

Liquidus phase relations on the quasi-binary join $\text{Cu}_2\text{S-Sb}_2\text{S}_3$: Implications for the formation of tetrahedrite and skinnerite

L. TARAS BRYNDZIA,* ANDREW M. DAVIS

The James Franck Institute, The University of Chicago, 5640 S. Ellis Avenue, Chicago, Illinois 60637, U.S.A.

ABSTRACT

Binary behavior along the join $\text{Cu}_2\text{S-Sb}_2\text{S}_3$ is observed for compositions between stibnite and chalcostibite, i.e., $X_{\text{Cu}_2\text{S}} = 0$ to 0.50 at 895 K. For compositions more Cu_2S -rich than $X_{\text{Cu}_2\text{S}} = 0.50$, nonbinary behavior manifested itself as anomalously large exothermic heats of mixing in the high-temperature (895 K) calorimetric study of solid and liquid phases along this join by Bryndzia and Kleppa (1988). This nonbinary behavior is attributed to the precipitation of a solid Sb-Cu alloy with $X_{\text{Sb}} \approx 0.92$. This alloy is believed to be the same as the phase reported as pure Sb metal by previous investigators of the Cu-Sb-S system. Sb metal was interpreted by these investigators to form by subsolidus breakdown of tetrahedrite or skinnerite.

A textural and compositional examination of liquidus and subliquidus phase relations on the join $\text{Cu}_2\text{S-Sb}_2\text{S}_3$ shows that the alloy is the earliest phase to crystallize, consistent with its precipitation from $\text{Cu}_2\text{S-Sb}_2\text{S}_3$ melts at 895 K. Early precipitation of an Sb-Cu alloy from a bulk composition with $X_{\text{Cu}_2\text{S}} \approx 0.75$ on the quasi-binary join $\text{Cu}_2\text{S-Sb}_2\text{S}_3$ would result in the residual composition entering the ternary solid-solution field of tetrahedrite and forming an assemblage of Sb metal, skinnerite, and tetrahedrite. This is exactly what has been documented by Karup-Møller and Makovicky (1974) in a natural skinnerite-bearing sample from the type locality in Greenland.

The apparent rarity of skinnerite in nature appears to be controlled by a combination of two factors: (1) the low probability of successfully quenching from high temperature a bulk composition corresponding to skinnerite and (2) the numerous subsolidus peritectic breakdown reactions involving skinnerite conspire to remove much of any that crystallizes. For these reasons, natural samples of appropriate bulk composition often contain tetrahedrite as the dominant phase, with subordinate amounts of Sb metal (\pm minor famatinite and/or chalcostibite), but rarely any skinnerite.

INTRODUCTION

In their high-temperature calorimetric investigation of solid and liquid phases on the join $\text{Cu}_2\text{S-Sb}_2\text{S}_3$, Bryndzia and Kleppa (1988) observed that truly binary behavior along the join at 895 K was restricted to melt compositions with $X_{\text{Cu}_2\text{S}} \leq 0.50$. For more Cu_2S -rich compositions, anomalously large exothermic enthalpies of mixing were observed. These were attributed to the precipitation of an Sb-rich solid Sb-Cu alloy, a phase not previously recognized in the ternary system Cu-Sb-S or in the binary system Sb-Cu. In previous experiments in this ternary system, Sb metal was the only similar phase recognized. It was always interpreted to have formed as a subsolidus breakdown product of skinnerite and/or tetrahedrite (Skinner et al., 1972; Tatsuka and Morimoto, 1973, 1977).

Bryndzia and Kleppa (1988) also observed a dramatic discontinuity in the heat of mixing along the $\text{Cu}_2\text{S-Sb}_2\text{S}_3$ join at exactly $X_{\text{Cu}_2\text{S}} = 0.765$, corresponding to the precipi-

tation of solid Cu_2S . The phase diagram for the join $\text{Cu}_2\text{S-Sb}_2\text{S}_3$ used as a guide in the calorimetric study (Fig. 1, taken from Cambi and Elli, 1965) indicated that at 622 °C (895 K) and at the composition of the discontinuity ($X_{\text{Cu}_2\text{S}} = 0.765$), only a single liquid phase should be present. Thus, the topology of the liquidus surface in Figure 1 must be incorrect. In their comprehensive study of phase relations in the ternary system Cu-Sb-S, Skinner et al. (1972) noted several other discrepancies with the results reported by Cambi and Elli (1965), particularly with respect to the composition-stability relationships of tetrahedrite (summarized in Bryndzia and Kleppa, 1988). This study aims to reconcile some of the contradictory phase relations that exist at high temperature along the join $\text{Cu}_2\text{S-Sb}_2\text{S}_3$.

Previous work in the system Cu-Sb-S

Figure 2, taken from Skinner et al. (1972), shows the phases of interest in the ternary system Cu-Sb-S. Minerals on the binary join $\text{Cu}_2\text{S-Sb}_2\text{S}_3$ include Cu_2S (chalcocite), Cu_3SbS_3 (skinnerite), CuSbS_2 (chalcostibite), and Sb_2S_3 (stibnite). As noted by Skinner et al. (1972), two

* Present address: Department of Geological Sciences, Northwestern University, Locy Hall, Evanston, Illinois 60208, U.S.A.

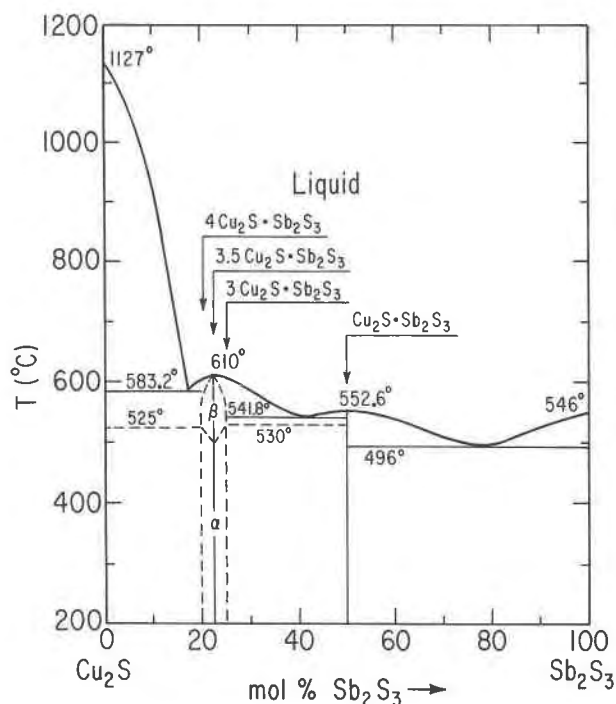


Fig. 1. Temperature vs. composition diagram for condensed phases on the quasi-binary join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, from Cambi and Elli (1965). Note particularly the two tetrahedrite polymorphs (α and β) and the extensive solid solution range of β -tetrahedrite along the join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$.

factors dominate and control phase relations in this system: (1) the join between Cu_2S and Sb is stable from the liquidus down to room temperature and (2) all the ternary phases are confined within the narrow compositional area bounded by Sb_2S_3 , Cu_2S , and CuS . The compositional field of tetrahedrite as determined by Skinner et al. (1972) defines a narrow arcuate band, subparallel to the $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ join, with the most Cu-rich tetrahedrite having nearly the same composition as skinnerite (Cu_3SbS_3).

The liquidus surface along the join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ was determined by Cambi and Elli (1965) from heating curves on mixtures of phases on the join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$. The mixtures were prepared by sulfidizing hydrous mixtures of Sb_2O_3 and Cu_2O at 312 °C and 100-atm pressure. Their phase diagram (Fig. 1) contains three eutectics: at 583.2 °C and 83.28 mol% Cu_2S , at 541.8 °C and 58.73 mol% Cu_2S , and at 496.0 °C and 20.12 mol% Cu_2S . The solid phases reported by Cambi and Elli (1965) as belonging to this join include chalcocite, tetrahedrite solid solution, chalcostibite, and stibnite. Their tetrahedrites ranged in composition from $4\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ to $3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$, i.e., $\text{Cu}_3\text{Sb}_2\text{S}_7$ to Cu_3SbS_3 , along the join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, completely at variance with several subsequent studies that showed that tetrahedrite is a ternary phase, lying off the binary join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ (e.g., see Fig. 2, and Tatsuka and Morimoto, 1973, 1977; Makovicky and Skinner, 1978,

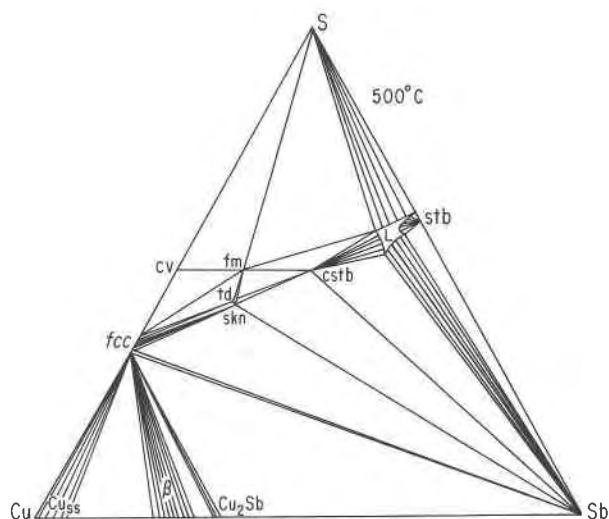


Fig. 2. Phase relations in the ternary system $\text{Cu}-\text{Sb}-\text{S}$ at 500 °C, from Skinner et al. (1972). Compositions are plotted in atom percent. Note that tetrahedrite (td) compositions sensu stricto lie off the binary join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ and are collinear with skinnerite (skn) and Sb . $\text{Cu}_{3\text{S}}$ = Cu-dominant solid solution; β = Cu-Sb alloy; cstab = chalcostibite; cv = covellite; fcc = face-centered cubic; fm = famatinitite; L = liquid.

1979; Lind and Makovicky, 1982). These references should be consulted for a detailed explanation of tetrahedrite phase relations.

Cambi and Elli (1965) reported the existence of two tetrahedrite phases with different unit-cell edges but apparently with the same symmetry. They interpreted this to mean that tetrahedrite had two polymorphs, a high-temperature β form and a low-temperature α form, and that mixtures of the two simply arose from the incomplete conversion on quenching. On heating, loss of the α form was explained as being due to complete transformation of the low-temperature form to the high-temperature form. This transformation was observed to occur at ~ 500 to 530 °C (Fig. 1). Skinner et al. (1972) interpreted these same thermal effects as being due to the breakdown of tetrahedrite by reaction at ~ 543 °C to famatinitite + skinnerite + a cation-disordered face-centered cubic phase (fcc). However, Cambi and Elli (1965) did not observe any of these breakdown phases in their experiments. They instead reported that the high-temperature β -tetrahedrite phase broke down by melting at ~ 610 °C. This is the same temperature at which the mineral skinnerite (Cu_3SbS_3) congruently melts.

The compound Cu_3SbS_3 was first reported by Gaudin and Dicke (1939). Verduch and Wagner (1957) determined the free energy of formation of Cu_3SbS_3 at 400 °C, showing it to be more stable than its component simple sulfides, Cu_2S and Sb_2S_3 . It is clear that Cambi and Elli (1965) were not aware of the existence of Cu_3SbS_3 or any previous synthesis work involving this phase. Our results will show that the β -tetrahedrite phase observed by them

TABLE 1. Liquidus phase relations on the join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$

Run	Melt composition $X_{\text{Cu}_2\text{S}}$	Phases present
In quenched sulfide melts		
1	0.88	Sb-Cu, Cu_2S
2	0.85	Cu_2S , Cu_3SbS_3 , Sb-Cu
3	0.82	Cu_2S , Cu_3SbS_3 , Sb-Cu
4	0.79	Cu_2S , Cu_3SbS_3 , Sb-Cu
5	0.76	Cu_2S , Cu_3SbS_3 , Sb-Cu
6	0.72	Cu_3SbS_3
7	0.61	Cu_3SbS_3 + CuSbS_2
8	0.56	Cu_3SbS_3 , CuSbS_2
9	0.55	Cu_3SbS_3 , CuSbS_2 , Sb-Cu
10	0.50	CuSbS_2
11	0.50	CuSbS_2
12	0.43	} Single homogeneous Cu_2S + Sb_2S_3 phase
13	0.35	
14	0.32	
15	0.22	
16	0.10	
In slow-cooled sulfide melts		
17	0.80	Cu_2S , Cu_3SbS_3 , Sb-Cu
18	0.772	Cu_2S , Cu_3SbS_3 , Sb-Cu
19	0.774	Cu_2S , Cu_3SbS_3 , Sb-Cu

* Phases: Sb-Cu: Sb + Cu alloy; Cu_2S : chalcocite; Cu_3SbS_3 : skinnerite; CuSbS_2 : chalcostibite.

is in fact the mineral skinnerite (phase B of Skinner et al., 1972).

Cambi and Elli (1965) also observed a thermal minimum at 541.8 °C between their β -tetrahedrite and chalcostibite that they interpreted as a "eutectic." Skinner et al. (1972) suggested that this was not a eutectic but rather the peritectic reaction



a reaction they observed at 543 ± 2 °C.

Experimental techniques

In this study we were particularly interested in re-examining the liquidus phase relations on the join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ for compositions with $X_{\text{Cu}_2\text{S}} \geq 0.50$, i.e., between chalcostibite (CuSbS_2) and chalcocite (Cu_2S). We have not attempted to measure the liquidus temperatures, however.

Pelletized charges containing variable proportions of Cu_2S and Sb_2S_3 were prepared from commercially available sulfides (see Bryndzia and Kleppa, 1988, for details) and were sealed under vacuum in silica tubes (6-mm outside diameter, 1-mm-thick wall) using standard techniques as described by Scott (1974). The mixtures were melted in a furnace ~900 K (close to the calorimeter operating temperature of 895 K in Bryndzia and Kleppa, 1988) for ~15 hours. The charges were quenched by immersion into an ice-water bath. Polished sections of the quenched sulfides were prepared and examined using a JEOL JSM-35 scanning electron microscope equipped with a backscattered-electron detector and a KeveX 7077 energy-dispersive X-ray microanalysis system. In some cases it was possible to deduce subliquidus phase relations by comparing rapidly quenched sulfide melts from this study with melts of identical composition from the calorimetric study of Bryndzia and Kleppa (1988). The latter were not quenched, but allowed to cool slowly to room temperature.

RESULTS

As indicated by the data in Table 1, almost all charges more Cu_2S -rich than $X_{\text{Cu}_2\text{S}} = 0.50$ contain a Sb-Cu alloy.

TABLE 2. Energy-dispersive electron-microprobe analyses of Sb-Cu alloy from quenched (runs 1, 2, and 4) and slowly cooled (run 17) sulfide melts on the join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$

Sample:	1	4	2	17
$X_{\text{Cu}_2\text{S}}$:	0.88	0.79	0.85	0.80
n:	3	1	1	1
S (wt%)	0.16 ± 0.07	0.26	0.91	0.32
Cu (wt%)	3.65 ± 0.52	4.49	5.90	3.06
Sb (wt%)	97.46 ± 0.26	99.00	96.67	96.29
Sum	101.27	103.75	103.48	99.67
S (at.%)	0.59 ± 0.23	0.91	3.11	1.18
Cu (at.%)	6.65 ± 0.89	7.91	10.14	5.67
Sb (at.%)	92.77 ± 1.07	91.18	86.75	93.04
X_{Sb}	0.93	0.92	0.90	0.94

It was very difficult to obtain good analytical data for this phase owing to its very fine grain size and intimate intergrowth with other phases. Analyses from four samples in which it was possible to obtain reasonable analyses of the alloy are given in Table 2. There may be minor fluorescence from surrounding sulfides even in these analyses. The important point is that the Cu/S ratio in these analyses is far too high to be accounted for by fluorescence from surrounding Cu-bearing sulfides. The average composition of the alloy is $\text{Sb}_{0.2}\text{Cu}_3$ (average $X_{\text{Sb}} = 0.92 \pm 0.01$).

There appears to be no systematic variation in the composition of the alloy with the bulk composition of the melt from which it crystallized. The presence of the Sb-Cu alloy in quenched sulfide melts strongly suggests that the anomalously large exothermic enthalpies of mixing observed by Bryndzia and Kleppa (1988) at 895 K for melt compositions more Cu_2S -rich than $X_{\text{Cu}_2\text{S}} \approx 0.50$ may be attributable to the precipitation of this solid phase at 895 K. We tentatively suggest that the Sb-Cu alloy may have precipitated from an immiscible Sb-Cu liquid, present on the join Sb-Cu at 895 K, since there is no solid solution between Sb and Cu (Skinner et al., 1972).

Bryndzia and Kleppa (1988) observed an abrupt thermal discontinuity in melts on the join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ at 895 K, at exactly $X_{\text{Cu}_2\text{S}} = 0.765$. SEM photographs of quenched sulfide melt textures for melts with $X_{\text{Cu}_2\text{S}} > 0.765$ show quite clearly that the thermal discontinuity was due to the precipitation of solid Cu_2S . As Figures 3 and 4 show, the quenched melts contain immiscible droplets of Cu_2S in a matrix that consists dominantly of skinnerite, with subordinate amounts of fine-grained interstitial Sb-Cu alloy.

We feel that the obvious interpretation of these data is that at 895 K (622 °C) Cu_2S begins to precipitate because the liquidus surface along the join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ has been intersected at $X_{\text{Cu}_2\text{S}} = 0.765$. This interpretation is clearly at odds with the phase diagram in Figure 1 from Cambi and Elli (1965).

The first five melt compositions in Table 1 encompass the entire range of tetrahedrite solid solutions reported by Cambi and Elli (1965) as well as their first eutectic at 583.2 °C and 83.28 mol% Cu_2S . Compositions of all the

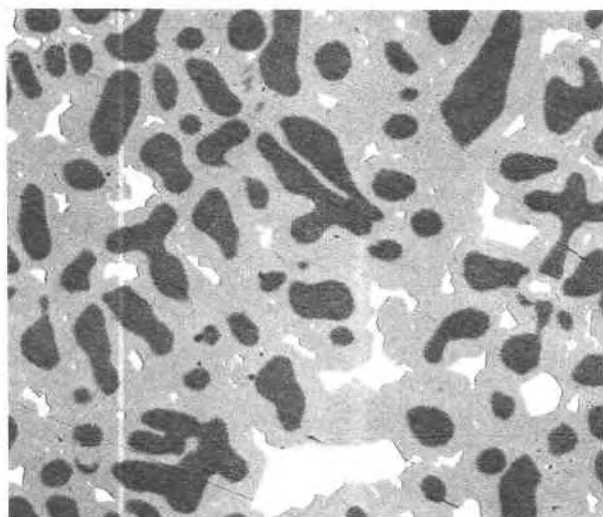


Fig. 3. Backscattered-electron photograph of textures in a slowly cooled melt with $X_{\text{Cu}_2\text{S}} = 0.772$ (run 18, Table 1), from Bryndzia and Kleppa (1988). Three phases are present. In order of decreasing backscattered-electron albedo, they are Sb-Cu alloy, skinnerite, and chalcocite. According to Figure 1, Cu_2S should not crystallize as a major phase in a melt of this composition. Width of field of view = 1.27 mm.

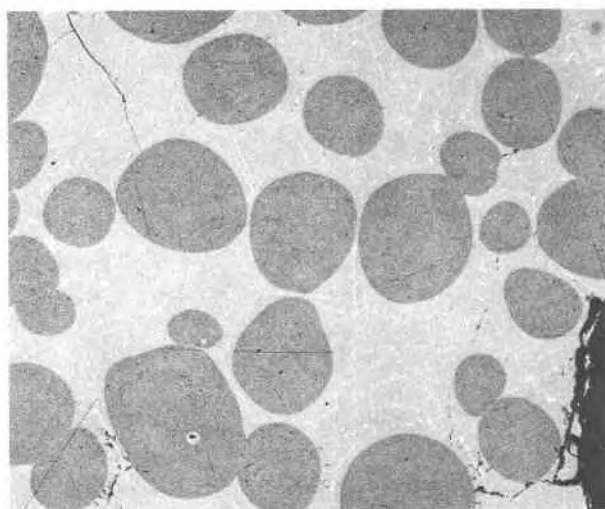


Fig. 4. Backscattered-electron photograph of textures in a quenched melt with $X_{\text{Cu}_2\text{S}} = 0.82$ (run 3, Table 1). Three phases are present. In order of decreasing backscattered-electron albedo, they are Sb-Cu alloy (fine-grained, interstitial phase), skinnerite, and chalcocite. Note that chalcocite occurs as immiscible droplets in a matrix of skinnerite. Width of field of view = 400 μm .

phases in Table 1 have been confirmed by electron-microprobe analysis. Our results, summarized in Table 1, clearly indicate that skinnerite, not tetrahedrite, is the dominant stable liquidus phase on the join $\text{Cu}_2\text{S-Sb}_2\text{S}_3$ for melts with $X_{\text{Cu}_2\text{S}} > 0.75$. The β -tetrahedrite phase reported by Cambi and Elli (1965 and Fig. 1) to melt at $\sim 610^\circ\text{C}$ is therefore skinnerite.

Recent experimental work by Tatsuka and Morimoto (1973, 1977) in the ternary system Cu-Sb-S is instructive in better understanding the tetrahedrite solid solutions reported by Cambi and Elli (1965). The xRD patterns for $4\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3$, $3.5\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3$, and $3\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3$, the range of tetrahedrite compositions reported by them, are almost identical. More significant, however, their xRD patterns are also nearly identical to the xRD pattern for pseudotetrahedrite (i.e., Cu_3SbS_3) reported by Tatsuka and Morimoto (1977, their Fig. 7). In other words, Cambi and Elli (1965) observed only one "tetrahedrite-like" phase (their β -tetrahedrite) on the join $\text{Cu}_2\text{S-Sb}_2\text{S}_3$, and this phase, Cu_3SbS_3 , is now recognized to be the mineral skinnerite (Karup-Møller and Makovicky, 1974). As demonstrated by Tatsuka and Morimoto (1977), the xRD patterns for tetrahedrite *sensu stricto* and Cu_3SbS_3 are so similar that confusion of the two phases is easily understood.

Quench textures from run 3 with $X_{\text{Cu}_2\text{S}} = 0.82$ are shown in Figure 4. This melt composition is almost the same as that at which Cambi and Elli (1965) reported their first eutectic (83.28 mol% Cu_2S). Textures in Figure 4 do not support such an interpretation, but rather indicate the presence of blebs of immiscible Cu_2S in a matrix of skinnerite, with fine-grained interstitial Sb-Cu alloy.

Our interpretation of the heat effect observed by Cambi and Elli (1965) at 583.2°C and 83.28 mol% Cu_2S is based in large measure on the textures present in the slowly cooled melts from calorimetric experiments with $X_{\text{Cu}_2\text{S}} = 0.80$ and 0.772 shown in Figures 5 and 3, respectively. Textures in Figure 5 clearly show that nowhere is the Sb-Cu alloy in contact with Cu_2S . Skinnerite always occurs between these two phases, suggesting that it formed according to the following reaction:



The textures in Figure 3 suggest that the reaction has essentially gone to completion. This reaction is remarkably similar to the peritectic breakdown reaction



reported by Skinner et al. (1972) to occur at $588 \pm 3^\circ\text{C}$. We propose that the latter interpretation is the correct explanation for the heat effect observed by Cambi and Elli (1965) and interpreted by them to be a eutectic. Our textural data support a peritectic relationship for phases below the liquids for melt compositions more Cu_2S -rich than $X_{\text{Cu}_2\text{S}} = 0.75$. We find no evidence to suggest that a eutectic exists between Cu_2S and skinnerite.

Melt compositions in runs 6–11 in Table 1 cover the range between skinnerite and chalcostibite, i.e., $X_{\text{Cu}_2\text{S}} = 0.75$ to 0.50, and encompass the range of "eutectic two," reported by Cambi and Elli (1965) to occur at 541.8°C and 58.73 mol% Cu_2S . Figures 6 and 7 are the quench textures from runs 5 and 7, respectively. In Figure 6 ($X_{\text{Cu}_2\text{S}} = 0.72$), there are two phases, the dominant one being skinnerite, as expected. The other phase is probably chal-

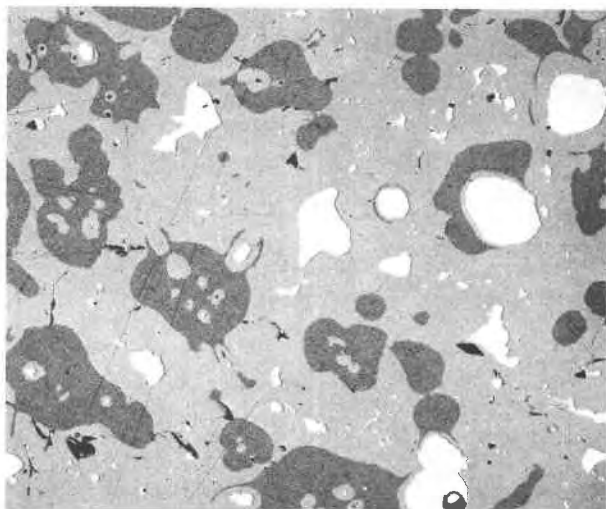


Fig. 5. Backscattered-electron photograph of textures in a slowly cooled melt with $X_{\text{Cu}_2\text{S}} = 0.80$ (run 17, Table 1) from Bryndzia and Kleppa (1988). Three phases are present. In order of decreasing backscattered-electron albedo, they are Sb-Cu alloy, skinnerite, and chalcocite. Note that nowhere is the Sb-Cu alloy in contact with chalcocite. Skinnerite always occurs between these two phases. The textures in this figure represent an intermediate reaction stage between that in Figures 4 and 3. Textures in Figures 4 and 5 do not support the presence of a eutectic for Cu_2S -rich compositions on the join $\text{Cu}_2\text{S-Sb}_2\text{S}_3$ (see Fig. 1). Width of field of view = $400 \mu\text{m}$.

costibite, but owing to its very fine grain size its composition could not be confirmed by electron-microprobe analysis. Figure 7 reveals the quench texture for a melt with composition of $X_{\text{Cu}_2\text{S}} = 0.61$ and confirms the pres-

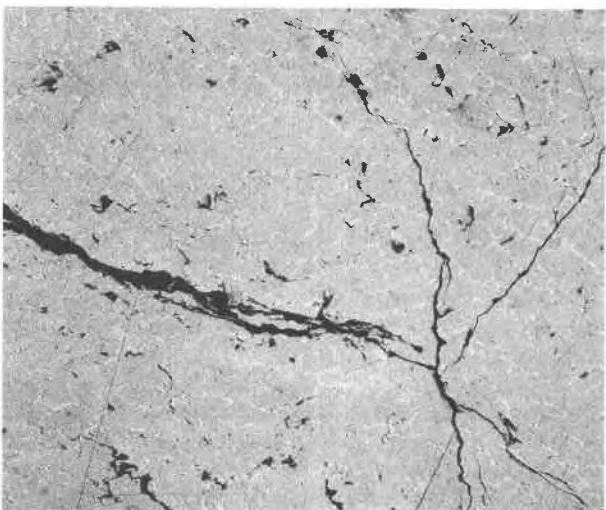


Fig. 6. Backscattered-electron photograph of textures in a quenched melt with $X_{\text{Cu}_2\text{S}} = 0.72$ (run 6, Table 1). Two phases are present. In order of decreasing backscattered-electron albedo, they are chalcostibite (very minor phase) and skinnerite (the dominant phase). Note, no chalcocite occurs in melts with $X_{\text{Cu}_2\text{S}} < 0.75$. Width of field of view = $400 \mu\text{m}$.

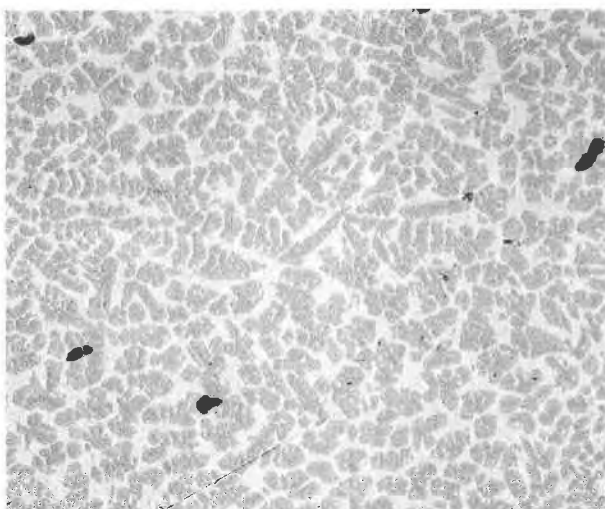


Fig. 7. Backscattered-electron photograph of textures in a quenched melt with $X_{\text{Cu}_2\text{S}} = 0.61$ (run 7, Table 1). Two phases are present. In order of decreasing backscattered-electron albedo, they are chalcostibite and skinnerite. We interpret this as a eutectic texture, in agreement with "eutectic two" in Figure 1. Width of field of view = $400 \mu\text{m}$.

ence of a eutectic at almost the same composition as the eutectic composition reported by Cambi and Elli (1965). These data do not support the observation made by Skinner et al. (1972) that the peritectic reaction



occurs at $543 \pm 2^\circ\text{C}$, almost the same temperature (541.8°C) at which "eutectic two" of Cambi and Elli (1965) is observed. It is of interest to note that the Sb-Cu alloy that is obvious in Figures 3, 4, and 5 is not as obvious in Figures 6 and 7. The reason for this is not clear, but it appears that the abundance of the Sb-Cu alloy decreases in more Sb_2S_3 -rich melt compositions.

DISCUSSION

Based on a detailed SEM and electron-microprobe study of quenched sulfide melts along the join $\text{Cu}_2\text{S-Sb}_2\text{S}_3$ it has been possible to resolve many of the uncertainties that have plagued phase relations along this join. With knowledge gained as a result of this study we have constructed a more realistic phase diagram for the Cu_2S -rich portion of this join, shown in Figure 8. The most significant changes are as follows: (1) The liquidus surface at 622°C (895 K) shifts from $X_{\text{Cu}_2\text{S}} = 0.83$ to $X_{\text{Cu}_2\text{S}} = 0.765$ and continues to the melting point of skinnerite at 610°C . (2) The eutectic at 583.2°C and $X_{\text{Cu}_2\text{S}} = 0.83$ from Cambi and Elli (1965) has been replaced with a peritectic at $588 \pm 3^\circ\text{C}$ determined by Skinner et al. (1972). Our observation that an Sb-Cu alloy forms at high temperature in melts near skinnerite in composition (i.e., $X_{\text{Cu}_2\text{S}} \approx 0.75$) has significant implications for the formation of skinnerite and tetrahedrite (*sensu stricto*) in nature. Removal of an Sb metal from a sulfide melt whose bulk composition

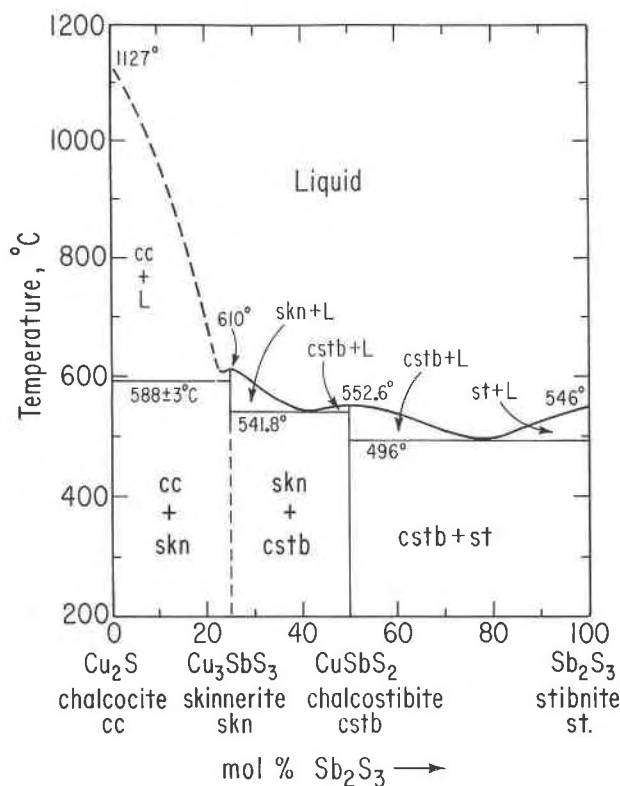


Fig. 8. Modified temperature vs. composition diagram for condensed phases on the quasi-binary join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ consistent with observed textures and phase compositions from this study. The liquidus between Cu_3SbS_3 and Sb_2S_3 is from Cambi and Elli (1965). Modifications are described in the text.

falls exactly at $X_{\text{Cu}_2\text{S}} = 0.75$ (i.e., Cu_3SbS_3) will result in the composition of the residual sulfide melt becoming slightly more enriched in S. This is exactly where the field of tetrahedrite solid solution lies as defined by Skinner et al. (1972) and Tatsuka and Morimoto (1973, 1977) and also explains why the most Cu-rich tetrahedrites have nearly the same composition as skinnerite (Skinner et al., 1972). In the studies mentioned above, as well as in the products of experiments by Cambi and Elli (1965, their Fig. 4), Sb metal is obvious in compositions containing tetrahedrite as the dominant mineral. Tatsuka and Morimoto (1977) interpreted the Sb metal to be a decomposition product of pseudotetrahedrite with composition Cu_3SbS_3 . Our interpretation of this texture, based on our own observations, is that Sb metal was probably the first phase to precipitate in their experiments in which the bulk composition was close to Cu_3SbS_3 , after which tetrahedrite crystallized from the residuum. Interpretation of textures is often ambiguous, but our interpretation is consistent with early precipitation of Sb as an Sb-Cu alloy in melts of similar bulk composition at high temperature.

Skinnerite is a rare mineral in nature, prompting Tatsuka and Morimoto (1977) to suggest that natural skinnerite is a metastable phase. Karup-Møller and Mako-

vicky (1974) suggested that an unusual combination of decomposition and cooling rate or stabilization by small concentrations of Ag could explain the occurrence of skinnerite in nature. However, Bryndzia and Kleppa (1988) inferred that skinnerite should be a stable mineral at 298 K. Its rarity in nature, therefore, must be attributed to other factors. Important among these must be the numerous peritectic breakdown reactions that involve skinnerite on cooling from high temperature (Skinner et al., 1972). These peritectic reactions are probably why Karup-Møller and Makovicky (1974) did not observe skinnerite in mineralized samples from the Tuperssuait Bay locality (Greenland) that contained the assemblage (in order of abundance) valentinite + senarmontite + Fe-rich tetrahedrite + Ag-rich tetrahedrite + native antimony and minor amounts of famatinite + argentite + polybasite.

Mineralized samples from the type locality for skinnerite contain the assemblage senarmontite + valentinite + native antimony + tetrahedrite + chalcostibite + galena + traces of loellingite (Karup-Møller and Makovicky, 1974; p. 890, their Figs. 1 and 2). The tetrahedrite is intergrown with skinnerite, suggesting that early precipitation of Sb metal, documented by Karup-Møller and Makovicky (1974, p. 894), was the reason tetrahedrite crystallized with skinnerite. The significance of this inference is that even if the original bulk composition did lie on the join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ at $X_{\text{Cu}_2\text{S}} \approx 0.75$, it is likely to end up in the ternary field of tetrahedrite solid solution merely by first precipitating Sb metal and may even end up not crystallizing any skinnerite at all. This mechanism undoubtedly operates to low temperatures ($\leq 350^\circ\text{C}$) as indicated by several of the experimental studies and numerous natural examples in which tetrahedrite commonly occurs with native antimony, but without any trace of skinnerite.

ACKNOWLEDGMENTS

This research has been supported by NSF CHE-8700937, awarded to O. J. Kleppa, and has benefited from the Central Facilities of the University of Chicago Materials Research Laboratory. We are indebted to Dr. C. Cermignani of the University of Toronto for providing us with a thorough translation from Italian, into English, of the Cambi and Elli (1965) paper. Discussions with O. J. Kleppa are also appreciated.

REFERENCES CITED

- Bryndzia, L.T., and Kleppa, O.J. (1988) High-temperature reaction calorimetry of solid and liquid phases in part of the quasi-binary system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, *American Mineralogist*, 73, 707-713.
- Cambi, L., and Elli, M. (1965) Processi idrotermali. Sintesi di solfosali da ossidi di metalli e metalloidi. Nota II-cuprosolfoantimoniti. *La Chimica e l'Industria*, 47, 136-147.
- Gaudin, A.M., and Dicke, G. (1939) The pyrosynthesis microscope study and iridescent filming of sulfide compounds of copper with arsenic, antimony and bismuth. *Economic Geology*, 34, 49-81, 214-232.
- Karup-Møller, S., and Makovicky, E. (1974) Skinnerite, Cu_3SbS_3 , a new sulfosalt from the Ilimaussaq alkaline intrusion, South Greenland. *American Mineralogist*, 59, 889-895.
- Lind, I.L., and Makovicky, E. (1982) Phase relations in the system $\text{Cu}-\text{Sb}-\text{S}$ at 200°C , 10^8 Pa by hydrothermal synthesis. Microprobe analyses

- of tetrahedrite—A warning. *Neues Jahrbuch für Mineralogie Abhandlungen*, 145, 134–156.
- Makovicky, E., and Skinner, B.J. (1978) Studies of the sulfosalts of copper: VI. Low-temperature exsolution in synthetic tetrahedrite solid solution. $\text{Cu}_{12+x}\text{Sb}_{4+y}\text{S}_{13}$. *Canadian Mineralogist*, 16, 611–623.
- (1979) Studies of the sulfosalts of copper: VII. Crystal structures of the exsolution products $\text{Cu}_{12.3}\text{Sb}_4\text{S}_{13}$ and $\text{Cu}_{13.8}\text{Sb}_6\text{S}_{13}$ of unsubstituted synthetic tetrahedrite. *Canadian Mineralogist*, 17, 619–634.
- Scott, S.D. (1974) Experimental methods in sulfide synthesis. *Mineralogical Society of America Short Course Notes*, 1, S1–S38.
- Skinner, B.J., Luce, F.D., and Makovicky, E. (1972) Studies of the sulfosalts of copper: III. Phases and phase relations in the system Cu-Sb-S. *Economic Geology*, 67, 924–938.
- Tatsuka, K., and Morimoto, N. (1973) Composition variation and polymorphism of tetrahedrite in the Cu-Sb-S system below 400 °C. *American Mineralogist*, 58, 425–434.
- (1977) Tetrahedrite stability relations in the Cu-Sb-S system. *Economic Geology*, 72, 258–270.
- Verdusch, A.G., and Wagner, C. (1957) Contributions to the thermodynamics of the systems PbS-Sb₂S₃, Cu₂S-Sb₂S₃, Ag₂S-Sb₂S₃, and Ag-Sb. *Journal of Physical Chemistry*, 61, 558–562.

MANUSCRIPT RECEIVED MAY 11, 1988

MANUSCRIPT ACCEPTED SEPTEMBER 21, 1988