

PHASE RELATIONS AND MINERAL ASSEMBLAGES
IN THE COPPER-LEAD-SULFUR SYSTEM

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ABSTRACT

Above 600°C the system Cu-Pb-S is dominated by two-liquid fields in both the sulfur-rich and metal-rich portions. A central liquid phase prohibits coexistence of galena and copper sulfides above 523°C. This sulfide liquid, which may be important in the genesis of certain ores, remains stable to $508 \pm 2^\circ\text{C}$, at which temperature a monotectic reaction forms galena, digenite ss, and sulfur liquid. A new ternary phase, A, of the composition $\text{Cu}_{14}\text{Pb}_2\text{S}_{9-x}$ ($0 < x < 0.15$) has been synthesized and is stable between $528 \pm 2^\circ\text{C}$ and $486 \pm 4^\circ\text{C}$. Between about 435° and $271 \pm 5^\circ\text{C}$ the stable assemblages include galena, chalcocite ss, and native lead; galena, chalcocite ss, and digenite ss; and galena, digenite ss, and covellite. Below 271°C the chalcocite-native lead pair reacts to form galena and native copper.

The phase relations as determined at 200°C must be modified at low temperatures due to the appearance of other copper sulfides such as blue-remaining covellite and djurleite. Experiments containing Fe or Zn in addition to Cu and Pb sulfides indicate that these elements do not stabilize the sulfide liquid phase to temperatures below the minimum in the pure Cu-Pb-S system. Furthermore, the addition of H_2O , which has been called upon to depress sulfide melting temperatures, does not have measurable effect on melting relations.

INTRODUCTION

Knowledge of phase relations in the Cu-Pb-S system is important in the understanding and interpretation of natural assemblages of copper and lead sulfides, in the smelting processes involved in the beneficiation of copper and lead-bearing ores, and in the development and understanding of more complex sulfide and sulfide-oxide systems such as As-Cu-Pb-S, Cu-Fe-Pb-S, Cu-Fe-Pb-Zn-S, and Cu-Fe-Pb-S-O. Nine minerals—including galena, the principal source of lead; and chalcocite, digenite, and native copper, three of the principal sources of copper—are reported within the system.

Although widespread geographically, mutual associations of copper and lead sulfides are most commonly restricted to low-temperature environments. Since the present study was directed primarily toward the mineralogical relations in the Cu-Pb-S system, and since high-temperature relations of interest to the smelting industry have been examined by several previous workers, the emphasis of the present paper is placed on assemblages stable below 600°C .

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PREVIOUS WORK

Cu-Pb system. Phase relations in the Cu-Pb system have been reviewed by Hansen and Anderko (1958) and Elliott (1965). A eutectic exists at 326°C and 99.94 weight percent Pb. Solubility of Cu in Pb liquid increases to about 2 weight percent at 700°C and about 7.5 weight percent at 900°C. At 954°C a two-liquid field exists between 64 and 13 weight percent Cu. Closure of the two-liquid field occurs at 990°C. No binary solid phases are known.

Pb-S system. The Pb-S system has been examined by Kullerud (1965*a*), who also reviewed previous work. The only compound, PbS, analogous to the mineral galena, melts congruently at $1015 \pm 2^\circ\text{C}$. Two regions of liquid immiscibility exist, one above $1043 \pm 2^\circ\text{C}$, between 4.0 and 9.5 weight percent S, and the other above $799 \pm 2^\circ\text{C}$, between 27.0 and >95.0 weight percent S.

Cu-S system. Phase relations in the Cu-Cu₉S₅ portion of the Cu-S system have been examined by Roseboom (1966), who also reviewed previous work. The stable phases, their mineral equivalents, and maximum stabilities in the presence of vapor are: Cu₂S (chalcocite, orthorhombic, 103.5°C), Cu₂S (hexagonal, 435°C), Cu₂S (cubic, 1129°C), Cu_{1.96}S (djurleite, 93°C), Cu₉S₅ (digenite, pseudo-cubic, 83°C), Cu₉S₅ (cubic, complete solid solution with cubic Cu₂S above 435°C),¹ CuS_{1-x} (blue-remaining covellite, 157°C), and CuS (covellite, hexagonal, 507°C). Regions of liquid immiscibility exist between 2 and 20 weight percent S above 1105°C and between 26 and >98 weight percent S above 813°C. Naturally occurring copper sulfides in addition to those listed above are reported by Morimoto and Koto (1966). Other copper sulfides, which are not known as minerals, have been synthesized under conditions of high confining pressure in the absence of vapor (Skinner, Boyd, and England, 1964; Munson, 1966); such phases have not been encountered in the present study.

Cu-Pb-S system. Phase relations in the Cu₂S-PbS-Pb-Cu portion of the Cu-Pb-S system above 900°C have been studied by Guertler and Meissner (1921), Leitgeb and Miksch (1934), Guertler and Landau (1934), and Dice, Oldright, and Brighton (1936). All these workers confirmed the existence of a region of two immiscible liquids which spans the metal-rich portion² of the system; one of these liquids contains 17–19 weight percent S and lies nearly on the Cu₂S-PbS join, whereas the other contains less than 2 weight percent S and lies along the Cu-Pb join. Friedrich (1907) reported a eutectic on the Cu₂S-PbS join at about 51 weight percent Cu₂S and 540°C but was unable to synthesize any of the ternary phases (9Cu₂S·2PbS, 9Cu₂S·5PbS, 3Cu₂S·PbS, and 3Cu₂S·2PbS) predicted previously by Danner (1894). Guertler (1920) presented a tentative low-temperature diagram in which are indicated the assemblages Cu+Pb+Cu₂S, Pb+Cu₂S+PbS, PbS+Cu₂S+CuS, and PbS+CuS+S.

Wagner and Wagner (1957), in an electrochemical study, determined that the reaction $2\text{Cu} + \text{PbS} \rightarrow \text{Cu}_2\text{S} + \text{Pb}$ took place between 250° and 350°C. On the basis of the derived thermochemical data they calculated the temperature of reaction as $279 \pm 4^\circ\text{C}$.

¹ For convenience the Cu₂S-Cu₉S₅ solid solution will hereafter be referred to as *cc*_{ss}. This solid solution extends from stoichiometric Cu₂S to a composition approximately 0.6 weight percent more sulfur rich than Cu₉S₅ at 500°C (Kullerud and Yund, 1960).

² "Metal-rich portion" here designates that portion of the system which contains more metal than along the PbS-Cu₂S join. In contrast, "sulfur-rich portion" will designate that portion of the system containing more sulfur than along the PbS-Cu₉S₅ join.

EXPERIMENTAL TECHNIQUES AND REACTANTS

Reactants in this study were Pb and Cu of 99.999+% purity as determined by analyses by the supplier (American Smelting and Refining Co.) and S of 99.993% purity, obtained from Dr. W. N. Tuller of the Freeport Sulfur Co.

The majority of the experiments were conducted in evacuated rigid silica-tube reaction vessels, which were heated in nichrome-wound resistance furnaces controlled to within $\pm 2^\circ\text{C}$. At the termination of each experiment the samples were rapidly cooled by plunging them into ice water. Temperatures were recorded and read with chromel-alumel thermocouples. Differential thermal analysis was conducted in the manner described by Kullerud and Yund (1962). The synthetic phases encountered in this study, with the exception of phase A, were identical in X-ray and optical characteristics to analogous naturally occurring phases. Experimental products were examined by X-ray diffraction techniques and by reflected light microscopy. High-temperature phases and phase assemblages, except for the sulfide liquid and the cc_{ss} which broke down on cooling, were preserved during chilling.

EXPERIMENTAL RESULTS AND DISCUSSION

Phase relations within the Cu-Pb-S system are discussed below in the sequence from high to low temperature. The relations at 1130°C are schematic and are based upon previous workers' concepts of the bounding binary and the ternary system. Diagrams at lower temperatures are based on the data given in Tables 1, 2, and 4 and on inferences drawn from the known binary systems. All diagrams are "condensed" in that they represent phase assemblages stable in the presence of a vapor, although the vapor phase is not shown on the diagrams. Additional experiments defining the existence of the phase assemblages shown in each isothermal section have been performed but are unlisted for the sake of brevity.

At 1130°C (Fig. 1) three separate homogeneous liquid fields exist which span the ternary system. One liquid field is sulfur rich and contains more than 98 weight percent S; the second is sulfide rich¹ and contains 20–26 weight percent S on the Cu-S join and 9–27 weight percent S on the Pb-S join; the third is metal rich and contains less than 2 weight percent S. Regions of liquid immiscibility exist between the sulfur-rich and sulfide-rich liquids and between the sulfide-rich and the metal-rich liquids. With decreasing temperature, Cu_2S appears at 1129°C and PbS appears at 1115°C . The metal-rich two-liquid field present between Cu_2S and Cu withdraws from the Cu-S join into the ternary system at 1105°C . Withdrawal of the same two-liquid field into the ternary system from the Pb-S join occurs at 1043°C (Kullerud, 1965a). With the appearance of Cu at 1083°C the metal-rich liquid field along the Cu-Pb join withdraws toward Pb. The sulfur-rich two-liquid field withdraws from the Cu-S join into the ternary system at 813°C and from the Pb-S join at 799°C .

¹ This central sulfide-rich liquid will hereafter be referred to as the "sulfide liquid."

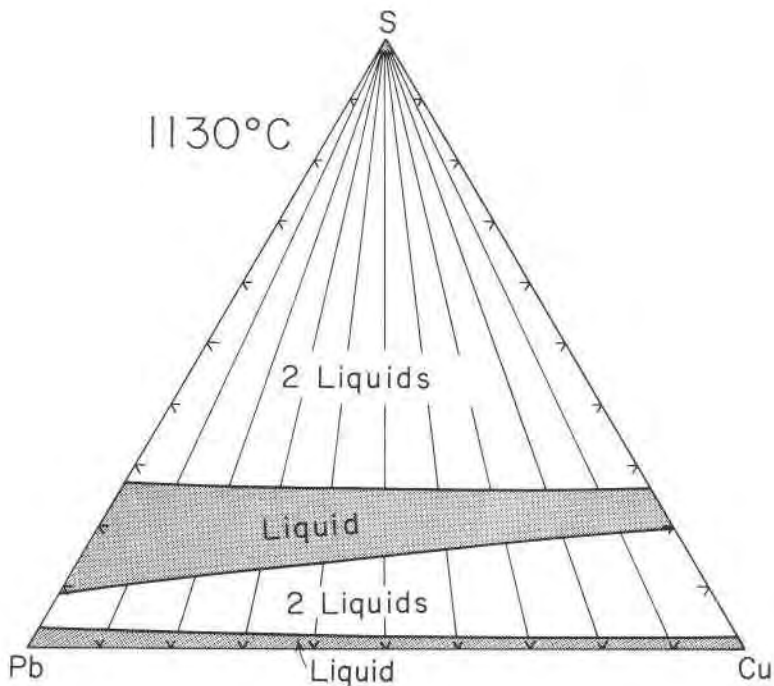


FIG. 1. Schematic phase relations in the condensed Cu-Pb-S system at 1130°C.

The reduction in size of the two-liquid fields and the appearance of Pbs, cc_{ss} , and Cu result in phase relations at 600°C as shown in Figure 2. At 600°C the central sulfide liquid is reduced to a small four-sided area and the metal-rich liquid has been nearly confined to the Pb corner of the diagram. The exact boundaries of these liquid fields have not been determined.

With decrease in temperature below 600°C the sulfide liquid field continuously diminishes in size, particularly in the metal-rich portion of the system. At $528 \pm 2^\circ\text{C}$ a ternary phase appears through reaction of the sulfide liquid and the cc_{ss} as shown schematically in Figure 3A, B. This phase has not been previously described and is here designated as phase A. The composition of phase A is 26.5 ± 0.5 weight percent Pb, 55.5 ± 0.5 weight percent Cu, and 18.0 ± 0.5 weight percent S. This composition is slightly more Pb rich and Cu and S deficient than the stoichiometric composition $\text{Cu}_{14}\text{Pb}_2\text{S}_9$ ($7\text{Cu}_2 \cdot 2\text{PbS} = 26.02$ weight percent Pb, 55.86 weight percent Cu, 18.12 weight percent S). An experiment prepared with the exact $\text{Cu}_{14}\text{Pb}_2\text{S}_9$ composition contained phase A plus approximately 5% PbS and cc_{ss} . The best chemical formula to apply to phase

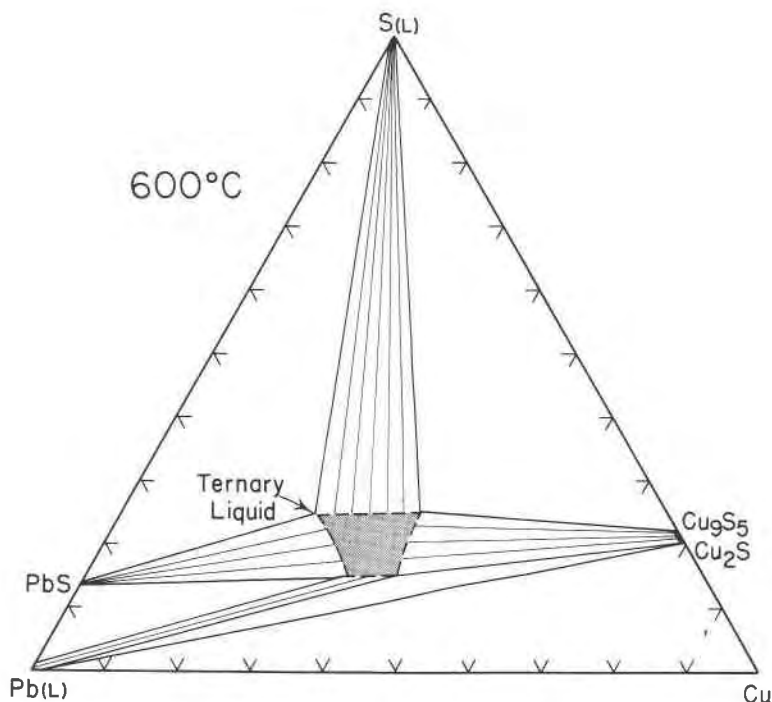


FIG. 2. Schematic phase relations in the condensed Cu-Pb-S system at 600°C.

A is thus $\text{Cu}_{14}\text{Pb}_2\text{S}_{9-x}$, where $0 < x < 0.15$. The density of phase A as measured on a Berman balance is $8.42 \pm 0.08 \text{ g/cm}^3$. Experiments defining the composition and stability of phase A are given in Table 1.

Phase A is softer than galena and very brittle; in reflected light it is beige, moderately birefractant, and moderately anisotropic (blue to beige). Its crystal structure is not known. Room-temperature X-ray powder diffraction data obtained from diffractometer charts with silicon ($a = 5.4305 \text{ \AA}$) as an external standard and from films exposed in a 114.59 mm diameter Straumanis-type mounting camera are presented in Table 2. Phase A is readily preserved in quench-type experiments that are rapidly cooled in ice water and shows no sign of breakdown even after being kept in a vacuum at room temperature for 4 months. If it is left exposed to the air, however, an iridescent surface film develops in a few days.

Between $528^\circ \pm 2^\circ\text{C}$, the temperature of appearance of phase A, and $523^\circ \pm 2^\circ\text{C}$, the temperature at which $\text{cc}_{\text{ss}}\text{-PbS}$ tie lines are established, four reactions involving phase A take place. Reactions 2–4 represent invariant points whereas reaction 1 represents a singular point. These

TABLE 1. EXPERIMENTS DEFINING THE COMPOSITION AND STABILITY OF PHASE A

Composition, wt %			Temp., °C	Time, days	Phases ^a at Temperature
Cu	Pb	S			
59.0	23.0	18.0	510	6	A+cc _{ss} +Pb liq
57.0	25.0	18.0	510	6	A+cc _{ss} +Pb liq
56.5	25.5	18.0	510	9	A+cc _{ss} +Pb liq
56.2	26.2	17.6	510	30	A+cc _{ss} +Pb liq
55.9	26.0	18.1	510	6	A+cc _{ss} +gn
55.6	26.3	18.1	500	20	A+cc _{ss} +gn
55.3	26.6	18.1	500	20	A+cc _{ss} +gn
55.0	27.1	17.9	510	9	A+gn+Pb liq
53.2	28.9	17.9	510	6	A+gn
53.1	29.0	17.9	510	4	A+gn+cc _{ss}
51.9	30.1	18.0	510	7	gn+cc _{ss}
53.2	29.0	17.8	526	0.2	A+liq
53.2	29.0	17.8	530	0.2	cc _{ss} +liq
53.1	29.0	17.9	530	0.3	cc _{ss} +liq
53.2	28.9	17.9 ^b	490	6	A+gn+cc _{ss}
53.2	28.9	17.9	490	13	A+gn+cc _{ss}
53.2	29.0	17.8 ^b	483	90	gn+cc _{ss} +Pb liq
53.2	28.9	17.9	483	104	gn+cc _{ss}
51.3	31.2	17.5 ^b	478	20	gn+cc _{ss} +Pb liq
53.2	29.0	17.8	475	117	gn+cc _{ss}

^a gn = PbS; cc_{ss} = Cu₂S-Cu₉S₅ solid solution; liq = ternary sulfide liquid.

^b Reaction of Cu+Pb+S; all other experiments first melted at 750°C and then annealed at temperatures indicated.

reactions in the probable order of occurrence with decreasing temperature are:

- (1) cc_{ss} + liq → A
- (2) cc_{ss} + liq → A + Pb liq
- (3) liq + Pb liq → A + PbS
- (4) A + liq → PbS + cc_{ss}

Reaction 1 (see Fig. 3A, B) indicates the incongruent melting of phase A to cc_{ss}+sulfide liquid (liq). Reaction 2 (Fig. 3B, C) represents the establishment of tie lines between phase A and Pb liquid. Reaction 3 (Fig. 3C, D) is the breakdown of sulfide liquid+Pb liquid tie lines to form the assemblage phase A+PbS. Reaction 4 (Fig. 3D, E) shows the establishment of tie lines between PbS and cc_{ss} through reaction of phase A and the sulfide liquid. The 523°±2°C value of maximum PbS+cc_{ss} coexistence is significantly lower than that (540°C) given by Fredrich

(1907). The sulfide liquid remains stable down to $508^{\circ} \pm 2^{\circ}\text{C}$, at which temperature it is involved in a monotectic reaction to form PbS, cc_{ss} , and S liquid. On cooling, the sulfide liquid crystallizes, depending upon composition, to a fine ($1-5 \mu$) myrmekitic intergrowth of PbS and phase A and/or cc_{ss} and/or Pb. The composition of the sulfide liquid at the monotectic temperature is $34 \pm 2\%$ Cu, $43 \pm 2\%$ Pb, $23 \pm 2\%$ S (Table 3). This ternary monotectic reaction involves five phases (liq, PbS, cc_{ss} , S liq, vapor) and thus represents invariancy. Any change in temperature or pressure requires elimination of one or more phases. The sulfur vapor pressure at the invariant point is not known precisely but probably nearly approximates the vapor pressure over CuS which appears on the

TABLE 2. X-RAY POWDER DIFFRACTION DATA OF TERNARY Cu-Pb-S PHASE A

$d(\text{obs})$	$I(\text{obs})$	$d(\text{obs})$	$I(\text{obs})$	$d(\text{obs})$	$I(\text{obs})$
8.56	w	3.16	vw	2.24	w
5.34	m	2.98	m	2.22	m
4.37	m	2.92	vs	2.19	w
4.29	m	2.85	vs	2.09	s
3.99	w	2.81	m	1.99	m
3.83	m	2.76	s	1.96	w
3.77	w	2.71	w	1.88	m
3.74	w	2.65	m	1.87	m
3.63	w	2.58	w	1.83	w
3.36	s	2.47	m	1.79	w
3.33	s	2.41	m	1.71	w
3.27	m	2.36	w	1.66	w
3.23	w	2.29	w	1.55	w

CuK α , Ni filtered radiation. $\lambda = 1.5418 \text{ \AA}$.

vs, very strong; s, strong; m, moderate; w, weak; vw, very weak.

Cu-S join between Cu_9S_5 and S liq at 507°C . The sulfur vapor pressure over CuS at 507°C has been estimated as 1.5 ± 0.3 bars by Kullerud (1957, 1965*b*) and determined by a "dew-point" method as 1.4 bars by Dickson, Shields, and Kennedy (1962).

Phase relations in the Cu-Pb-S system at 510°C , which is immediately above the temperature of sulfide liquid crystallization, are shown in Figure 4. At this temperature tie lines extend from the sulfide liquid to PbS, Cu_9S_5 , and S liquid. Tie lines exist between PbS and sulfur-rich compositions of cc_{ss} and between PbS and phase A; copper-rich compositions of cc_{ss} coexist with phase A but not with PbS. Tie lines also exist between phase A and Pb liquid and between Cu_2S and Pb liquid. Phase relations at 510°C involving phase A are shown schematically in the inset of Figure 4.

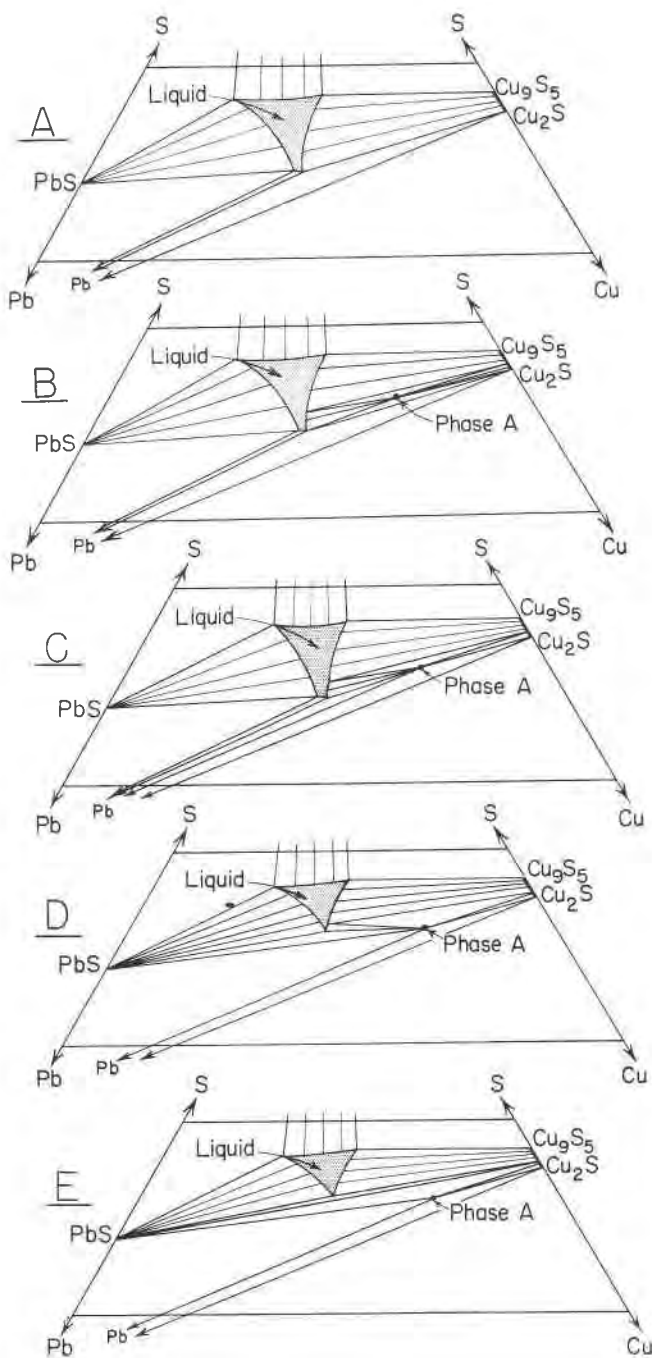


FIG. 3. Schematic presentation of changes in phase relations between $528^{\circ} \pm 2^{\circ}\text{C}$ and $523^{\circ} \pm 2^{\circ}\text{C}$. The four reactions involving phase A which occur between successive portions of the figure are described in the text. Figs. A-E are not drawn to scale.

TABLE 3. EXPERIMENTS DEFINING THE T - X FIELD OF THE TERNARY LIQUID

Composition, wt %			Temp., °C	Time, hours	Phases* at Temperature
Cu	Pb	S			
40.9	37.1	22.0 ^b	510	20	gn+cc _{ss} +liq
38.2	40.2	21.6 ^b	510	20	gn+cc _{ss} +liq
37.3	42.5	20.2 ^b	510	1.0	gn+cc _{ss} +liq
40.8	34.1	25.1 ^b	510	1.0	liq+cc _{ss} +S liq
36.9	38.0	25.1 ^b	510	1.0	liq+cc _{ss} +S liq
33.0	44.0	23.0 ^b	510	1.0	liq+gn+S liq
29.0	49.0	22.0 ^b	510	20	liq+gn+S liq
25.1	52.9	22.0 ^b	510	20	liq+gn+S liq
33.3	43.2	23.5 ^c	505	0.5	gn+cv
33.3	43.2	23.5 ^c	511	0.5	gn+liq
37.3	42.5	20.2 ^d	502	0.5	gn+cc _{ss} +cv
37.3	42.5	20.2 ^d	506	0.5	gn+cc _{ss} +cv
37.3	42.5	20.2 ^d	510	0.5	gn+cc _{ss} +liq
31.4	41.5	27.1 ^e	506	0.5	gn+cv+S liq
31.4	41.5	27.1 ^e	510	0.5	gn+liq+S liq
34.0	43.0	23.0 ^d	500	1440	gn+cv+cc _{ss}
34.0	43.0	23.0 ^d	505	48	gn+cv+cc _{ss}
34.0	43.0	23.0 ^d	510	48	liq+cc _{ss}
39.9	43.3	16.8 ^f	519	0.5	gn+cc _{ss}
39.9	43.3	16.8 ^f	525	0.5	gn+liq
59.9	21.6	18.5 ^f	520	0.5	gn+cc _{ss}
59.9	21.6	18.5 ^f	526	0.5	cc _{ss} +liq

* gn=PbS; cc_{ss}=Cu₉S₅-Cu₂S ss; cv=CuS; liq=ternary sulfide liquid.

^b Prepared with Cu+Pb+S.

^c Prepared with cv+gn.

^d Prepared with cv+gn+cc_{ss}.

^e Prepared with cv+gn+S.

^f Prepared with cc_{ss}+gn.

Unit-cell determinations (with silicon, $a = 5.4305 \text{ \AA}$, as an internal standard) on PbS synthesized, respectively, in coexistence with CuS, with cc_{ss}, with phase A, and with the sulfide liquid, in the temperature interval 500°–550°C, yield $a = 5.936 \pm 0.002 \text{ \AA}$. This value is identical with the a value of pure PbS given by Swanson and Fuyat (1953), indicating little or no solubility of the copper sulfides in PbS. A slight solubility of PbS in cc_{ss} is suggested in polished sections by the presence of small amounts (<1%) of exsolved PbS in samples cooled rapidly from 500° and from 510°C. Experiments prepared with 1 percent Pb, 78 percent Cu, and 21 percent S and with 1 percent Pb, 78.5 percent Cu, and 20.5 percent S and reacted at 500°C contained small amounts of primary

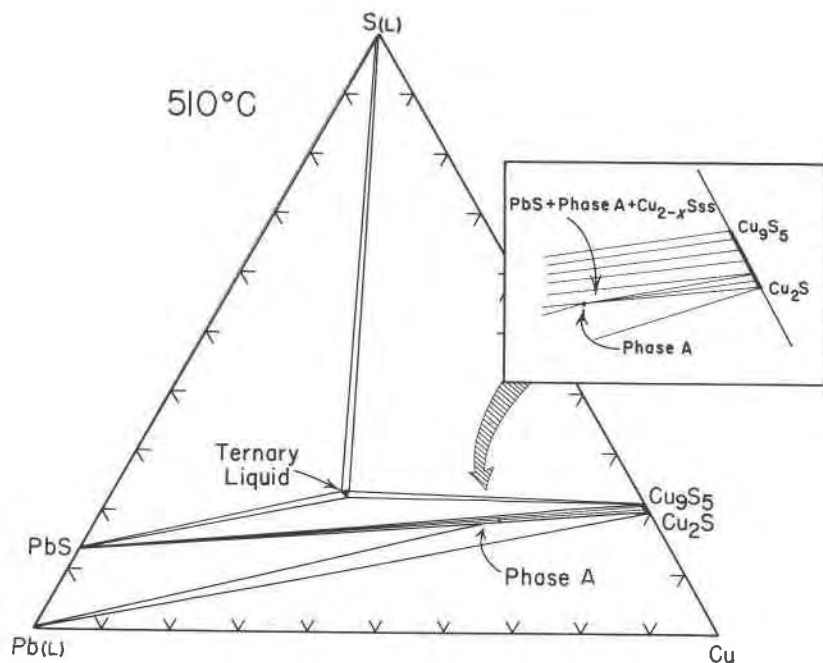


FIG. 4. Phase relations in the condensed Cu-Pb-S system at 510°C. Relations surrounding phase A composition are shown schematically in the inset, which is not to scale.

PbS as well as cc_{ss} with exsolved PbS, indicating that the solubility of Pb is less than 1 percent.

Covellite, CuS, becomes stable on the Cu-S join at 507°C. Differential thermal analysis indicates that CuS and PbS form a stable assemblage below $506^\circ \pm 2^\circ\text{C}$. No evidence of solubility of Pb in CuS has been observed in polished sections or in X-ray patterns.

Phase A breaks down to form PbS, cc_{ss} , and Pb liq as the temperature drops below $486^\circ \pm 4^\circ\text{C}$. Phase assemblages occurring immediately above and below the temperature of this invariant reaction are shown schematically in Figure 5.

Phase relations at 450°C inferred from experimental data at higher and lower temperatures are shown in Figure 6A. At 450°C tie lines exist between PbS and CuS, PbS and cc_{ss} , and Pb liq and cc_{ss} . Below 435°C the cc_{ss} breaks down into distinct $\text{Cu}_2\text{S ss}$ and $\text{Cu}_9\text{S}_5 \text{ ss}$ phases, each of which coexists stably with PbS. These phase assemblages remain stable down to $271^\circ \pm 5^\circ\text{C}$, at which temperature $\text{Cu}_2\text{S} + \text{Pb}$ react to give the low-temperature $\text{Cu} + \text{PbS}$ assemblage. In order to determine the temperature of this invariant reaction (Table 4), a Cu-Pb alloy was prepared by

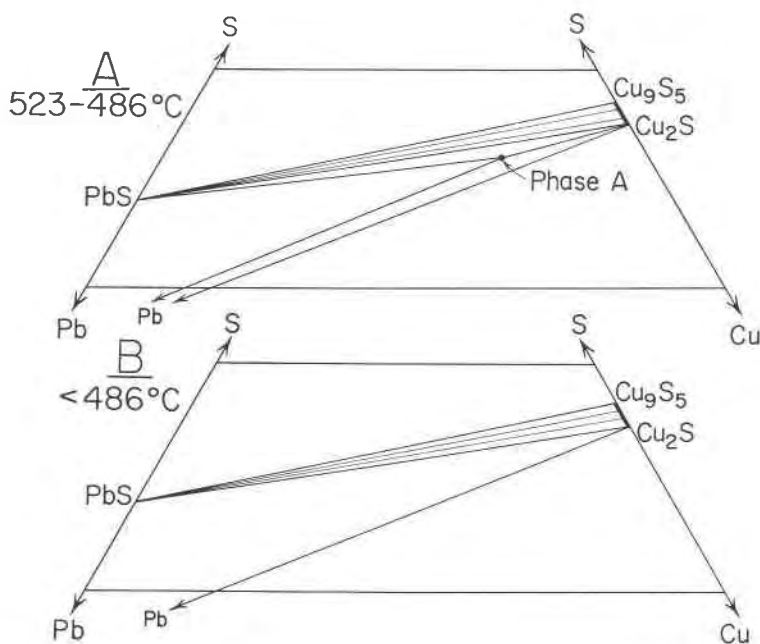


FIG. 5. Diagrammatic presentation of breakdown of phase A to $\text{PbS} + \text{cc}_{\text{ss}} + \text{Pb liq}$ at 486°C . This diagram is not to scale.

melting the elements above 1000°C and then rapidly cooling the molten mass. Filings of this sample, which consisted of very finely intergrown Pb and Cu, were mixed with sulfur and reacted at various temperatures. At 276°C and above, the assemblages observed were $\text{Cu} + \text{Pb} + \text{cc}_{\text{ss}}$ and $\text{cc}_{\text{ss}} + \text{Pb} + \text{PbS}$, whereas at 266°C and below, the assemblages were $\text{Cu} + \text{PbS} + \text{cc}_{\text{ss}}$ and $\text{Pb} + \text{PbS} + \text{Cu}$. At 272°C all four phases, Cu, PbS, cc_{ss} , and Pb, persisted. Experiments performed with $\text{Cu} + \text{PbS}$ and $\text{Pb} + \text{Cu}_2\text{S}$ indicated the same stable assemblages but showed only a few percent reaction after 2–3 months. Some solubility of Cu_2S toward Cu_9S_5 and toward PbS between 272° and 310°C is indicated by the growth of small amounts of Cu wire in experiments prepared with Cu_2S and Pb at these temperatures. When small amounts of PbS were added to $\text{Cu}_2\text{S} + \text{Pb}$ mixtures, Cu wire formed at 250° and 272°C but not at 288° and 310°C ; these observations are compatible with the results of Cu-Pb alloy + sulfur reactions. The maximum temperature of $\text{Cu} + \text{PbS}$ coexistence determined here is in very good agreement with the value of $279^\circ \pm 4^\circ\text{C}$ calculated by Wagner and Wagner (1957).

The effect of pressure on the stability of the $\text{Cu} + \text{PbS}$ assemblage has not been investigated, but judging from the molar volumes given by

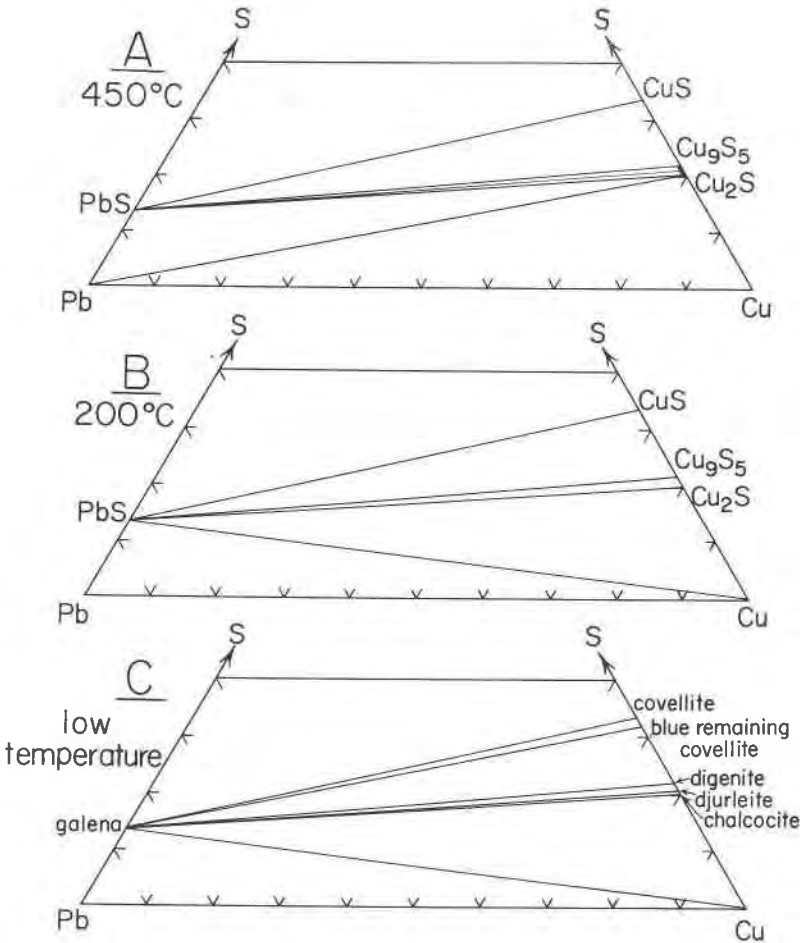
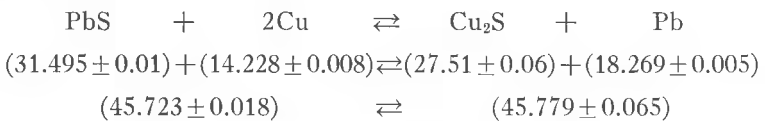


FIG. 6. Phase relations in the condensed Cu-Pb-S system at (A) 450°; (B) 200°C (note that the Cu₂S-Pb assemblage stable at 450°C has broken down to give PbS+Cu); and (C) low temperature, as observed in ores.

Robie *et al.* (1966), and neglecting differences in thermal expansion, the value of ΔV (in cm³) for the reaction



is 0.056 ± 0.083 cm³. The small magnitude of ΔV indicates that pressure has little effect on the stability of the PbS+Cu assemblage. Because of

TABLE 4. EXPERIMENTS DEFINING TEMPERATURE OF $\text{Pb} + \text{Cu}_2\text{S} \rightleftharpoons 2\text{Cu} + \text{PbS}$ REACTION

Reactants	Temp., °C	Time, days	Products
Cu+PbS	400	3	cc _{ss} +Pb
Cu+PbS	346	0.1	cc _{ss} +Pb
Cu+PbS	324	13	cc _{ss} +Pb
PbS+Cu ₂ S+Pb	310	30+	no reaction
Cu+PbS	310	255	cc _{ss} +Pb+Cu
CuPb ^a +S	310	40	cc _{ss} +Pb+gn
Cu+PbS	300	46	partial reaction to cc _{ss} +Pb
CuPb ^a +S	288	43	cc _{ss} +Pb+Cu
Cu+PbS	288	46	partial reaction to cc _{ss} +Pb
Cu+gn+cc _{ss} ^b	288	13	cc _{ss} +Pb+Cu (trace)
Cu ₂ S+Pb+PbS	288	30	no reaction
Cu+gn+cc _{ss} ^c	276	17	cc _{ss} +Pb (+trace amounts of gn+cu)
Cu ₂ S+Pb+PbS	272	30	Cu wire forming
CuPb ^a +S	272	40	Cu+gn+cc _{ss} +Pb
cc _{ss} +Pb+Cu ^d	272	40	Cu+gn+cc _{ss} +Pb
CuPb ^a +S	266	7	Cu+gn+cc _{ss} (+small amounts of Pb)
cc _{ss} +Pb+Cu ^d	266	25	Cu+gn (+small amounts of unreacted cc _{ss} +Pb)
Cu+PbS	250	14	no reaction
Cu ₂ S+Pb+PbS	250	17	Cu wire forming
CuPb ^a +S	225	17	gn+Cu+cc _{ss}

^a Cu+Pb in proportions (38:62) melted at >1000°C and rapidly cooled; filings reacted with S in proportions approximating composition of 2Cu+PbS.

^b Cu+gn+cc_{ss} formed by reaction of CuPb+S at 225°C.

^c Cu+gn+cc_{ss} formed by reaction of CuPb+S at 266°C.

^d cc_{ss}+Pb+Cu formed by reaction of CuPb+S at 288°C.

the large uncertainty associated with this value, it is not possible to predict whether the slope of the reaction curve in P - T space is positive or negative.

Stable phase assemblages at 200°C, the lowest temperature of experimentation, are shown in Figure 6B. These assemblages are inferred to be identical with those at 25°C (Fig. 6C) except for the complications induced by the appearance of blue-remaining covellite, djurleite, and additional Cu sulfides described by Morimoto and Koto (1966). No phase analogous to a pure Cu-Pb-S betekhtinite (reported by Schüller and Wohlmann, 1955, as Cu₁₀[Fe,Pb]S₆) was observed in our experiments; in view of these results we conclude that betekhtinite is not stable in the Cu-Pb-S system above 200°C.

GEOLOGICAL CONSIDERATIONS

Occurrence of minerals of the Cu-Pb-S system is widespread in various types of ore deposits. Primary mineralization rich in copper and lead

occurs in many sulfide ores such as those at Broken Hill, Australia; Concepción del Oro, Peru; Sierra de Cordoba, Spain; Butte, Montana, and many others. In all or most such ores, associations of primary copper and lead sulfides are absent due to incorporation of the copper in copper-iron and/or copper-arsenic sulfides. On the other hand, occurrences of galena and the copper sulfides corresponding to the low-temperature synthetic assemblages discussed above are frequently observed in the supergene zones of numerous deposits. In such occurrences, the copper sulfides generally have replaced galena along fractures and cleavages, as has been shown in photomicrographs from Broken Hill, Australia (Stillwell, 1927; Ramdohr, 1955); Mount Isa, Australia (Grondijs and Schouten, 1937); Reichenbach in Odenwald, Germany (Ramdohr, 1955); Tintic District, Utah (Cameron, 1961); and Heath Steel Mine, N.B., Canada (Dechow, 1960). In addition, mutual occurrences of galena and copper sulfides have been described from Morachoca and Cerro de Pasco, Peru (Petersen, 1965); Mt. Sopris, Colorado (Schwartz and Park, 1930); and Devonian sandstones in Pennsylvania (McCauley, 1958).

Occurrences of native copper in the lavas of the Keweenaw Peninsula, Michigan, and in the oxidized zones of numerous copper deposits are well known. Native lead, on the other hand, is very rare and known from only a few localities in which extremely reducing conditions prevailed. The only locality known to the authors in which native copper and native lead coexist is Franklin, New Jersey (Foote, 1898). Disregarding the effects of high confining pressures, crystallization of the copper-lead mineral pair must have taken place below 326°C , the eutectic temperature (Hansen and Anderko, 1958).

The ternary Cu-Pb-S phase, A, has not been observed in ores. However, Ramdohr (1955) has noted the existence of myrmekitic intergrowths of chalcocite and galena. Such intergrowths could form through breakdown of a natural analogue of phase A on cooling below $486^{\circ}\pm 4^{\circ}\text{C}$. It is likely, however, that during the slow cooling of an ore body such a breakdown texture would not be preserved. Typical myrmekitic textures were not observed as a result of breakdown of synthetic phase A.

Native copper and galena have been established as a stable assemblage below $271^{\circ}\pm 5^{\circ}\text{C}$. To our knowledge this mineral pair has not been reported in nature.

Effects of Additional Components on Copper-Lead-Sulfide Magmas. Field observations by several geologists (e.g., Spurr, 1923; Hutchinson, 1965; Clark, 1965) have led them to the conclusion that some iron-, lead-, and zinc-rich ores may have crystallized from homogeneous sulfide liquids at temperatures as low as $500^{\circ}\text{--}600^{\circ}\text{C}$. Brett and Kullerud (1967), after

showing that a sulfide melt appears in the Fe-Pb-S system at 716°C, stated, "additional components may lower this temperature so that . . . pyrite-galena ores may melt at temperatures below 700°C." The observation of a sulfide melt in the Cu-Pb-S system at 508°C demonstrates that copper is, indeed, a constituent which may significantly lower the temperature of melting in iron, lead, and zinc ores.

Two series of experiments were conducted to determine whether the presence of Fe or Zn (the metallic components of the common sulfides other than Cu and Pb) would lower the temperature of appearance of the ternary Cu-Pb-S melt.

In one series of experiments 7.2 weight percent ZnS was added to samples containing 34% Cu, 43% Pb, and 23% S. In the other series of experiments 5.0 weight percent Fe_{1-x}S (61.5 weight percent Fe) was added to samples containing the same Cu-Pb-S composition used in the first series. Both series were then heated for 1/2-hour periods at 502°, 505°, 507°, and 511°C. No liquid appeared in either series of experiments at 502°, 505°, or 507°C, but nearly total melting occurred in the ZnS-containing experiment at 511°C. In the experiment containing Fe_{1-x}S only small amounts of a sulfide liquid were present at 511°C, most of the Fe_{1-x}S having reacted with the Cu_2S to form a bornite phase.

These series of experiments demonstrate that the presence of Zn or Fe does not stabilize a Cu-Pb-S liquid to temperatures below that at which it is stable in the pure ternary system. The solubility of Fe and Zn in the Cu-Pb-S melt appears to be small (<1–2%) at 511°C. In many natural environments, in which Fe and/or Zn predominate over Cu and Pb, large-scale emplacement cannot be attributed to a Cu-Pb sulfide melt. In more restricted environments, however, in which Cu and Pb do constitute a major portion of the ores, Cu-Pb sulfide melts could serve as effective mechanisms of ore emplacement or remobilization.

It has been suggested that volatiles such as H_2O may lower the melting temperature of the appropriate sulfide assemblages. To test this hypothesis an additional experiment was conducted in which H_2O was sealed in a silica tube containing PbS, CuS, and cc₈₈ of bulk composition 34% Cu, 43% Pb, and 23% S. This experiment was performed at 500°C for 1 hour with an external supporting pressure of 500 bars to prevent bursting of the silica tube due to the internal H_2O pressure. Slight oxidation (<<0.01%) but no melting was observed. Thus, the presence of H_2O in this system does not lower the temperature of melting of sulfide assemblages and cannot be called upon to stabilize such melts to low temperature.

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