ag}_3\text{AuS}_2$  and  $\text{AgAuS}$  invert to primitive cubic structures ( $\text{Pn}3m$ ) at  $185^\circ$  and  $310^\circ\text{C}$ , respectively.

Folmer et al. (1976) present several types of evidence which suggest that the transition from the body-centered to the primitive cell may be of second or higher order: (1) there is no observed miscibility gap, no detectable heat of transition, and no discontinuity in the cell volumes; (2) the space groups of the two forms are such that a second-order transition is allowable by Landau's (Landau and Lifshitz, 1959) theory of second-order transitions; (3) the transition is easily reversible and does not show undercooling; (4) the primitive structure will occur in regions where it is metastable with respect to the body-centered structure plus low-temperature  $\text{Ag}_3\text{AuS}_2$ ; and (5) although there is no detectable heat of transition, the heat capacity ( $C_p$ ) is discontinuous, consistent with second-order behavior. In this study no evidence was observed for the primitive to body-centered transition on either the differential scanning calorimetry or the high-temperature X-ray runs of  $\text{Ag}_3\text{AuS}_2$ . For this reason, and others discussed below, it is thought that this transition intersects the solidus at a more silver-rich composition than  $\text{Ag}_3\text{AuS}_2$ .

At high-temperatures ( $586^\circ$  to  $622^\circ\text{C}$  in the silver

end member) there is a transition from the body-centered structure to a face-centered structure. No thermal effect was noted for this transition in the differential thermal analysis runs, perhaps because the heat of transition is very small (Mills, 1974, gives 0.10 kcal for the  $\text{Ag}_2\text{S}$  II-I transition). Because the high-temperature X-ray pattern for the most silver-rich composition ( $\text{Ag}_{1.65}\text{Au}_{0.35}\text{S}$ ) failed to show this transition, the boundary between the body-centered and the face-centered phases is thought to rise steeply with increasing gold content.

Folmer et al. (1976) propose a structural model for the solid solutions at temperatures below  $500^\circ\text{C}$  which is based on Rahlfs' (1935) statistical model of  $\text{Ag}_2\text{S}$  II. In the body-centered structure the sulfur atoms are statistically distributed over sites 6(b), 12(d), and 24(h), with the sulfur atoms at the origin and center of the cell and the gold atoms at the 8(c) sites (space group  $\text{Im}3\text{m}$ ). Addition of gold is thought to cause a decrease in the occupancy of the 6(b) site alone until it is empty. When all the 6(b) silver has been removed, it appears that the addition of more gold begins the selective depopulation of the 12(d) sites. If this interpretation is correct—the evidence from Folmer et al. (1976) is contestable because they give no interpretation beyond the emptying of the 6(b) sites—the 12(d) sites are completely emptied at approximately the limit of the solid solution— $\text{Ag}_{0.9}\text{Au}_{1.1}\text{S}$  (using Folmer et al.'s site occupancies). This scheme, in which silver of higher coordination is removed first, is consistent with the preference of transition metals with nearly filled d-orbitals for low coordination numbers. At a point corresponding to the transition from body-centered to primitive structure, the 8(c) sites in  $\text{Im}3\text{m}$  split into the 4(b) and 4(c) sites of  $\text{Pn}3\text{m}$  (see the *International Tables for X-ray Crystallography*, vol. 1, space group # 224). With increasing gold content these sites change in relative population, with one accepting most of the gold and the other approaching zero occupancy. Metastable  $\text{Au}_2\text{S}$  is the limiting case of this trend; the space group is  $\text{Pn}3\text{m}$  and all the gold is either in the 4(b) or 4(c) sites (these are the alternate centers of the eight small cubes in the unit cell—gold is linearly coordinated by sulfur; Hirsch et al., 1966). A highly schematic illustration of the population trends is given in Fig. 4.

The slope of the  $\text{Im}3\text{m}$ - $\text{Pn}3\text{m}$  transition (Fig. 3) is consistent with this structural model because increasing temperature favors the  $\text{Im}3\text{m}$  structure which has eight equivalent gold sites for mixing whereas the  $\text{Pn}3\text{m}$  structure has two disjoint sets of four equivalent gold sites. The composition  $\text{Ag}_{1.5}\text{Au}_{0.5}\text{S}$  is the likely limit of the body-centered

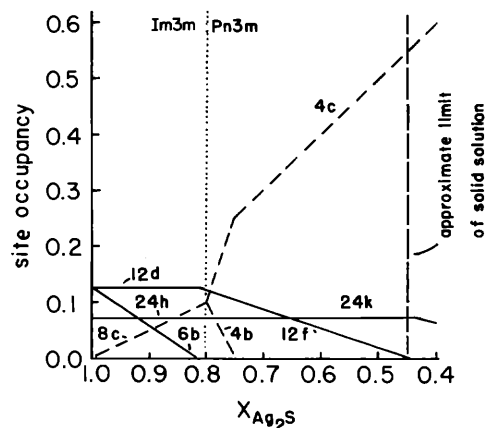


FIG. 4. Schematic site population trends in  $(\text{Ag}, \text{Au})_2\text{S}$ . The dashed lines are for the gold-bearing sites, the solid lines are for the silver-bearing sites (sites are labeled as in *International Tables for X-ray Crystallography*, vol 1). The site occupancy is the occupancy (fraction of one) for one site; e.g., an occupancy of 0.125 for the 12(d) sites means there are  $12 \times 0.125 = 1.50$  silver atoms, on the average, in the d positions in each unit cell. This diagram is based on data from Folmer et al. (1976).

lattice at any temperature. At this composition there is one gold atom per unit cell; a second gold atom added to any unit cell would prefer the subset of four sites of the first gold atom (i.e., 4(b) or 4(c) in  $\text{Pn}3\text{m}$ ), because there it would not be adjacent to another gold atom.

With this structural model there should be a higher order transition when the 6(b) sites are emptied and the 12(d) sites begin to lose silver, because at that point there would be a discontinuity in the change of entropy with composition, hence a discontinuity in the second derivative of free energy. This transition would not appear in any physical measurements of first-order properties or in X-ray patterns (no symmetry change). One might ask, concerning this model, why sites depopulate individually when none is full to begin with, and also how the gold-rich sulfides maintain  $\text{Pn}3\text{m}$  symmetry when the sum of the radii of the atoms along the body diagonal is about  $11 \text{ \AA}$  but the length of the body diagonal calculated from the cell edge is only about  $9 \text{ \AA}$ .

Because the nonstoichiometry of the sulfide increases with temperature in the Ag-S system, similar behavior is expected for the ternary sulfides. Necessarily though, as required by the phase rule, the width of the sulfide field must narrow to zero at the edge of the four-phase region (vapor + liquid sulfur + sulfide + electrum).

Data from Table 1 are plotted in Figure 5 to correlate the electrum composition with metal-saturated sulfide composition. Isothermal curves calculated using the model in the next section are also plotted. Although the  $100^\circ\text{C}$  data points

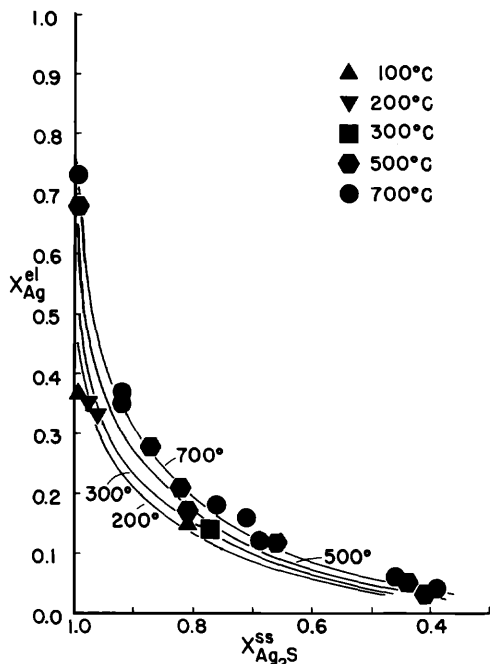


FIG. 5. Electrum-sulfide tie line data. The curves are calculated from equation (5), see text.

represent metastable existence of the solid solution, these points are included because they are consistent with the higher temperature data. Figure 6 shows four isothermal ternary sections.

The melting relations for the sulfides were determined entirely by differential thermal analysis. Agglomeration of fine-grained aggregate into beads was observed in all runs. Along the binary, melting temperatures were determined for metal- and sulfur-saturated parts as well as for stoichiometric compositions (see Figs. 3 and 6). Determinations for compositions that were metal- or sulfur-saturated were made using sulfide that had been equilibrated with excess metal or sulfur at 700°C for 2 weeks. These charges were ground as fine as possible and cycled through the melting interval several times. Fluctuations in the transition temperatures appeared to be random and were within measurement error.

There is a minimum in the stoichiometric sulfide liquidus at 720°C and  $\text{Ag}_{1.3}\text{Au}_{0.7}\text{S}$ ; this shifts to more silver-rich compositions and lower temperatures for metal- and sulfur-saturated sulfide compositions, although the details are not clearly defined (see Fig. 7). Tavernier et al. (1967) reported the melting temperature of  $\text{Ag}_3\text{AuS}_2$  to be 755°C; Smit et al. (1970) reported the melting temperature of  $\text{AgAuS}$  to be about 730°C (both differential thermal analysis measurements). Neither temperature corresponds closely to those obtained here. The invariant point  $S_{\text{vapor}} + S_{\text{liquid}}$

+  $(\text{Au, Ag})_{\text{ss}} + (\text{Au, Ag})_2\text{S}_{\text{ss}} + (\text{Ag, Au})_2\text{S}_{\text{liq}}$  is at  $756^\circ \pm 10^\circ\text{C}$ .

Although compositions were not measured, the liquid on the metal- and sulfur-saturated sides of the binary should be farther removed from the binary than the coexisting solid sulfides. Above the invariant point the limiting sulfide liquid moves to more silver-rich compositions with increasing temperature (Figs. 3 and 7).

### Thermodynamics

The thermodynamic properties of gold-silver alloys are well known (e.g., White et al., 1957; Hultgren et al., 1973b), as are those for the silver-sulfur binary (e.g., Wagner, 1953; Mills, 1974; Rau, 1974). Barton and Skinner (1979) estimate the temperature-dependent free energy of formation of  $\text{Au}_2\text{S}$ . There is sparse information for the ternary: Smit et al. (1970) estimated heats of transition and the work of Barton and Toulmin (1964) allows calculation of  $f_{\text{S}_2}$  over an electron + sulfide assemblage but specifies only the composition of the electrum.

In this study the primary data available for calculation of the thermodynamic properties of the sulfide are the electrum-sulfide tie lines. The

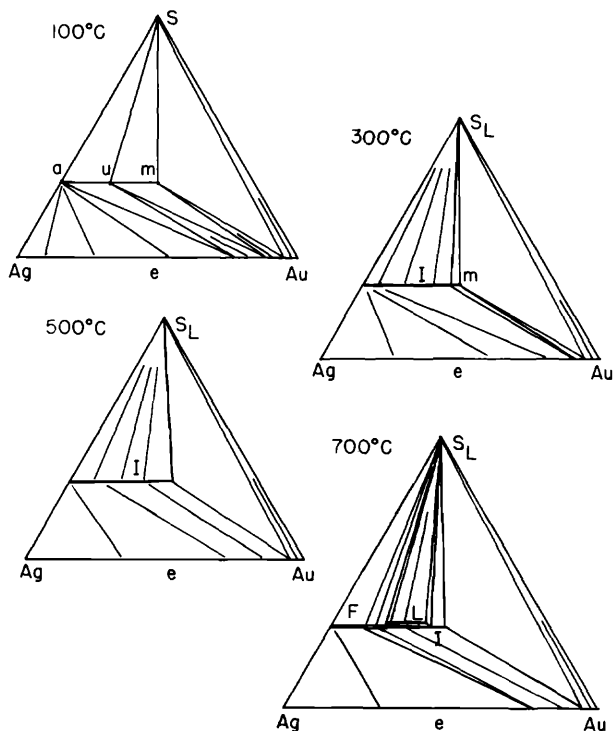


FIG. 6. Isothermal ternary sections for the system Ag-Au-S at 100°, 300°, 500°, and 700°C. Phases are denoted as in Figure 3, except that P is included with I. Vapor is present throughout.



quality of the data is such that numerous, alternative theoretical or empirical models could be admitted. For two reasons the sulfide solid solution will be modeled as a symmetrical regular solution with components  $\text{AgS}_{0.5}$  and  $\text{AuS}_{0.5}$ : (1) this model fits all the experimental data within the error for those data, and (2) it is a simple model as might be expected for solid solutions with an argentite ( $\text{Ag}_2\text{S}$  II) structure ( $\text{MS}_{0.5}$ , not  $\text{M}_2\text{S}$ , components are used here because the cations, not the anions, are mixing). At an earlier stage of this study (Barton, 1978) an empirical scheme was used which gave comparable results.

Equation (1) represents an exchange reaction between electrum and sulfide.



The equilibrium constant for this reaction is given by equation (2), where  $a_i^p$ ,  $X_i^p$ , and  $\gamma_i^p$  are, respectively, the activity, mole fraction, and activity coefficient of component  $i$  in phase  $p$ ; ss indicates sulfide solid solution and el indicates electrum.

$$K = \frac{(a_{\text{AuS}_{0.5}}^{\text{ss}})(a_{\text{Ag}}^{\text{el}})}{(a_{\text{AgS}_{0.5}}^{\text{ss}})(a_{\text{Au}}^{\text{el}})} = \frac{(1 - X_{\text{AgS}_{0.5}}^{\text{ss}})(X_{\text{Ag}}^{\text{el}})\gamma_{\text{AuS}_{0.5}}^{\text{ss}}\gamma_{\text{Ag}}^{\text{el}}}{(1 - X_{\text{Ag}}^{\text{el}})(X_{\text{AgS}_{0.5}}^{\text{ss}})\gamma_{\text{AgS}_{0.5}}^{\text{ss}}\gamma_{\text{Au}}^{\text{el}}} \quad (2)$$

The standard states are the pure end members at the temperature of interest (e.g.,  $\text{AgS}_{0.5}$  II and hypothetical  $\text{AuS}_{0.5}$ ). In a symmetrical regular solution activity coefficients are of the form given in equation (3), where  $W_G$  is an interaction parameter related to the excess free energy of mixing (Thompson, 1967).

$$\ln \gamma_i = (1 - X_i)^2 W_G / RT \quad (3)$$

Several sources of information can be used to evaluate  $K$ . 1. White et al. (1957) give analytical expressions for the activity coefficients of silver and gold in electrum which are consistent with the

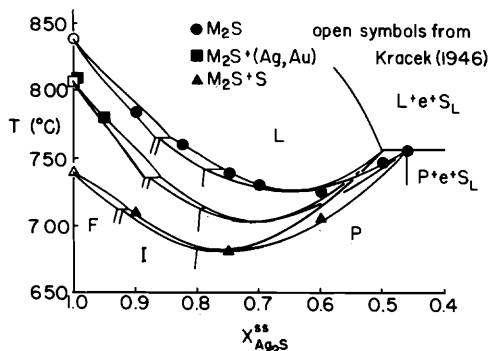


FIG. 7. Sulfide melting relations. Vapor is present throughout. Phases are denoted as in Figure 3.

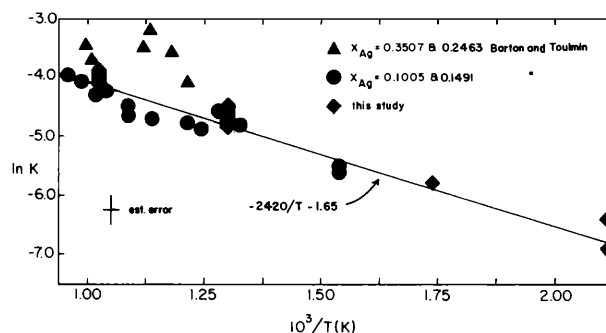


FIG. 8. The  $\ln K$  versus  $1,000/T$  (K) plot for the equation  $\text{AgS}_{0.5}^{\text{ss}} + \text{Au}^{\text{el}} = \text{AuS}_{0.5}^{\text{ss}} + \text{Ag}^{\text{el}}$ . The 0.3507 and 0.2463 points were not used in determining the best fit line which is the average of the least squares fits for the data from this study and the 0.1005 and 0.1491 experiments of Barton and Toulmin (1964). Each point from Barton and Toulmin represents one tarnish-fresh reversal of an electrum. No straightforward manipulation of the model was found that would bring the high  $X_{\text{Ag}}^{\text{el}}$  points into line; this discrepancy is consistent with that found in Figure 12.

Ag-Au data from Hultgren et al., 1973b. 2. Mole fractions for use in equation (2) come from the experimentally determined tie lines. 3. The electrum-tarnish calibration method of Barton and Toulmin (1964) provides values for  $a_{\text{AgS}_{0.5}}^{\text{ss}}$  from which, given a model for the sulfide solution and a relationship between  $X_{\text{Ag}}^{\text{el}}$  and  $X_{\text{AgS}_{0.5}}^{\text{ss}}$ , one can obtain  $a_{\text{AuS}_{0.5}}^{\text{ss}}$ .

Calculated values of  $K$ , one for each electrum-sulfide pair, best converge for  $W_G = -1,000$  calories using only the two most intensively studied isotherms,  $500^\circ$  and  $700^\circ\text{C}$ . It is difficult to give a meaningful uncertainty to this value, but for  $W_G$ 's of  $-500$  and  $-1,500$  calories the differences between the maximum and minimum  $K$ 's, calculated for the electrum-sulfide pairs, are about doubled. Negative interaction energies, on the order of several kilocalories, are also found for electrum (White et al., 1957), so perhaps a large negative interaction energy for the sulfide is not as surprising as it might first seem. In Figure 8,  $\ln K$  is plotted versus  $1/T$  (K) with a chosen best fit line.

The standard free energy of reaction (1) is given by equation (4).

(calories,  $350(?) < T(\text{K}) < 1,050$ )

$$\Delta G = -RT \ln K = 4,810 + 3.28T(\text{K}) \quad (4)$$

The error of fit for this equation is about 200 calories, while the total error, which arises primarily from the tie line determinations, is about 1,000 calories. Standard free energies of formation for  $\text{Au}_2\text{S}$ , high  $\text{Ag}_3\text{AuS}_2$ , and high  $\text{AgAuS}$  can be derived directly from (4) and the free energy of formation of argentite given by Kubaschewski

TABLE 5. Free Energies of Formation<sup>1</sup>

Reaction	T limits		$\Delta G^\circ_{T,F}$	$\Delta G^\circ_{298,F}$	Estimated error	Reference
	min	max				
4Ag + S <sub>2</sub> = 2Ag <sub>2</sub> S	?	450	-43,880 + 20.8T	-37,680	1,000	This study
"	?	450	-44,800 + 22.1T	-38,200	1,000	Barton and Skinner (1979)
"	450	1,100	-41,980 + 16.52T	-27,060	1,000	Kubaschewski et al. (1967)
3Ag + Au + S <sub>2</sub> + Ag <sub>3</sub> AuS <sub>2</sub>	?	458	-40,410 + 20.8T	-34,210	1,500	This study
"	458	1,000	-37,910 + 15.3T	-33,350	1,500	This study
2Ag + 2Au + S <sub>2</sub> = 2AgAuS	?	583	-36,740 + 23.4T	-29,780	2,000	This study
"	583	1,020	-33,340 + 17.6T	-28,100	2,000	This study
4Au + S <sub>2</sub> = 2Au <sub>2</sub> S	?	?	-12,500 + 24T	-5,340	5,000	Barton and Skinner (1979)
"	?	?	-22,700 + 29.6T	-13,880	4,000	This study

<sup>1</sup> T = K; standard states are pure Ag metal, pure Au metal, and ideal S<sub>2</sub> gas at temperature and 1 atmosphere pressure; all values in units of calories.

et al. (1967) (Table 5).<sup>1</sup> Furthermore, use of the expression relating T and the equilibrium constant K can be used with the solution model ( $W_G = -1,000$  calories) to give expression (5) which relates  $X_{Ag}^{el}$  to  $X_{AgS_{0.5}}^{ss}$ .

$$1 = \frac{(1 - X_{AgS_{0.5}}^{ss})(X_{Ag}^{el})}{(X_{AgS_{0.5}}^{ss})(1 - X_{Ag}^{el})} \times \exp \left[ \frac{1,208X_{Ag}^{el^2} + 3,271X_{Ag}^{el} + 885 - 1,000X_{AgS_{0.5}}^{ss}}{T} - 1.384X_{Ag}^{el} + 2.34 \right] \quad (5)$$

The isothermal curves in Figure 5 were obtained by an iterative solution of this equation. The error of fit in  $X_{AgS_{0.5}}^{ss}$  to the experimental data is  $\pm 0.03$ .

Barton and Skinner (1979) propose a linear, temperature-dependent, free energy equation for Au<sub>2</sub>S (Table 5) based on 25°C solubility data (Cugnac-Pailliotet and Pourdier, 1972) and an estimated entropy. Both equation (5) and the equation of Barton and Skinner show that Au<sub>2</sub>S is metastable with respect to liquid or solid sulfur-saturated vapor plus gold at all temperatures of interest, in agreement with the experimental evidence cited earlier. The calculated standard volume change for the formation of Au<sub>2</sub>S is 0.10 cal/bar at 25°C; (data from Hirsch et al., 1966; Robie et al., 1978); therefore, Au<sub>2</sub>S would not be expected to be stabilized with increasing pressure (unless  $d\Delta V/dP$  or  $d\Delta V/dT$  is large and negative), an interpretation supported by the various high-pressure sulfidation experiments discussed earlier.

<sup>1</sup> It should be noted that the free energies calculated here are actually for the metal-saturated sulfides, which deviate slightly from M<sub>2</sub>S stoichiometry. Use of Rau's (1974) data to integrate the change in free energy across the width of the Ag<sub>2+x</sub>S field to Ag<sub>2</sub>S shows that the maximum error introduced is less than 150 calories. The errors for the solid solution should be comparable. As this error is much less than the other errors, it is neglected.

Combination of the measured enthalpies of transition for Ag<sub>2</sub>S, Ag<sub>3</sub>AuS<sub>2</sub>, and AgAuS with the calculated standard free energies of formation for the higher temperature forms (Table 5) provides estimates of the standard free energies of formation of the lower temperature forms (Table 5). Two types of checks can be made on these results—both show agreement within experimental error. 1. Calculation of electrom compositions and sulfur

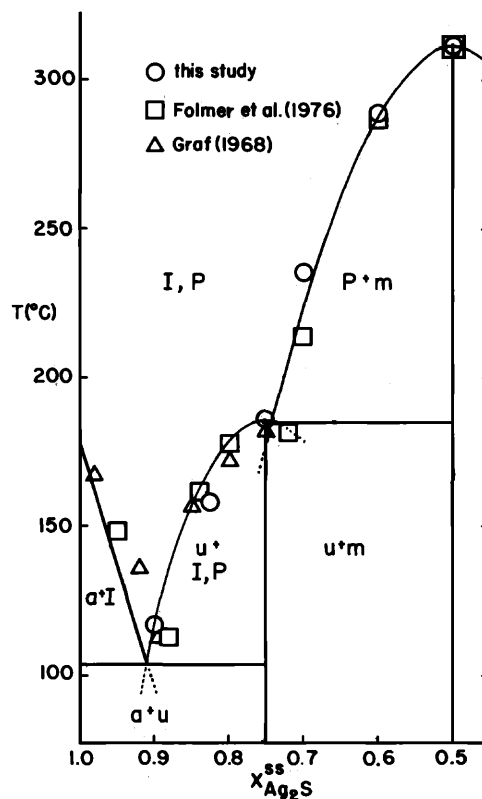


FIG. 9. Differential thermal analysis and resistivity results from Graf (1963), Folmer et al. (1976), and this study and the calculated phase diagram for Ag<sub>2</sub>S-Au<sub>2</sub>S binary between Ag<sub>2</sub>S and AgAuS. Phases are denoted as in Figure 3.

fugacities along the limbs of the eutectoids allow free energies of formation to be calculated directly—these are consistent within 250 calories. 2. Enthalpies of transition and the solution model enable calculation of the limbs of the eutectoids. In this case, experimental values agree with the calculated curves to within 10°C (Fig. 9). The positions of the calculated curves are sensitive to the values chosen for the  $\Delta H$ 's—here the averages of the measured values were used. If the maximum value for the AgAuS transition were used,  $Ag_3AuS_2$  would bear a reaction relationship with the solid solution. In other words,  $Ag_3AuS_2$  would react to AgAuS plus solid solution with increasing temperature rather than inverting congruently; the experimental data (Fig. 9) suggest, but hardly prove, the congruent alternative.

Calculated positions of the electrom-saturated  $Ag_2S$ - $Ag_3AuS_2$  and  $Ag_3AuS_2$ -AgAuS univariant equilibria are shown in Figure 10 which is a  $\log f_{S_2}$  versus  $1/T$  plot showing the stability fields of the various low-temperature phases and some of the coexisting electrom compositions. Apart from the change in the nature of the upper stability limit of low  $Ag_3AuS_2$  (above) variations in these curves due to the uncertainties in the enthalpies are less than 0.2 log units in  $f_{S_2}$ . Figure 11 is a projection of the metal-saturated phase relations onto the silver-gold binary.

Utilization of the available volumes and enthalpies of transition and the Clausius-Clapeyron relation allows calculation of the pressure effect on the temperature of several of the transitions (Table 6). The errors in all of these are substantial due to the difficulty in determining precisely the volumes of reaction. Reasonable errors in  $a$  (the

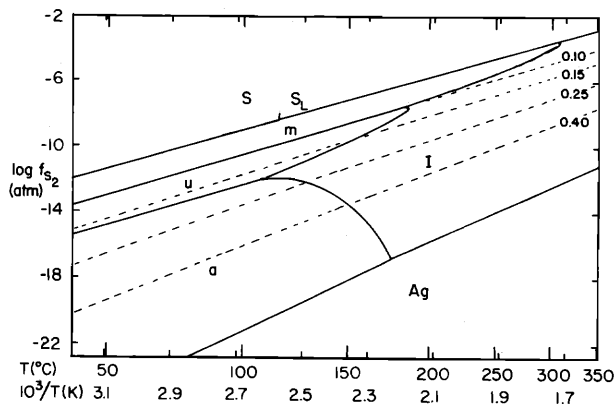


FIG. 10.  $\log f_{S_2}$  versus  $1,000/T(K)$  plot showing the stability of metal-saturated sulfides with some coexisting electrom compositions (dashed lines, mole percent Ag). Phases are denoted as in Figure 3 except that I includes both  $a$  and P.

TABLE 6. P-T Slopes for Inversion Reactions

Transition	Slope (°C/kbar)	Comments
$Ag_2S$ III-II	1.57	Experimentally determined; Clark and Rapoport (1970)
"	$9 \pm 15$	Calculated, based on volumes from data in Table 4; enthalpies of this study from Table 3
$Ag_3AuS_2$ low-high	$9 \pm 15$	"
$AgAuS$ low-high	$17 \pm 15$	"

order of 0.05 Å) for the high-temperature phases result in an error in  $\Delta V$ , on the order of  $\Delta V$ .

It is difficult to rationalize the apparently simple behavior of the solid solution with the complex structural model of Folmer et al. (1976). Evidently, the energetic contributions of alternative site occupancies are too small to be resolved in the types of experiments used here. Perhaps an emf study (cf. Potter and Barnes, 1978) would be sensitive enough to test the model.

The minimum in the sulfide liquidus indicates that the liquid mixes even more readily than the solid. Related to this is the probability that the liquid has a significantly more negative  $W_G$ , because a rigid sulfur lattice does not exist and there is a greater chance for Ag-Au interaction. Such interactions are indicated by similar behavior for

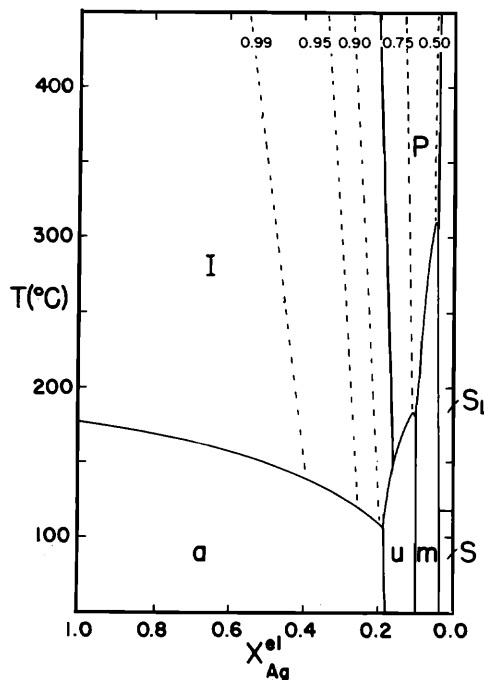


FIG. 11. Projection of the metal-saturated phase relations onto the Ag-Au binary. Vapor and electrom are present throughout. Phases are denoted as in Figure 3. Dashed lines are isopleths of  $Ag_2S$  (mole fraction).

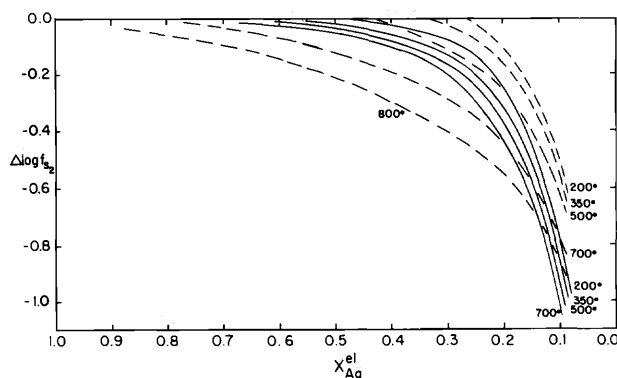


FIG. 12. A comparison of correction factors ( $\Delta \log f_{S_2}$ ) to equation (10) of Barton and Toulmin (1964). The dashed lines are the empirically derived correction factors of Barton and Toulmin. The solid lines are the correction factors calculated from the thermodynamic information derived in this study.  $T = ^\circ\text{C}$

Ag-Au solutions (White et al., 1957; Hultgren et al., 1973b).

Similar behavior to that found on the  $\text{Ag}_2\text{S-Au}_2\text{S}$  join is found in the Ag-Cu-S system on the  $\text{Ag}_2\text{S-Cu}_2\text{S}$  join. This is another 2:1-M:S join along which the sulfide components form a solid solution at intermediate temperatures, the liquidus has a minimum displaced toward  $\text{Ag}_2\text{S}$ , and several ordered compounds form at low temperature (Skinner, 1966). Perrot and Jeannot (1971), using a gas mixing technique, determined the activity of  $\text{Ag}_2\text{S}$  (not  $\text{AgS}_{0.5}$ ) in silver-copper sulfides as a function of composition. Their results show remarkable agreement with a model in which  $\log \gamma_{\text{Ag}_2\text{S}}$  is the linear function of  $X_{\text{Ag}_2\text{S}}$ , behavior not found in this study for Ag-Au-S. The interaction parameters they propose vary from  $-2,050$  to  $-3,000$  calories depending on temperature and composition. Whereas Perrot and Jeannot model  $a_{\text{Ag}_2\text{S}}$  as a function of composition,  $a_{\text{AgS}_{0.5}}$  can be more simply be modeled as ideal ( $a_i = X_i$ ), while still obtaining a reasonably good fit ( $\pm 15\%$ ). An improved fit ( $\pm 8\%$ ) over the ideal mixing model can be obtained by a symmetrical regular solution model, still based on  $\text{AgS}_{0.5}$ , in which case  $W_G$  is of the order of  $-2,000$  calories.

With the thermodynamic information above, the correction to equation (10) of Barton and Toulmin (1964) can be calculated.

$$\log f_{S_2} = \frac{1}{4.576T} [-41,980 + 16.52T - 18.296T \log X_{\text{Ag}}^{\text{el}} + 4(1 - X_{\text{Ag}}^{\text{el}})^2(5,650 - 1,600(1 - X_{\text{Ag}}^{\text{el}}) - 1.375T)]$$

Considering the uncertainties, reasonable agreement is found between the calculated curves of

this study and the empirically determined curves of Barton and Toulmin for the correction for  $X_{\text{Ag}}^{\text{el}} \leq 0.30$ , as shown in Figure 12. (Figure 6 of Barton and Toulmin is similar, but note that their vertical scale is mislabeled by 0.1 log unit.) The region  $X_{\text{Ag}}^{\text{el}} \leq 0.30$  contains most of Barton and Toulmin's calibration points. The only a priori restriction on the shape of these curves is that they must approach zero as  $X_{\text{Ag}}^{\text{el}}$  approaches zero. However, since the correction is proportional to  $\ln \gamma_{\text{AgS}_{0.5}}^{\text{ss}}$  and from the tie line data  $X_{\text{AgS}_{0.5}}^{\text{ss}}$  becomes close to unity by about  $X_{\text{Ag}}^{\text{el}} = 0.4$ , from Raoult's law the correction should approach zero in this region (at least for temperatures below the solidus). The indicated changes in the calibration factor will make small systematic differences in the calculated sulfur fugacities where silver-rich electrum was used at high temperatures for electrum tarnish studies (e.g., a few of the runs in Toulmin and Barton, 1964).

#### Application to Mineral Deposits

In many silver-gold deposits the dominant minerals of the silver-gold-sulfur system are acanthite and electrum. The recently described mineral uytenbogaardtite (low-temperature  $\text{Ag}_3\text{AuS}_2$ ) has been found in specimens from three localities where it occurs in a low-temperature, precious metal paragenesis with acanthite and electrum (Barton et al., 1978). In all natural assemblages the electrum is more silver rich ( $0.40 < X_{\text{Ag}}^{\text{el}} < 0.65$ ) than predicted for the three-phase assemblage acanthite + electrum + uytenbogaardtite (Fig. 11). Electrum + acanthite assemblages without uytenbogaardtite are also found in these deposits, with the electrum having the same (or higher) gold contents. One possible interpretation is that the uytenbogaardtite-bearing assemblages represent the disequilibrium cooling of a high-temperature, gold-bearing argentite + electrum assemblage. On cooling the argentite might have exsolved uytenbogaardtite, ultimately leaving a disproportionately silver-rich electrum with acanthite plus uytenbogaardtite. Some electrum grains from the Comstock lode, Nevada, have silver-rich cores and gold-rich rims which, in turn, are partially surrounded by uytenbogaardtite and acanthite, suggesting that the uytenbogaardtite is breaking down to acanthite plus gold-rich electrum or that uytenbogaardtite is reacting with silver-rich electrum to yield assemblages more compatible with the phase diagram. Graphic intergrowths of uytenbogaardtite and acanthite from Tambang Sawah, Indonesia, could represent a eutectoid intergrowth resulting from the cooling of a high-temperature, gold-bearing argentite.

Because the inversions of the high-temperature phases in the Ag-Au-S system are rapid, it is unlikely that the high-temperature phases will be found in nature. There may, however, be textures such as those described above which indicate the former presence of higher temperature phases.

Uytendogaardite will occur where there is abundant sulfur, a high gold to silver ratio (Figs. 10 and 11), and an absence of elements which tend to form competing compounds with either gold or silver, e.g., Sb, As, Bi, Se, or Te. AgAuS has not yet been reported in nature, presumably because it would be stable only at even higher sulfur fugacities and Au/Ag ratios, although such conditions are by no means improbable for some natural environments.

### Summary

Study of the Ag-Au-S system shows that all ternary sulfides lie on or close to the  $\text{Ag}_2\text{S}-\text{Au}_2\text{S}$  join. At temperatures below  $310^\circ\text{C}$  a eutectoid exists between the compounds  $\text{Ag}_2\text{S}$  and  $\text{Ag}_3\text{AuS}_2$ ; another may exist between  $\text{Ag}_3\text{AuS}_2$  and  $\text{AgAuS}$ . Sulfide melts form at temperatures in the interval  $680^\circ$  to  $838^\circ\text{C}$  with a minimum in the sulfide liquidus at  $\text{Ag}_{1.3}\text{Au}_{0.7}\text{S}$ .

Measured enthalpies of transition are in reasonable agreement with the phase diagram. The sulfide solid solution can be modeled, within experimental error, as a symmetrical regular solution with  $W_G \cong -1,000$  calories. This model is too insensitive to discriminate the intricate structure for the solid solution proposed by Folmer et al. (1976).

Several natural assemblages in the Ag-Au-S system can be interpreted in terms of disequilibrium cooling. Due to rapid inversion rates only the low-temperature phases in the system are likely to be found in nature, and the ternary phases only in environments with unusually high sulfur concentrations and high gold to silver ratios.

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