

## BINARY AND TERNARY SULPHOSALT ASSEMBLAGES IN THE $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{PbS}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$ SYSTEM

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### ABSTRACT

The  $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{PbS}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$  system has 18 ternary sub-systems which contain sulphosalts. Phases and natural assemblages reported in the literature are plotted on ternary composition diagrams of these sub-systems. Tie line variations provided by extensive solid solutions suggest numerous potential geothermometers. Facies changes are also indicated in certain systems by tie line switches as suggested from natural assemblages. Sequences of assemblages from a deposit have the potential of indicating relative metal and/or semi-metal fugacity changes.

This type of data analysis suffers from the ambiguities inherent in sulphosalt identification. Additionally, detailed analyses of phases having variable compositions are almost completely lacking. Qualifications concerning the meaning of an assemblage, and the degree of attainment of equilibrium are also noted.

The potential interest of detailed investigations on sulphosalt assemblages is emphasized.

### INTRODUCTION

The purpose of the present study is to derive ternary compatibility diagrams for a large portion of sulphosalt chemistry using previously-reported data concerning natural assemblages of sulphosalts. Many sulphosalt compositions can be expressed as combinations of simple sulphide components, and the system considered here is  $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{PbS}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$ . Phases present in the sulphosalt binaries and ternaries of this system are listed in Tables 1 and 2, respectively, and phases are plotted on ternary composition diagrams using all combinations of these sulphides as end-member components of sulphosalt systems. Reported natural assemblages are then indicated as tie lines on the composition diagrams. Reference is made to phase equilibrium studies where they are relevant to interpretation of natural assemblages, or in some cases to fill in where reported assemblages are lacking. As such, this study might be considered an extension of work initiated by McKinstry on the  $\text{Cu}-\text{Fe}-\text{S}-\text{O}$  (McKinstry 1959) and  $\text{Cu}-\text{Fe}-\text{As}-\text{S}$  (McKinstry 1963) systems, and continued by

Petersen (1962). This work has the same limitations and qualifications expressed in the previous studies, plus a few peculiar to sulphosalt mineralogy.

Having indicated above the purpose of the present work, it is important to note also what it will not include. This study is not intended to be a review of sulphosalt mineralogical data nor phase relations. The details of mineralogical problems within so large a group of minerals is beyond the scope of this endeavor. The documentation of the consistent or conflicting patterns of assemblages of sulphosalts is, rather, the object of this study. The resulting diagrams are useful to investigators of sulphosalt mineralogy and geochemistry, and in pointing out sulphosalt systems of potential geochemical interest. As sulphosalts are often found within, or adjacent to, important ore deposits, knowledge of the genesis of this family of minerals can be useful in mineral exploration.

The most severe limitations encountered when relying on the literature for sulphosalt assemblages is the question of identification of species. Sulphosalt systems commonly have a multiplicity of phases present, and many phases have similar properties and appearance. Most studies before 1955 relied solely upon microchemical and microscopic techniques, which have since proved not diagnostic for many sulphosalts. Some studies reported assemblages of 8 or 10 sulphosalts, with many conflicting tie lines and disregard for the Phase Rule limitation on the number of possible coexisting phases in a system. X-ray identifications can generally be relied on, but the literature suffers from the scarcity of such critical studies.

The second question raised in the present study of sulphosalt assemblages, and the reservation shared with the earlier studies of McKinstry and Petersen, is what is meant by an assemblage. The relations between assemblages, associations, and true equilibrium are discussed further by Barton *et al.* (1963). In the present work the terms 'found with' or 'associated with' as used in the literature are accepted to mean assemblage. Unfortunately, it is all too often left un-

specified whether these terms mean intimate grain to grain contact, or found together in the same polished section, hand sample, paragenetic zone, or merely in the same mining district. Ideally, the use of the term assemblage indicates compatibility and equilibrium, but as McKinstry (1959) pointed out, two minerals which occur together are not an absolute guarantee of compatibility. Another term used in the literature is 'replacement', but this term generally does not indicate an equilibrium assemblage. The textural

establishment of replacement versus coprecipitation is, furthermore, a matter of conjecture in certain cases.

The assemblages noted in this study have been obtained from a number of sources. The standard references are Palache *et al.* (1944), Ramdohr (1969), Schouten (1962), Traill (1970), and Uytendogaardt (1951). Original sources were sought in instances of reported conflicting tie lines, and a review of the pertinent literature for the past twenty years was made. Conflicting assemblages are indicated on the diagrams by dashed lines. Undoubtedly, some reported assemblages have been missed, and the author would appreciate hearing of any such omissions.

In spite of the reservations which have been mentioned above, and in light of the increasing mineralogic, crystallographic, phase equilibrium, and thermodynamic data on sulphosalts that are becoming available, it is strongly felt that we must come to a better understanding of the natural occurrences of these species. In the idea of McKinstry (1963), "Chemistry, however precise, is not geology until natural occurrences are correlated and reconciled with it." In addition to assemblages, paragenetic sequences of sulphosalts are also noted, as such data are relevant to an understanding of the genesis of the mineralization.

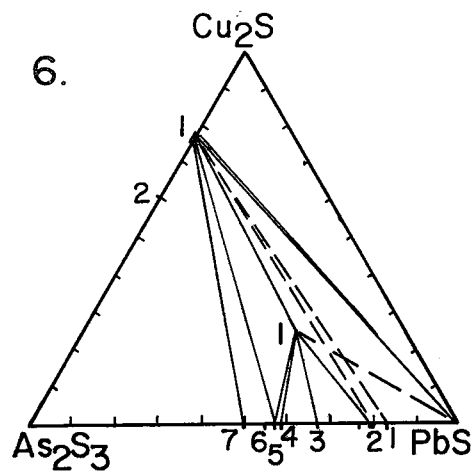
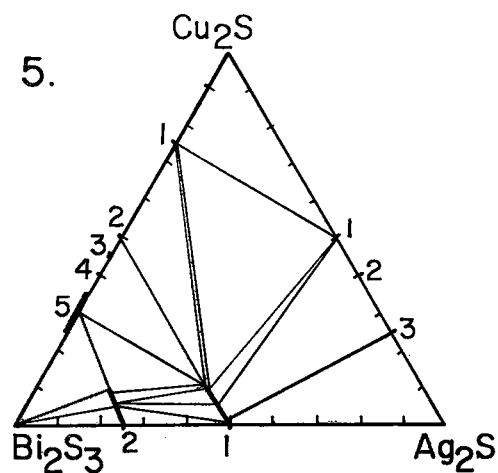
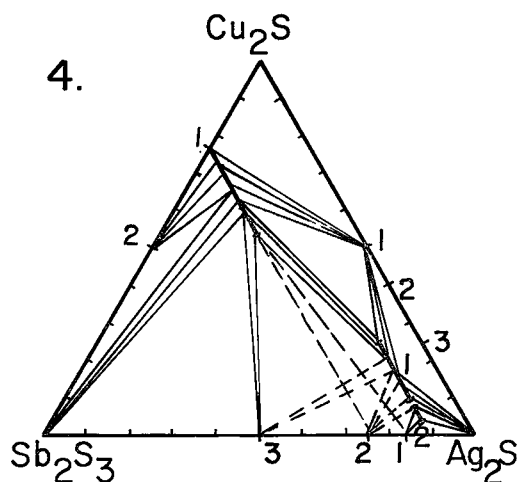
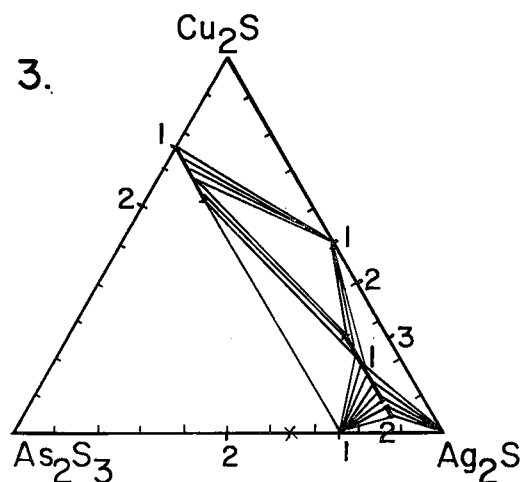
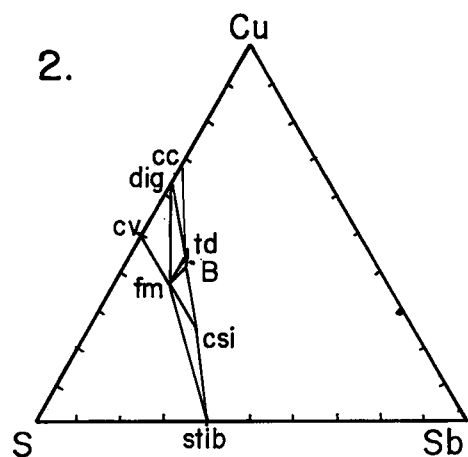
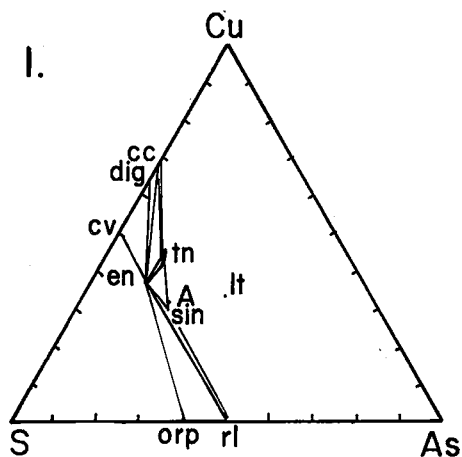
In the tables and figures which follow, metal-rich phases and sub-systems are listed first, with progressively more semi-metal-rich phases and sub-systems following. When more than one metal or semi-metal constituent appears in a system, as in the ternaries, each appears in the order of the atomic weights of the metallic or semi-metallic element. Binaries and then ternaries are discussed, and at each successive step new phases appearing in a system are listed in table form according to the above-described order. The numerical appearance of a phase in these tables is then used for reference in the accompanying composition diagrams, and is indicated in parentheses when a species is referred to in the text. It is hoped that this binary and ternary numerical reference scheme will keep the diagrams relatively uncluttered; however, the interested reader may find it useful to write his own abbreviations on the figures.

## BINARY SYSTEMS

Table 1 lists the sequence of binaries, and the formulas and metal/semi-metal ratios of the species in each of the 15 binaries. Only the more important of these are discussed below. References to the most recent phase equilibrium studies can be found in Craig & Barton (1973), and

TABLE 1. PHASES PRESENT ALONG THE BINARY SYSTEMS IN THE  $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{PbS}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$  SYSTEM (see text for special notes)

Binary system	Phases present	Formula	Component ratios, A : B
1. $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}$	1. stromeyerite 2. mckinstryite 3. jalpaite	$\text{CuAgS}$ $\text{Cu}_{0.84}\text{Ag}_{1.2}\text{S}$ $\text{CuAg}_3\text{S}_2$	1:1 2:3 1:3
2. $\text{Cu}_2\text{S}-\text{PbS}$	1. betekhtinite	$\text{Cu}_{10}(\text{Fe,Pb})\text{S}_6$	5:1
3. $\text{Ag}_2\text{S}-\text{PbS}$	none		
4. $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$	1. tennantite (projected)  enargite, luzonite Phase A (Maske & Skinner 1971)  2. sinnerite	$\text{Cu}_{12}\text{As}_4\text{S}_{13}$ $z=0.1, y=0.08$ $\text{Cu}_3\text{AsS}_4$ $\text{Cu}_{24}\text{As}_{12}\text{S}_{31}$ $\text{Cu}_6\text{As}_4\text{S}_9$	43:1 3:1 2:1 3:2
5. $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$	1. tetraedrite (projected)  Phase B (skinnerite) (Skinner <i>et al.</i> 1972) fennite 2. chalcocottite	$\text{Cu}_{12}\text{Sb}_4\text{As}_4\text{S}_{13}$ $z=0.1, y=0.02, x=0.27$ $\text{Cu}_3\text{SbS}_3$ $\text{Cu}_3\text{SbS}_4$ $\text{CuSbS}_2$	1244:244 3:1 3:1 1:1
6. $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$	mineral #2 (Honnorez-Guerrero 1971)  1. wittichenite 2. omphacite 3. cuprobismutite 4. hodrichite 5. 'elchbergite'	$\text{Cu}_9\text{Bi}_{11}\text{S}_{16}$ $\text{Cu}_3\text{BiS}_3$ $\text{CuBiS}_2$ $\text{Cu}_{11}\text{Bi}_{12}\text{S}_{22}$ $\text{Cu}_8\text{Bi}_{12}\text{S}_{22}$ $\text{CuBi}_3\text{S}_5$	9:31:1 3:1 1:1 5:6 2:3 1:3
7. $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$	As-billingsleyite As-stephantite (Hall 1966) 1. proustite, xanthoconite 2. smithite, trichomanite	$\text{Ag}_7\text{AsS}_5$ $\text{Ag}_5\text{AsS}_4$ $\text{Ag}_3\text{AsS}_3$ $\text{AgAsS}_2$	7:1 5:1 3:1 1:1
8. $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$	Sb-billingsleyite 1. stephanite 2. pyrrhotite, pyrostilpnite 3. ulargyrite	$\text{Ag}_7\text{SbS}_6$ $\text{Ag}_5\text{SbS}_4$ $\text{Ag}_3\text{SbS}_3$ $\text{AgSbS}_2$	7:1 5:1 3:1 1:1
9. $\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3$	1. wittichenite 2. pavonite	$\text{AgBiS}_2$ $\text{AgBi}_3\text{S}_5$	1:1 1:3
10. $\text{PbS}-\text{As}_2\text{S}_3$	1. graytonite 2. Jordanite  3. dufrénoysite 4. rathite 5. baumhauerite 6. liveingite 7. sartorite (scleroclase)	$\text{Pb}_3\text{As}_4\text{S}_{15}$ $\text{Pb}_{13}\text{As}_7\text{S}_{23}$ $\text{Pb}_{14}\text{As}_7\text{S}_{24}$ $\text{Pb}_3\text{As}_5\text{S}_8$ $\text{Pb}_9\text{As}_{13}\text{S}_{28}$ $\text{Pb}_4\text{As}_6\text{S}_{13}$ $\text{Pb}_3\text{As}_6\text{S}_{10}$ $\text{PbAs}_2\text{S}_4$	9:2 25:7 28:7 2:1 18:13 4:3 6:5 1:1
11. $\text{PbS}-\text{Sb}_2\text{S}_3$	goacronite (schulzite)  1. boulangierite 2. semseyite madocite 3. dadsonite 4. heteromorphite 5. launayite 6. piagontite 7. robinsonite 8. zinkenite 9. fulopite	$\text{Pb}_{27}(\text{Sb,As})_{14}\text{S}_{48}$ (As essential) $\text{Pb}_2\text{SbS}_{11}$ $\text{Pb}_3\text{SbS}_{21}$ $\text{Pb}_{17}(\text{Sb,As})_{16}\text{S}_{41}$ $\text{Pb}_{11}\text{Sb}_{12}\text{S}_{29}$ $\text{Pb}_7\text{SbS}_{19}$ $\text{Pb}_{22}(\text{Sb,As})_{26}\text{S}_{61}$ $\text{Pb}_5\text{SbS}_{17}$ $\text{Pb}_7\text{Sb}_{12}\text{S}_{25}$ $\text{Pb}_6\text{Sb}_{14}\text{S}_{27}$ $\text{Pb}_3\text{SbS}_{15}$	27:7 5:2 9:4 17:8 11:6 7:4 22:13 5:4 7:6 6:7 3:4
12. $\text{PbS}-\text{Bi}_2\text{S}_3$	heyrovskyite 1. titanite 2. bursite 3. cosalite 4. 'bonchevite'	$\text{Pb}_6\text{Bi}_{12}\text{S}_{29}$ (Ag, Cu present) $\text{Pb}_3\text{Bi}_2\text{S}_6$ $\text{Pb}_2\text{Bi}_4\text{S}_{11}$ $\text{Pb}_2\text{Bi}_2\text{S}_5$ $\text{PbBi}_2\text{S}_4$ $\text{PbBi}_4\text{S}_7$	6:1 3:1 5:2 2:1 1:1 1:2
13. $\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$	wakabayashinite 1. getchelite	$\text{As}_{10}\text{Sb}_{18}$ $\text{AsSbS}_3$	10:1 1:1
14. $\text{As}_2\text{S}_3-\text{Bi}_2\text{S}_3$	none		
15. $\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$	bismuthinite solid solution	$(\text{Sb}_{0.55}\text{Bi}_{0.45})_2\text{S}_3$ $\text{Bi}_2\text{S}_3$ (Springer 1971)	11:9:0:1



recourse should be made to this work for a list of critical points and stability ranges of binary assemblages.\*

The natural phases appearing on the  $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$  and  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  joins are given in Table 1, #4 and #5, along with the synthetic phases which might be recognized in natural assemblages in the future. These two important joins are also among the more complicated ones, in that they necessitate the projection of compositions from sulphur onto the join of interest. Natural assemblages in the  $\text{Cu}-\text{As}-\text{S}$  and  $\text{Cu}-\text{Sb}-\text{S}$  systems are given in Figures 1 and 2. Sinnerite is the only phase which plots exactly on the  $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$  join, so that the tennantite field is projected away from sulphur onto this join. Digenite and djurelite project onto the  $\text{Cu}_2\text{S}$  position. Enargite and luzonite project onto the tennantite field and also have substitution of As by Sb (Springer 1969a). Their presence indicates high sulphur fugacity conditions, and their coexistence has the possibility of providing geothermometric measurements (Skinner 1960). A particularly important assemblage is that of enargite-realgar, which precludes the coexistence of orpiment with tennantite. These observations are compatible with equilibria studies down to  $300^\circ\text{C}$  (Maske & Skinner 1971), and the assemblages indicated in Figure 1 are in agreement with their work. Sinnerite has been found with tennantite at its only natural occurrence, the Lengenbach Quarry, Switzerland. Tennantite-chalcocite (digenite) is a not uncommon assemblage.

The assemblages for the  $\text{Cu}-\text{Sb}-\text{S}$  system given in Figure 2 present fewer complications. Digenite and the tetrahedrite field project away from sulphur onto the  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  join, and famatinite projects onto the tetrahedrite field, occurring under higher sulphur fugacity conditions. A recent review of phase relations is in Chen & Chang (1974). Phase B of Skinner *et al.* (1972) plots on the  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  join at the point where famatinite and ideal tetrahedrite are projected. Except for Phase B, all two-phase assemblages along the join are found in nature.

On the  $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$  join (Table 1, #6), mineral #2 (Honnorez-Guerstein 1971) falls on the sulphur-rich side of this join. Cuprobismutite, long thought to be dimorphic with emplectite, has been found to have a distinct composition in both synthetic (Buhlmann 1971) and natural

(Taylor *et al.* 1973) materials. Eichbergite, although thought to be discredited, has been found in synthesis studies in this system (Buhlmann 1971), and consequently is retained in the present work. The natural assemblages on this join are wittichenite(1)-emplectite(2), and wittichenite(1)-chalcocite, with this latter reported also with enargite (Ramdohr 1969, p. 711). It would be of interest to investigate this high-sulphur fugacity assemblage for the presence of mineral #2.

The sequence of phases on the  $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$  and  $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$  joins (Table 1, #7&8; Figs. 3&4) includes billingsleyite and its antimony analogue, although these phases lie on the sulphur-rich side of the joins. All two-phase assemblages of adjoining phases are reported in nature except that of smithite(trechmannite)(2)-proustite(xanthocobaltite)(1). Although smithite was reported (Palache *et al.* 1944) in association with orpiment, later studies (Graeser 1968) do not substantiate this assemblage. The three-phase assemblage argentite-stephanite(1)-pyrargyrite(2), not uncommon in the literature, is interpreted (Keighin & Honea 1969) to represent subsequent precipitation of stephanite on previously-deposited argentite-pyrargyrite, in one instance. Stephanite is stable below  $197^\circ\text{C}$ .

On the  $\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3$  join (Table 1, #9; Fig. 5), all adjoining phases have been observed; matildite-bismuthinite has also been reported (Schouten 1962), but this does not agree with phase equilibrium studies of the simple binary. The matildite polymorph stable above  $195^\circ\text{C}$  has a solid solution in both directions along the join, and is a potential geothermometer if found with acanthite or pavonite.

The  $\text{PbS}-\text{As}_2\text{S}_3$  and  $\text{PbS}-\text{Sb}_2\text{S}_3$  joins (Table 1, #10&11; Figs. 6&7) contain a profusion of phases. The four most arsenic-rich phases on the  $\text{PbS}-\text{As}_2\text{S}_3$  join were described from the Lengenbach Quarry, Binnatal, Switzerland. Dufrenoyite has been reported (Palache *et al.* 1944) with orpiment, realgar, sphalerite and gypsum. This is probably a low-temperature assemblage when compared with the Binnatal deposit. Jordanite(2)-dufrenoyite(3) has been reported from Binnatal, and this assemblage is stable below approximately  $480^\circ\text{C}$ . Gratonite(1) is considered by Roland (1968) to be a low-temperature dimorph of jordanite, which serves to explain the reported coexistence of jordanite and gratonite each with galena. This idea is supported by more detailed chemical analyses of gratonite (Burkart-Baumann *et al.* 1968). Jordanite is the arsenic end-member of the geocronite solid solution, which takes up to 58 atomic % Sb replacing As (Roland 1968; Walia

\*Reference should also be made to Sulfide Phase Equilibria, chapter 5 in the Short Course on Sulfide Mineralogy given by the Mineralogical Society of America, November, 1974.

& Chang 1973). A review of mineralogical and stability relations can be found in Chang & Bever (1973).

Numerous mineralogical and phase equilibrium studies have failed to resolve questions as to the nature and stability of phases within the  $\text{PbS}-\text{Sb}_2\text{S}_3$  system. Some of this work is reviewed in Chang & Bever (1973). Reported two-phase assemblages compatible with phase equilibrium studies include galena-boulangerite(1), boulangerite(1)-zinkenite(8) (below  $318^\circ\text{C}$ , Craig *et al.* 1973), and zinkenite(8)-stibnite. Boulangerite(1)-robinsonite(7)-stibnite, semseyite(2)-heteromorphite(4)-plagionite(6) (Jambor 1969), galena-zinkenite (8), and zinkenite (8)-fulöppite (9), are reported assemblages not compatible with phase equilibrium studies. Arsenic-free geocronite, madocite, and launayite have not been found. Jamesonite and meneghinite lie just off this join, having essential Fe and Cu, respectively.

A review of mineralogical and stability studies in the  $\text{PbS}-\text{Bi}_2\text{S}_3$  system can be found in Chang & Bever (1973). On this join (Table 1, #12; Fig. 8), the two-phase assemblages reported are galena-cosalite(2), cosalite(2)-bismuthinite, galena-galenobismutite(3), galenobismutite(3)-bismuthinite, and cosalite(2)-galenobismutite(3). Only the last two of these are compatible with phase equilibrium studies (Craig 1967). Bursaitite(1) and bonchevite(4) are rare, and giessenite apparently has copper and antimony as essential constituents that causes it to plot off of the join. Heyrovskyite is probably a member of this join (Klominsky *et al.* 1971; Craig 1967, Phase II), although a copper- and silver-free member has not been reported.

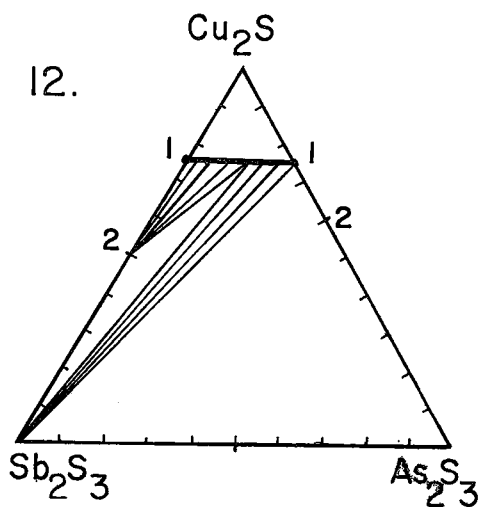
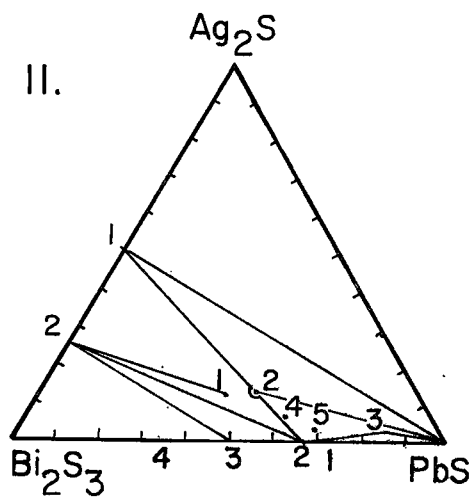
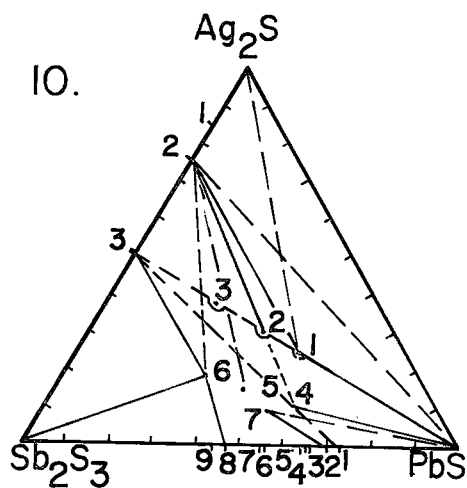
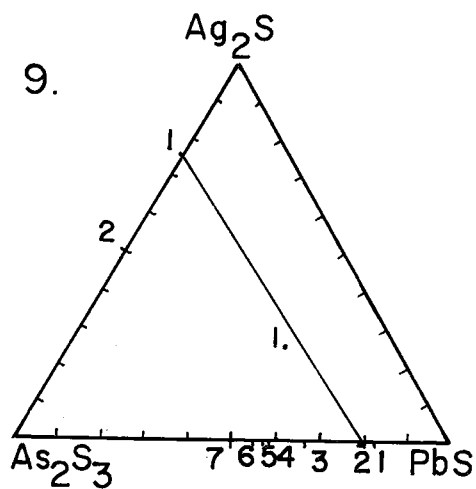
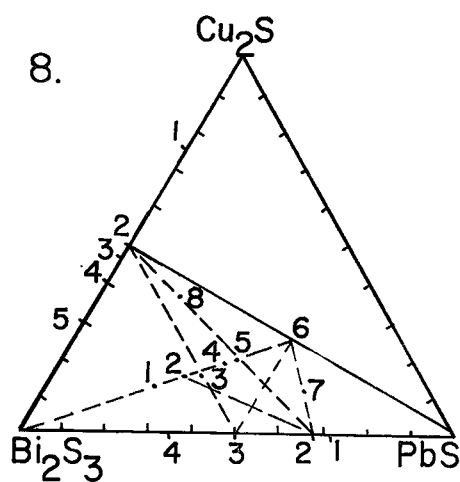
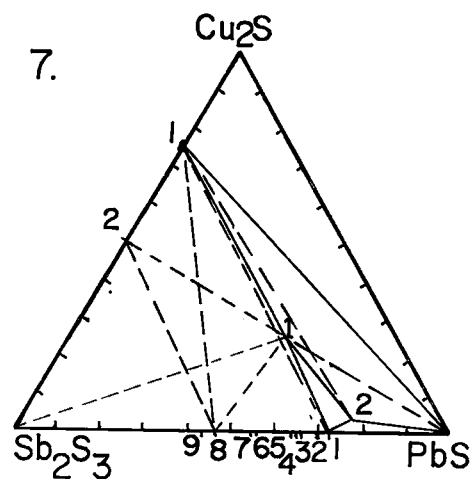
### TERNARY SYSTEMS

Ternary sulphosalt composition diagrams are considered in the order of two metal + one semi-metal sulphide components, followed by one metal + two semi-metal sulphide components. These components are listed according to the increasing atomic weights of their metallic and then semi-metallic elements. This same order of components is listed clockwise around the ternary composition diagrams. Binary phases are referred to by their identification number along a particular join, as listed in Table 1. Ternary phases are indicated in Table 2, and are noted on the diagrams by their number of appearance in the ternary. Natural assemblages are shown as tie lines on the composition diagrams. These assemblages are most often only of two phases; cases where

three phases have been reported are noted especially. In many cases solid solutions are present; however, very little data are available concerning coexisting compositions, so that the tie line distributions given are only schematic. Conflicting tie lines are dashed. The changes of tie line distributions suggest numerous potential geothermometers.

TABLE 2. TERNARY PHASES IN THE  $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{PbS}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$  SYSTEM, COEXISTING PHASES

Ternary system		Phases present	Formula	Reference
FIGURES 3-20				
1. $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$ (Fig. 3)	1. pearceite (Frondelet 1963) pearceite (111) (Harris <i>et al.</i> , 1965)	( $\text{Ag}_{14.7-20}\text{Cu}_{1.3-2}\text{As}_{21}$ )	variable	
	2. arsenopolybasite (Frondelet 1963) pearceite (222) (Harris <i>et al.</i> , 1965)	( $\text{Ag}_{15.4-20}\text{Cu}_{0.6-2}\text{As}_{21}$ )	variable	
2. $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ (Fig. 4)	1. antimonopercite (Frondelet 1963) polybasite (111) (Harris <i>et al.</i> , 1965)	( $\text{Ag}_{14.3-20}\text{Cu}_{1.7-2}\text{Sb}_{21}$ )	variable	
	2. polybasite (Frondelet 1963) polybasite (222) (Harris <i>et al.</i> , 1965)	( $\text{Ag}_{15.4-20}\text{Cu}_{0.6-2}\text{Sb}_{21}$ )	variable	
3. $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3$ (Fig. 5)	1. antimonopercite (Frondelet 1963) Cu-bearing pavonite (Pavonite 1971)	( $\text{Ag}, \text{Cu})\text{Bi}_{21}\text{S}_{25}$		
4. $\text{Cu}_2\text{S}-\text{PbS}-\text{As}_2\text{S}_3$ (Fig. 6)	1. seligmannite	$\text{CuPbAs}_3$	1:2:1	
5. $\text{Cu}_2\text{S}-\text{PbS}-\text{Sb}_2\text{S}_3$ (Fig. 7)	1. bourmonite 2. meneghinite	$\text{CuPbSb}_3$ $\text{CuPb}_{13}\text{Sb}_{24}$	1:2:1 1:26:7	
6. $\text{Cu}_2\text{S}-\text{PbS}-\text{Bi}_2\text{S}_3$ (Fig. 8)	1. gladiite 2. nezarynite 3. lindstromite 4. 7 (Welfin 1966) 5. hammarite 6. sikinitite 7. nuffieldite 8. 2 (Kupcik & Makovsky 1968)	$\text{CuPbBi}_3$ $\text{Cu}_6\text{Pb}_6\text{Bi}_{20}\text{S}_{39}$ $\text{CuPbBi}_3\text{S}_6$ $\text{Cu}_3\text{Pb}_6\text{Bi}_7\text{S}_{15}$ $\text{Cu}_2\text{Pb}_4\text{Bi}_4\text{S}_9$ $\text{CuPbBiS}_3$ $\text{Cu}_4\text{Pb}_{10}\text{Bi}_{10}\text{S}_{28}$ $\text{Cu}_4\text{PbBi}_5\text{S}_{11}$	1:2:5 3:6:10 1:2:3 3:6:7 1:2:2 1:2:1 2:10:5 4:2:5	
7. $\text{Ag}_2\text{S}-\text{PbS}-\text{As}_2\text{S}_3$ (Fig. 9)	1. wairdite	$\text{AgPbAs}_3$	1:2:1	
8. $\text{Ag}_2\text{S}-\text{PbS}-\text{Sb}_2\text{S}_3$ (Fig. 10)	1. freieslebenite 2. diaphorite 3. 7 (Hoda & Chang 1972) 4. oymacite 5. ramdohrite 6. andorite 7. ftezelyite	$\text{AgPbSb}_3$ $\text{Ag}_3\text{PbSb}_5\text{S}_8$ $\text{Ag}_2\text{PbSb}_5\text{S}_7$ $\text{Ag}_2\text{Pb}_5\text{Sb}_6\text{S}_{15}$ $\text{Ag}_2\text{Pb}_3\text{Sb}_6\text{S}_{13}$ $\text{AgPbSb}_3\text{S}_6$ $\text{Ag}_2\text{Pb}_5\text{Sb}_6\text{S}_{18}$	1:2:1 3:4:3 3:2:3 1:5:3 1:3:3 1:2:3 1:5:4	
9. $\text{Ag}_2\text{S}-\text{PbS}-\text{Bi}_2\text{S}_3$ (Figs. 11, 23)	1. gustavite X (Karup-Møller 1970) 2. schirmerite 3. heyrovskyite 4. X (Nedachi <i>et al.</i> 1973) 5. Z (Nedachi <i>et al.</i> 1973)	$\text{Ag}_3\text{PbBi}_{11}\text{S}_{24}$ $\text{Ag}_2\text{PbBi}_{10}\text{S}_{24}$ $\text{AgPbBi}_3\text{S}_7$ $6(\text{Pb}_{0.88}\text{Bi}_{1.08}(\text{Ag}, \text{Cu})_{0.04}\text{S}_{12})$ $0.9\text{Ag}_2\text{S} \cdot 8\text{PbS} \cdot 4.9\text{Bi}_2\text{S}_3$ $0.5\text{Ag}_2\text{S} \cdot 9\text{PbS} \cdot 4.3\text{Bi}_2\text{S}_3$	3:10:11 1:7:5 1:4:3 (6):1 0.9:8.5:4.9 0.5:9.9:4.3	
10. $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$ (Fig. 12)	none			
11. $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3-\text{Bi}_2\text{S}_3$ (Fig. 13)	none			
12. $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$ (Fig. 14)	none			
13. $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$ (Fig. 15)	none			
14. $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3-\text{Bi}_2\text{S}_3$ (Fig. 16)	none			
15. $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$ (Fig. 17)	1. aramayvite	$\text{Ag}(\text{Sb}, \text{Bi})\text{S}_2$	6:5:1	
16. $\text{PbS}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$ (Fig. 18)	1. baumhauerite 2. guettardite 3. berntite 4. veenite 5. stearryite 6. sorbyite 7. madocite 8. boulangerite 9. playfairite 10. geocronite	$\text{Pb}_4(\text{As}, \text{Sb})_6\text{S}_{13}$ $\text{Pb}_2(\text{Sb}, \text{As})_{10}\text{S}_{21}$ $\text{Pb}(\text{Sb}, \text{As})_2\text{S}_4$ $\text{Pb}_2(\text{Sb}, \text{As})_2\text{S}_2$ $\text{Pb}_{12}(\text{Sb}, \text{As})_{10}\text{S}_{27}$ $\text{Pb}_{17}(\text{Sb}, \text{As})_{22}\text{S}_{50}$ $\text{Pb}_{17}(\text{Sb}, \text{As})_{16}\text{S}_{41}$ $\text{Pb}_5(\text{Sb}, \text{As})_4\text{S}_{11}$ $\text{Pb}_{16}(\text{Sb}, \text{As})_{16}\text{S}_{43}$ $\text{Pb}_5(\text{As}, \text{Sb})_2\text{S}_9$	4:(8) 6:(5) 1:1 2:(1) 12:(5) 17:(11) 17:(8) 5:(2) 16:(9) 5:(1)	
17. $\text{PbS}-\text{As}_2\text{S}_3-\text{Bi}_2\text{S}_3$ (Fig. 19)	A (Walt & Chang 1973) B (Walt & Chang 1973)	$\text{Pb}_{27}(\text{As}, \text{Bi})_{12}\text{S}_{48}$ $\text{Pb}_2(\text{As}, \text{Bi})_2\text{S}_3$	27:(7) 2:(1)	
18. $\text{PbS}-\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$ (Fig. 20)	1. titchfieldite 2. koballite 3. ustaravite	$\text{Pb}_5(\text{Sb}, \text{Bi})_6\text{S}_{17}$ $\text{Pb}_2(\text{Bi}, \text{Sb})_2\text{S}_5$ $\text{Pb}(\text{Bi}, \text{Sb})_6\text{S}_{10}$	5:(4) 2:(1) 1:(3)	



$\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$  and  $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ 

Natural assemblages for these systems are shown in Figures 3 and 4. The substitution of silver for copper in tennantite and tetrahedrite dominates the copper-rich portion of the diagrams, the latter being the variety freibergite. These solubility limits have not yet been investigated by phase equilibrium studies; however, in natural material silver substitutes for copper up to 18 wt. % in tennantite, and from 3.5 to 23.8 wt. % silver in tetrahedrite from Japan (Shimada & Hirowatari 1972), and 18.4–42.5 wt. % silver in tetrahedrite from Mt. Isa, Australia (Riley 1974). Substitution of copper for silver in proustite or pyrrargyrite appears negligible.

The ternary phases in Table 2, #1 & #2, were defined by Frondel (1963) and Harris *et al.* (1965), and substantiated by Hall (1967) in synthesis studies. Frondel presents analyses of ternary phases coexisting with argentite and pyrrargyrite(2), and these have been used as a guide in drawing the tie lines in Figure 4. The three-phase assemblage argentite-polybasite(2)-pyrrargyrite(2), which has been reported several times, probably formed above 197°C, below which stephanite(1) is stable.

The  $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$  system (Fig. 3) has no conflicting assemblages except pearceite(1)-tennantite(1) (Palache *et al.* 1944) with stromeyerite(1)-proustite(1) (Petruck & staff 1971). (Only the former of these is shown in Figure 3).

The  $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$  system (Fig. 4) is topologically similar to its arsenic analogue in the antimony-deficient portion of the diagram. Ramdohr (1969, p. 654) reports miargyrite(3) with polybasite(2) and with stephanite(1), which both conflict with the common tetrahedrite(1)-polybasite(2) assemblages. These conflicting assemblages may indicate differing primary depositional conditions, or may result from the difference between primary and secondary environments. More study is needed on these assemblages. The ores of the East Tintic District, Utah, have an abundance of phases in these systems, as noted by Pape (1971) and Radtke *et al.* (1969). Most assemblages are applicable only to more complex sulphosalt systems.

The distribution of copper and silver between coexisting solid solutions in these systems provides a potential geothermometer. Solid-state diffusion might, however, result in low-temperature re-equilibration, negating such measurements (Barton *et al.* 1963). The quaternary  $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$  system includes the partitioning of copper-silver and arsenic-antimony between coexisting solid solutions, but it does not fall within the limits of this discussion.

 $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3$ 

Stromeyerite(1)-wittichenite(1) and copper-rich pavonite(2)-matildite(1)-bismuthinite, both from Cobalt-Gowganda, Ontario (Petruck & staff 1971), are the only assemblages reported in this system (Fig. 5). Additional tie lines shown in Figure 5 are taken from phase equilibrium studies at 454°C (Chen & Chang 1974), so are only meant to be suggestive. Each of the  $\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3$  phases has extensive solid solutions into the ternary at this temperature.

Phases on the  $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$  join are generally found in copper-rich zones, whereas phases on the  $\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3$  join are found in lead-rich zones. It may be that the lack of internal natural assemblages results from the geochemical separation of copper and lead in hydrothermal conditions.

 $\text{Cu}_2\text{S}-\text{PbS}-\text{As}_2\text{S}_3$ 

Seligmannite is a ternary phase (Fig. 6). The assemblages in the portion of the diagram more arsenic-rich than tennantite(1) and dufrénoyite(3) are restricted to the Lengenbach Quarry, Binnatal, Switzerland. A significant sequence of assemblages has been described by Markham (1959) from South West Africa as: 1. jordanite (2)-tennantite (1)-sphalerite, 2. jordanite (2)-tennantite (1)-galena, 3. jordanite (2)-enargite-galena. The third assemblage was reported as "narrow veinlets of galena, frequently accompanied by enargite, that intersect masses of jordanite, which suggests later replacement of jordanite by galena-enargite". Jordanite was verified by x-ray diffraction, whereas the other identifications were made by ore microscopy. The change from assemblage 2 to 3 reflects an increase in sulphur fugacity if at constant temperature, and the presence of enargite suggests a temperature greater than 320°C (Skinner 1960). Another three-phase assemblage (Ramdohr 1969, p. 748) is galena-tennantite(1)-gratonite(1) crystallized from Pb-As-Sb gels or glasses found at Cerro de Pasco, Peru. The glasses are thought to have formed at temperatures of approximately 100°C. The glasses show a large chemical variability, and a recent microprobe study (Burkart-Baumann *et al.* 1972) of crystalline inclusions gave a composition of  $\text{Pb}_{11}\text{As}_8\text{S}_{31}$  for the lead sulpharsenide phase, somewhat more arsenic-rich than jordanite.

The above discussion establishes one group of tie lines on Figure 6, whereas the following presents less carefully substantiated evidence for a conflicting galena-seligmannite(1) tie line. Referring to jordanite from Balmat, New York,

Ramdohr (1969, p. 745) states that it "partly decomposes into myrmekitic aggregates of seligmannite, galena, a little tennantite, and native arsenic". Copper, however, is not balanced in such a suggested decomposition. Seligmannite has been observed microscopically as a reaction product between galena and tennantite, with the reaction zone being porous (Sztrokay 1945). These apparently conflicting tie lines merit further investigation. Tennantite in these assemblages should be checked for the presence of antimony; alternatively, two primary facies may be present in the system.

Finally, Uytenbogaardt (1951) and Schouten (1962) report gratonite found with chalcocite, which conflicts with the common assemblage galena-tennantite. This reported association is apparently taken from Rust (1940) who considers the chalcocite to be supergene. This assemblage has not been indicated in Figure 6.

#### $Cu_2S-PbS-Sb_2S_3$

This system contains a number of conflicting assemblages (Fig. 7); however, tie lines to tetrahedrite(1) must be viewed with caution due to its solid solution with tennantite. Although lead has been reported in tetrahedrite in substantial amounts (10 wt. %, Palache *et al.* 1944), recent electron microprobe investigations have not found measurable quantities (Shimada & Hirowatari 1972; Riley 1974).

Bournonite(1) has been reported with most other phases in the system. Its coexistence with chalcocite is prevented by the common galena-tetrahedrite(1) assemblage. The phases appearing on the galena-stibnite join between semseyite(2) and zinkenite(8), although possibly compatible with bournonite, have been found only with jamesonite, which lies just off this plane toward FeS. The three-phase assemblage galena-tetrahedrite(1)-bournonite(1) is very common (standard references; Harada 1973) both in equigranular textures and as galena replacing tetrahedrite with a reaction rim of bournonite (Anderson 1940; Ramdohr 1969). This is in conflict with the repeatedly reported tetrahedrite(1)-meneghinite(2) (standard references) and tetrahedrite(1)-bournonite(1)-meneghinite(2) of Warren (1946). On the more antimony-rich portion of the diagram, boulangerite(1)-tetrahedrite(1) (standard references; Warren & Thompson 1944) conflicts with other assemblages of bournonite. These conflicts are explained if either there is a temperature range over which bournonite is unstable, or, more probably, if the tetrahedrite in certain of these

assemblages is arsenic-bearing.\* Petersen (1962) resolves these conflicts by suggesting the two different facies shown in Figure 21 which might represent the ends of a spectrum of *P-T* changes.

Paragenetic sequences frequently take a path from tetrahedrite to tetrahedrite-bournonite, or tetrahedrite-bournonite-galena to boulangerite-galena, making a series of steps across the diagram. This sequence, with minor mineralogical variations, reflects the differentiation of copper and lead.

A different paragenetic sequence has been documented from stibnite veins at Dubrava, Czechoslovakia (Jakes 1963, mainly microscopic observations). The assemblages are stibnite, to zinkenite(8)-bournonite(1), followed by tetrahedrite(1)-chalcostibite(2).

#### $Cu_2S-PbS-Bi_2S_3$

The profusion of ternary phases is listed in Table 2, #6, and Figure 8. Five phases plot on a line colinear with bismuthinite and aikinite (6), with their unit cells being a continuous sequence of ordered superstructures based on aikinite (Padera 1955; Welin 1966; Moore 1967). These intermediate phases, except rezbanyite(2), have been found only at Gladhammar, Sweden, and have been subjected to electron microprobe verification (Welin 1966). Little is known of their paragenesis, but they might be used as indicators of bismuth fugacity changes and/or temperature.

Aikinite is reported with a number of phases in the system. Emplectite(2) is found with cosalite(2) and galenobismutite(3) (Uytenbogaardt 1951), which would conflict with the phases on the bismuthinite-aikinite join. Primary facies changes are suggested for this system, in agreement with its antimony analogue. Berryite (Nuffield & Harris 1966) and larosite (Petruk 1972) are phases which lie off of this composition plane, with silver substituting for copper. Finally, it is noted that the Cu-Pb-Bi sulphosalt reported by Honnorez-Guerstein (1971) is too sulphur-rich to plot in this system.

#### $Ag_2S-PbS-As_2S_3$

No solid solutions and comparatively few assemblages are observed (Fig. 9). Marrite (1) (Table 2, #7) is the only ternary phase, and is

\*J. Wu & R. Birnie have found arsenic-bearing bournonite, which could also explain these conflicts, personal communication, 1974.



reported only from the Lengenbach Quarry, Binnatal, Switzerland. The only assemblage is that of proustite(1) - jordanite(2) (Uytenbogaardt 1951), each of which could contain antimony. Several of the phases on the arsenic-rich side of the tie line are found only at Binnatal; several additional phases closely related to this composition plane and found almost exclusively at Binnatal are lengenbachite, which has copper substituting for silver, hatchite with thallium substituting for lead, and hutchinsonite which has both substitutions taking place.

#### *Ag<sub>2</sub>S-PbS-Sb<sub>2</sub>S<sub>3</sub>*

The profusion of ternary phases in this system (Table 2, #8; Fig. 10) can be better-visualized by considering several colinearities. The galena-miargyrite(3) join appears as a complete solid solution in phase equilibrium studies at 500°C (Hoda & Chang 1972), but is more limited at lower temperatures. Phases reported here are freieslebenite(1), diaphorite(2), and synthetic  $\text{Ag}_3\text{PbSb}_3\text{S}_7$  (Hoda & Chang 1972). Another colinearity is a ray from galena to  $\text{AgSb}_3\text{S}_4$ , with andorite, ramdohrite, and owyheeite. Fizelyite, however, might be considered to plot on a colinearity between  $\text{Pb}_3\text{Sb}_2\text{S}_6$  ('falkmanite') and  $\text{Ag-PbSb}_2\text{S}_6$  (andorite), as suggested by Karup-Møller (1970). Crystallographic, electron microprobe, and phase equilibrium studies would help decipher which substitutional mechanisms are operational.

The compilation of reported assemblages in this system is complicated (Fig. 10). The association of phases on both the galena-miargyrite(3) and galena-andorite(6) joins with 'pyrargyrite' provides many crossing tie lines. As pyrargyrite(2) has a solid solution of arsenic substituting for antimony, it is possible that the phases on the galena-andorite(6) join coexist with a pyrargyrite more arsenic-rich than those on the galena-miargyrite(3) join. Alternatively, the phases on the galena-miargyrite(3) colinearity become unstable below 300°C (the lowest temperature of investigation of Hoda & Chang 1972), permitting the association of phases on the galena-andorite(6) join with pyrargyrite(2). A number of additional conflicting tie lines which are reported include argentite-freieslebenite(1) versus the more common galena-pyrargyrite(2), galena-fizelyite(7) versus boulangerite(1)-owyheeite(4), and stephanite(1)-andorite(6) (Williams 1968) versus several tie lines. Furthermore, the galena-miargyrite(3) coexistence (Ramdohr 1969, p. 653) can be explained only if all of the intervening phases are unstable over a certain *P-T* interval.

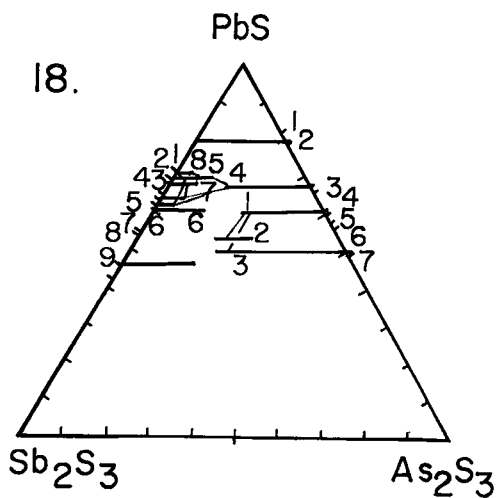
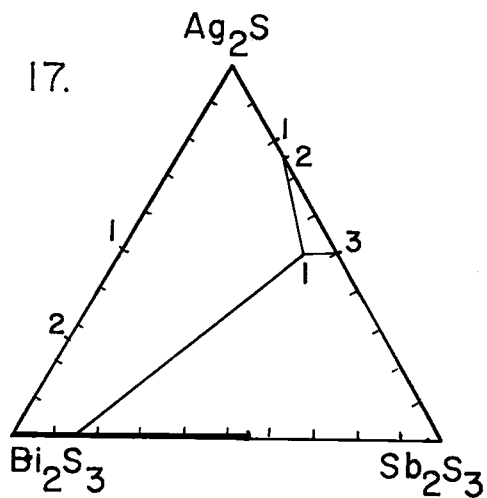
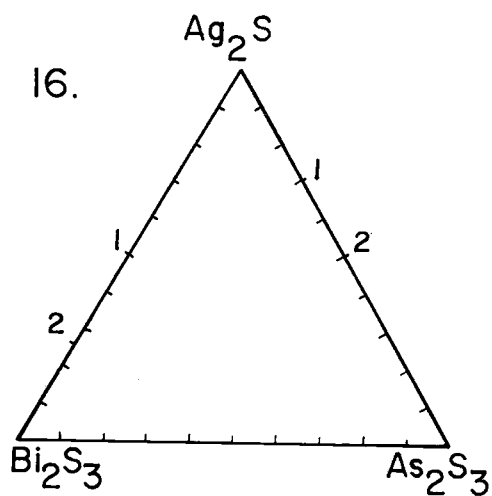
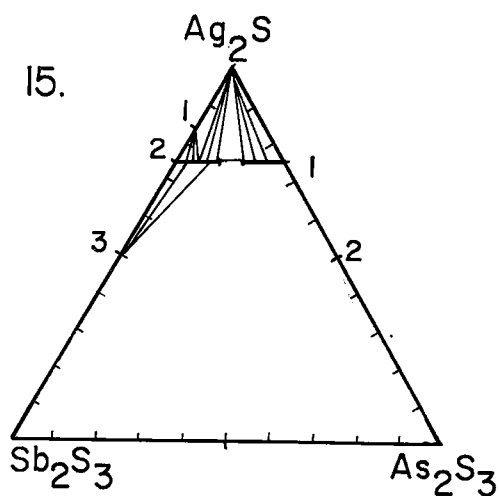
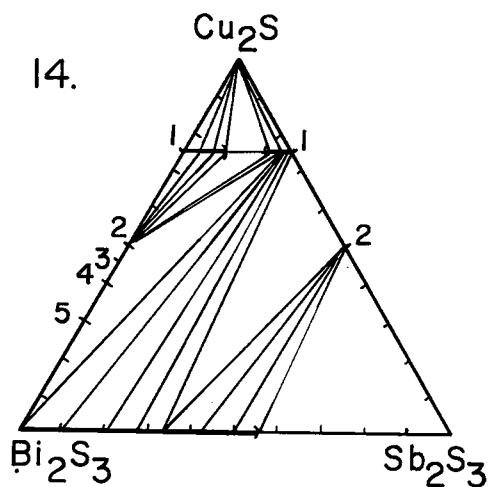
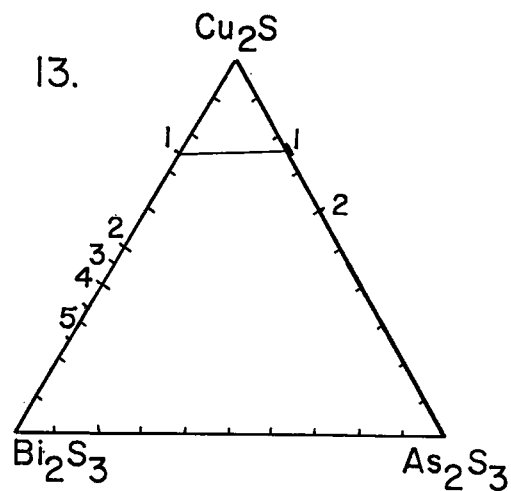
Three-phase assemblages reported are pyrargyrite(2)-miargyrite(3)-owyheeite(4) (Ramdohr 1969, p. 736), galena-stephanite(1)-pyrargyrite(2) (Oelsner 1961, Fig. 58), galena-argentite-freieslebenite(1), galena-pyrargyrite(2)-diaphorite(2), and stephanite(1)-pyrargyrite(2)-andorite(6) (last three from Palache *et al.* 1944). This last assemblage was again recognized by Williams (1968) in another study of the same area, Morey, Nevada. Williams describes a complex series of paragenetic changes starting with jamesonite and followed by owyheeite(4) or andorite(6). Andorite is then replaced by stephanite(1) and pyrargyrite(2) or by freieslebenite(1) and owyheeite(4), and this in turn is replaced by galena or pyrargyrite(2). No mention is made of identification techniques or replacement criteria, and the position of stephanite on the composition diagram is misplaced.

Phases and assemblages in this system are complicated and warrant further detailed study. The profusion of phases provides for the measurement of subtle changes in the relative fugacities of the components when sequences of assemblages are documented.

#### *Ag<sub>2</sub>S-PbS-Bi<sub>2</sub>S<sub>3</sub>*

Six ternary phases are reported (Table 2, #9; Fig. 11 & 23). None was found in synthesis studies down to 400°C (Craig 1967), with the implication that they appear at lower temperatures. Craig inferred from his work and from natural assemblages the lower temperature compatibilities given in Figure 11, to which the three-phase assemblage galena-cosalite-heyrovskyite (Klominsky *et al.* 1971), and the two-phase assemblages galena-schirmerite and gustavite-pavonite, have been added. A sequence of natural assemblages (Fig. 22) with some of these ternary phases has been described by Nedachi *et al.* (1973), who used an electron microprobe. Fluid inclusion filling temperatures in associated quartz have ranges between 87-142°C and 200-245°C; a maximum partial pressure of sulphur is approximately  $10^{-14}$ - $10^{-15}$  as inferred by extrapolation of higher-temperature data to 225°C, given the presence of pyrrhotite and native bismuth. Such detailed studies of sulphosalt assemblages are needed for further understanding of sulphosalt systems. The bismuthinite-pavonite(2)-gustavite(1) (Karup-Møller 1970) and galena-matildite(1)-schirmerite(2) (Karup-Møller 1973) assemblages are not incompatible with these low-temperature assemblages of Nedachi *et al.* (1973).

Numerous phases exist in the quaternary system which includes  $\text{Cu}_2\text{S}$ , but they are beyond the scope of the present study.



### $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$

The projection of the tennantite-tetrahedrite solid solution falls on this compositional plane (Fig. 12). Complete exchange of antimony for arsenic takes place above  $400^\circ\text{C}$ , but there is some suggestion that one or more solvi are present at lower temperatures (Wu, J., personal communication 1972). Tennantite-tetrahedrite compositions also have a significant variation off this plane towards sulphur, being limited by the compositions which coexist with the enargite-famatinite solid solution. Synthesis studies on these coexisting solid solutions have resulted in a geothermometer which has been applied to natural assemblages (Feiss 1974). Temperature and sulphur fugacity measurements are also potentially available from tennantite-tetrahedrite coexisting with both chalcocite and stibnite. Detailed analysis of mineral assemblages in the  $\text{Cu}-\text{As}-\text{Sb}-\text{S}$  system (Petersen 1962) indicates that this three-phase assemblage is a relatively sulphur-deficient one. It has yet to be adequately documented in natural material. Antimony-rich tetrahedrite is reported (Petruk 1971) coexisting with cobalt arsenides in an environment deficient in sulphur.

### $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3-\text{Bi}_2\text{S}_3$

No ternary phases are reported (Table 2, #11; Fig. 13) although a maximum of 15.9 wt. % bismuth in tennantite has been reported (Springer 1969). The only assemblage is a bismuthian tennantite-wittichenite tie line (Oen *et al.* 1973). This lack of assemblages might reflect a geochemical separation of arsenic and bismuth in iron-deficient environments, the latter qualification added because of the more common bismuthinite-arsenopyrite assemblage.

### $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$

Phase equilibrium studies in this system (Chen & Chang 1971) suggest a compositional variation of wittichenite on the  $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$  binary from 22 to 27 mole %. Substitution of 60 at. % Sb for Bi in wittichenite, but with very little converse substitution taking place, was found at  $450^\circ\text{C}$ . Similar semi-metal substitutions provide solid solutions into the ternary in chalcocite and 'eichbergite'.

Naturally occurring tetrahedrite has been found to contain 3.1 wt. % bismuth (Petruk 1971). A large number of coexisting phases has been reported (Fig. 14) with no conflicting tie lines. The solid solutions and tie line distributions are only topologically correct as no data on coexisting compositions are reported. Five

potential geothermometers exist from the compositional variations within the five three-phase assemblages.

Phase equilibrium studies of the solid solution of chalcocite into this ternary are not in agreement with the extreme rarity of this phase, and the relatively more abundant tetrahedrite-bismuthinite.

### $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$

This ternary system is dominated by the proustite-pyrargyrite solid solution which is complete down to at least  $300^\circ\text{C}$  (Toulmin 1963). Coexisting proustite and pyrargyrite have been reported several times, but information on coexisting compositions is lacking. Ramdohr (1969, p. 722) states that a miscibility gap exists between 13-97% proustite at room temperature. Reaction rates (Barton *et al.* 1963) suggest that high-temperature assemblages including proustite-pyrargyrite may redistribute arsenic and antimony in the solid state at lower temperatures. The tie lines shown in Figure 15 are schematic, and the composition of only one assemblage, argentite-pyrargyrite (Fronde1 1963), is reported. Pearceite and As-polybasite lie just off this plane towards chalcocite, and billingsleyite lies towards sulphur. These expanded systems contain assemblages of potential geochemical interest.

The assemblage proustite-stephanite (Petruk 1971) conflicts with the more common argentite-pyrargyrite.

### $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3-\text{Bi}_2\text{S}_3$

No ternary phases and no reported compatibilities are present in this system (Fig. 16).

### $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$

One ternary phase, aramayoite, has been reported, and is found with bismuthinite, with pyrargyrite(2), and coexisting with both miargyrite(3) and pyrargyrite(2) (Lewis 1964). Synthesis studies (Chen & Chang 1971) indicate a complete solid solution between matildite(1) and miargyrite(3) at  $450^\circ\text{C}$ . At  $300^\circ\text{C}$ , 56 mole % miargyrite is still soluble in matildite. Aramayoite may be an ordered phase cooled from this solid solution, and its compositional variations may prove to have geothermometric interest.

### $\text{PbS}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$

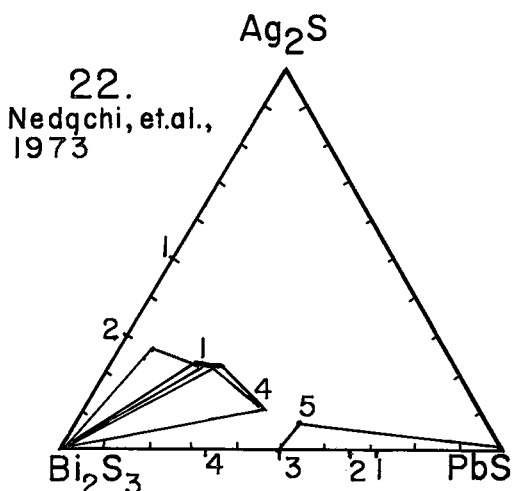
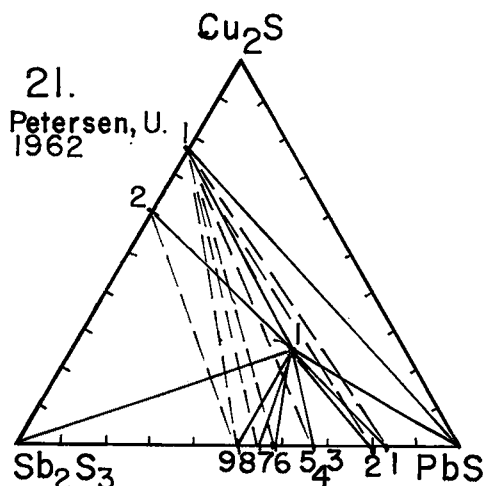
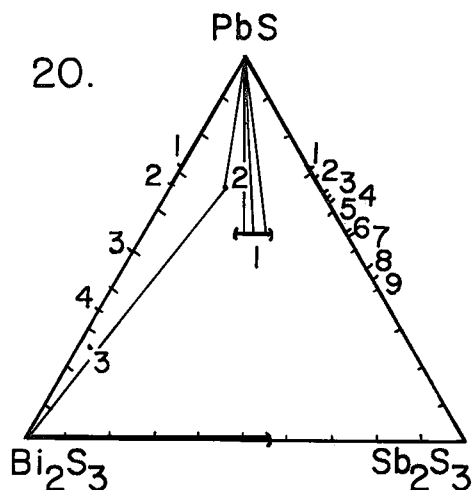
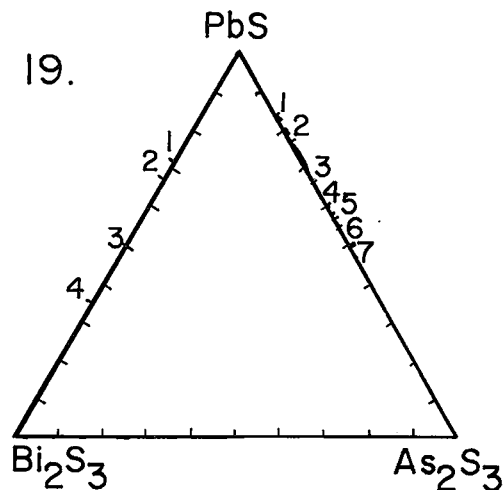
In spite of the fact that both of the lead-bearing binaries of this system are characterized by a profusion of phases, in all but a very few

cases have any coexisting phases in this system been reported. The geological environment in which the most common of these phases are generally found is in affiliation with hydrothermal ore deposits. The several compatibilities from this environment are the jordanite-geocronite solid solution associated with galena and semseyite, and with meneghinite which lies just off this plane towards  $\text{Cu}_2\text{S}$ .

In this system are a large number of phases which have been found only in a second, rare environment. Many of the lead sulpharsenides have been found only in the Lengenbach Quarry, Binnatal, Switzerland, whereas a majority of phases present in the ternary system under discussion have been found only at Madoc, Ontario (Jam-

bor 1967a, b, 1968). The suggested solid solutions, observed phases, and their associations are seen in Figure 18, based largely on Jambor's work. He reports a paragenetic sequence exhibiting decreasing As/Sb values, and points out one possible origin of such a complex mineralogy as the reworking of an original galena, arsenopyrite, sphalerite assemblage by antimony-rich solutions. This conclusion is similar to that of Graeser (1968) with respect to the origin of the complex mineralogy found in the Binnatal.

Phase equilibrium studies in the system at  $400^\circ\text{C}$  (Walia & Chang 1973) verify the existence of a number of solid solutions. Fifty-eight at. % antimony can substitute for arsenic in jordanite as the geocronite solid solution, 45 at. %



in dufrénosite towards the Sb end-member veinite, and 30 at. % antimony in zinkenite can be substituted by arsenic. Madocite has compositional ranges in both the As/Sb and Pb/(As+Sb) dimensions. The remaining phases of Jambor, except guettardite, were not found in the phase equilibrium studies down to 400°C.

Coexisting solid solutions in this system have potential for geothermometric or semi-metal fugacity measurements, but their extreme rarity limits their development and applicability.

#### *PbS-As<sub>2</sub>S<sub>3</sub>-Bi<sub>2</sub>S<sub>3</sub>*

No naturally occurring phases have been reported in this system, although Walia & Chang (1973) found two such phases (Table 2, #17) at 400°C. No assemblages have been reported.

#### *PbS-Sb<sub>2</sub>S<sub>3</sub>-Bi<sub>2</sub>S<sub>3</sub>*

Several ternary phases are reported (Table 2, #18; Fig. 20), and antimony substitutes for bismuth to a small extent in lillianite. Assemblages are kobellite(2) with galena, and with bismuthinite, and tintinaite(1) with galena. Solid solutions within the ternary are predicted on the basis of the diadochy of antimony and bismuth, and the partitioning of these elements between such solid solutions is of potential interest. This system is of the type which will prove more complicated and interesting when it receives more detailed study.

## DISCUSSION

The above study of natural sulphosalt assemblages has resulted in the derivation of 18 ternary sulphosalt composition diagrams. In general only those phases and assemblages which lie strictly on the ternaries have been considered. Exceptions are tennantite and tetrahedrite which have been projected onto the  $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3$  and  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  joins, and digenite which is projected to  $\text{Cu}_2\text{S}$ . This limitation prevents the inclusion of certain phases, notably jamesonite, which contains essential iron. In other cases the essential nature of a minor element is not known; in these instances a mineral may be mentioned in the text or tables, but is left off the related diagram. Examples of these are nøyite and berryite, which have small amounts of silver and consequently plot off the  $\text{Cu}_2\text{S}-\text{PbS}-\text{Bi}_2\text{S}_3$  plane.

Reported phases are plotted as being of end-member composition, in general, as only a few studies have reported assemblages with actual coexisting compositions. Tie lines to solid solu-

tions are extended along them in topological agreement with reported assemblages. Conflicting tie lines in these ternary systems might be explained by substitutions into quaternary or higher systems. An example of this is pyrrargyrite in the  $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$  and  $\text{Ag}_2\text{S}-\text{PbS}-\text{Sb}_2\text{S}_3$  systems, where arsenic substituting for antimony may resolve conflicting tie lines. Other such substitutions are Cu-Ag, 2Pb-AgSb, 2Pb-AgBi, As-Sb, Sb-Bi, and Pb-Bi (limited), although others occur also. Certain quaternary systems of particular interest resulting from such substitutions are  $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{PbS}-\text{Bi}_2\text{S}_3$ ,  $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$ ,  $\text{Cu}_2\text{S}-\text{PbS}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$ , and  $\text{Cu}_2\text{S}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$ .

With the above ideas in mind, and considering the composition diagrams as strictly ternaries, there are certain bivalent assemblages (in terms of pressure and temperature) in which solid solutions may vary enough to make them of potential geochemical interest. They can be identified on the figures as three-phase fields joined to one or more solid solutions, and they are listed in Table 3. The fact that many of these lie in the  $\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$  system makes it of particular interest, but as Barton *et al.* (1963) point out, postdepositional solid-state exchange may occur, modifying primary compositions. Ideally, calibration of compositional variations with physico-chemical parameters can be used to restrict degrees of freedom of natural assemblages (Barton & Skinner 1967). Such studies will be particularly useful when other variables can be fixed by an independent means. Certain other

TABLE 3

Listed below are bivalent assemblages (in terms of *P* and *T*) in which solid solutions may vary enough as to make them of potential geochemical interest. Study of certain two-phase assemblages among these might also be used to limit one or two degrees of freedom. These assemblages are arrived at from the topology of Figures 3 through 20.

System	Assemblages
$\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$	chalcocite-stromeyerite-tennantite stromeyerite-pearceite-tennantite pearceite-tennantite-proustite pearceite-proustite-arsenopybasite pearceite-arsenopybasite-argentite proustite-arsenopybasite-argentite
$\text{Cu}_2\text{S}-\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$	chalcocite-stromeyerite-tetrahedrite stromeyerite-tetrahedrite-antimonpearceite antimonpearceite-polybasite-argentite polybasite-argentite-sphalerite polybasite-sphalerite-pyrrargyrite polybasite-antimonpearceite-pyrrargyrite antimonpearceite-pyrrargyrite-miargyrite antimonpearceite-tetrahedrite-miargyrite pyrrargyrite-miargyrite-tetrahedrite miargyrite-tetrahedrite-stibnite tetrahedrite-stibnite-chalcocite
$\text{Cu}_2\text{S}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$	tennantite/tetrahedrite-stibnite-chalcocite
$\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$	chalcocite-tetrahedrite-wittichenite tetrahedrite-wittichenite-omphacite tetrahedrite-bismuthinite-chalcocite bismuthinite-chalcocite-stibnite
$\text{Ag}_2\text{S}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$	argentite-sphalerite-pyrrargyrite argentite-pyrrargyrite-proustite
$\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$ $\text{PbS}-\text{As}_2\text{S}_3-\text{Sb}_2\text{S}_3$ $\text{PbS}-\text{Sb}_2\text{S}_3-\text{Bi}_2\text{S}_3$	There are numerous potential bivalent assemblages in these systems. Natural assemblages, however, do not define the topology of the diagrams enough for them to be identified.

systems ( $\text{Cu}_2\text{S}$  and  $\text{PbS}$  with  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$  and  $\text{Bi}_2\text{S}_3$ ; and  $\text{Ag}_2\text{S}$  and  $\text{PbS}$  with  $\text{Sb}_2\text{S}_3$  and  $\text{Bi}_2\text{S}_3$ ); commonly possessing a number of ternary phases, indicate facies changes by tie line switches.

Phase equilibrium studies can theoretically determine the pressure and temperature ranges of sulphosalt facies, and such ranges can also be calculated from thermodynamic parameters (Craig & Barton 1973). The study of sulphosalt stability relations in temperature/sulphur-fugacity space has been initiated (Craig & Barton 1973; Craig *et al.* 1973), and can prove fruitful in defining conditions of formation. The present study of natural assemblages advances this work. Finally, documentation of sequences of primary assemblages in a deposit can serve as an indicator of the direction of fugacity changes during deposition.

It is emphasized that whereas many of the phases mentioned in this study are quite rare, taken as a group these sulphosalts are more significant. A common geologic setting of these species is within, or marginal to, base metal deposits, some of great value. Sulphosalt petrology can conceivably be used as a guide to exploration for and development of such deposits; consequently, an understanding of the environments of formation of these minerals is of interest. It is hoped that the present work will stimulate interest in and further study of natural assemblages of sulphosalts.

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