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INVESTIGATIONS IN THE Pb-Sb-S SYSTEM

JAMES R. CRAIG *, LUKE L. Y. CHANG ** AND WILLIAM R. LEES ***

ABSTRACT

The Pb-Sb-S system, with emphasis on the PbS-Sb_2S_3 join, has been examined by means of evacuated silica tube and differential thermal analysis techniques between 300 and 700°C. Five phases have been synthesized: Phase I (3PbS:Sb_2S_3) stable between 642 and 605°C; boulangerite (5PbS:$2Sb_2S_3$) stable below 638°C; Phase II (3PbS:Sb_2S_3) stable between 603 and 450°C; robinsonite (6PbS:$5Sb_2S_3$) stable between 582° and 318°C; zinckenite (PbS:Sb_2S_3) stable below 545°C. Each phase melts incongruently to the next more PbS-rich phase and a Sb_2S_3-enriched liquid. Eutectic relations exist between zinckenite and stibnite at 523 ± 3°C. Ternary eutectic relations exist among stibnite, zinckenite, antimony at 480°C and among galena, lead, antimony at 240°C. A ternary monotectic exists among stibnite, zinckenite and S-liquid at 474°C.

Limited S_2 activity data permit speculation about the thermochemical properties of the lead sulphantimonides.

INTRODUCTION

The lead-antimony-sulphur system contains the chemical compositions of a large number of mineral species. The lead sulphantimonides rarely constitute significant ore masses except in Bolivia but are widespread and commonly occur as accessory minerals in hydrothermal ore deposits. At least 15 distinct natural and synthetic lead sulphantimonides have been reported in the literature (Table 1). Some of the minerals have been discredited and others are of dubious validity; as a result the phase relations in the Pb-Sb-S system have remained unclear. The present study has been directed toward an understanding of these relations.

TECHNIQUES AND REACTANTS

Experiments were performed by means of conventional evacuated silica tube and differential thermal analysis techniques using elements of 99.999+% purity as specified by suppliers' analyses. Synthesis and annealing experiments were conducted in nichrome wound resistance furnaces controlled ±3°C. Experimental products were analyzed by means of *x*-ray diffraction, reflected light microscopic and electron microprobe techniques.

PREVIOUS INVESTIGATIONS

Pb-Sb-S system. The PbS-Sb_2S_3 join has been the subject of several previous investigations. Jaeger von Klooster (1912) and Iitsuka (1919) performed fusions of PbS and Sb_2S_3 in open systems. Schenck *et al.* (1939) measured H_2S/H_2 gas mixtures which had equilibrated with univariant Pb-Sb-S assemblages. Robinson (1948) reported syntheses by direct fusion of PbS and Sb_2S_3 in evacuated vitreosil tubes and by reaction of PbS and Sb_2S_3 in hydrothermal solutions of Na_2S, K_2S, CaS and HCl in graphite-lined iron crucibles. Kitakase (1968), Jambor (1968), Garvin (1973), Drafall & Koucky (1969) and Salanchi & Moh (1970) compiled their data

TABLE 1. PHASES REPORTED WITHIN THE Pb-Sb-S SYSTEM

Phases	Composition $PbS:Sb_2S_3$ ratio	Reference
Natural phases and synthetic phases with natural equivalent		
galena	1:0	(1)(2)(3)(4)(5)(6)(7)(8)(9)
boulangerite	5:2	(2)(3)(4)(5)(6)(7)(8)(9)
semseyite	9:4	(3)
dadsonite	11:6	(3)(11)
launayite	22:13	(7)
jamesonite[a]	2:1	(1)(6)(9)
heteromorphite	5:3	(4)
plagionite	5:4	(3)(4)(6)
tintinaite	5:4	(10)
robinsonite	7:6	(3)(5)(6)(8)(9)
zinckenite	1:1	(2)(3)(4)(5)(6)(8)(9)
fuloppite	3:4	(3)
stibnite	0:1	(1)(2)(3)(4)(5)(6)(7)(9)
Synthetic phases without known natural equivalent		
phase I	6:1	(3)
phase I	10:3	(5)
phase H, phase II	3:1	(5)(9)
phase K-1	12:5	(7)
phase F	2:1	(5)
phase E	5:3	(5)
phase D	8:5	(5)
phase IV	3:2	(1)
phase II	5:4	(3)

a: subsequently shown to contain addition necessary elements

(1)Jaeger & Van Klooster (1912); (2)Iitsuka (1919); (3)Robinson (1948); (4)Schenck *et al.* (1939); (5)Kitakaze (1968); (6)Drafall & Koucky (1969); (7)Jambor (1967); (8)Garvin (1973); (9)Salanchi & Moh (1970); (10)Harris *et al.* (1968); (11)Jambor (1969).

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* Dept. of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061.

** Dept. of Geology, Miami University, Oxford, Ohio 45056.

*** Dept. of Geosciences, Texas Tech University, Lubbock, Texas 79409.

from evacuated silica tube and differential thermal analysis techniques. Figure 1 summarizes some of the previously published phase relations in the system Sb_2S_3-PbS.

The wide variation in results in liquidus and subsolidus relations among the various workers clearly indicates the problems of, first, obtaining equilibrium in the Pb-Sb-S system, and secondly, of identifying the phases created. Barton's (1970) comment "it is evident that a given sulphosalt is not a great deal more stable than any of several alternative configurations representing the same bulk composition" and Craig & Lees' (1972) calculations of the very small differences in stabilizing free energies of the various lead-sulphantimonides, are clearly points to be considered in studies of the Pb-Sb-S system. We have tried to conduct the present study with the appropriate caution.

Pb-S system. The Pb-S system, the subject of several studies, has been most recently examined by Kullerud (1969). The system contains a single intermediate phase, PbS, analogous to galena, which melts congruently at 1115°C. Liquid immiscibility gaps exist in the metal-rich portion of the system (93.0 – 95.2 wt % Pb) above 1041°C and in the sulphur-rich portion of the system (72.8 – 6.8 wt % Pb) above 800°C.

Sb-S system. The Sb-S system has been summarized by Hansen & Anderko (1958), Shunk (1969) and Barton (1971). The system contains a single phase, Sb_2S_3, analogous to stibnite, which melts congruently at 555 ± 5°C. Liquid immiscibility fields exist in the sulphur-rich (31 – 98 wt % S) and sulphur-deficient (1.5 – 22.5 wt % S) portions of the system above 496°C and 615°C respectively.

Pb-Sb system. Phase relations in the Pb-Sb system have been summarized by Hansen & Anderko (1958) and Elliott (1965). A eutectic occurs at 11.1 wt (17.5 atomic) per cent Sb at 251°C. The maximum solubility of Sb in Pb is 3.5 wt (5.8 atomic) percent and of Pb in Sb is about 5 atomic per cent.

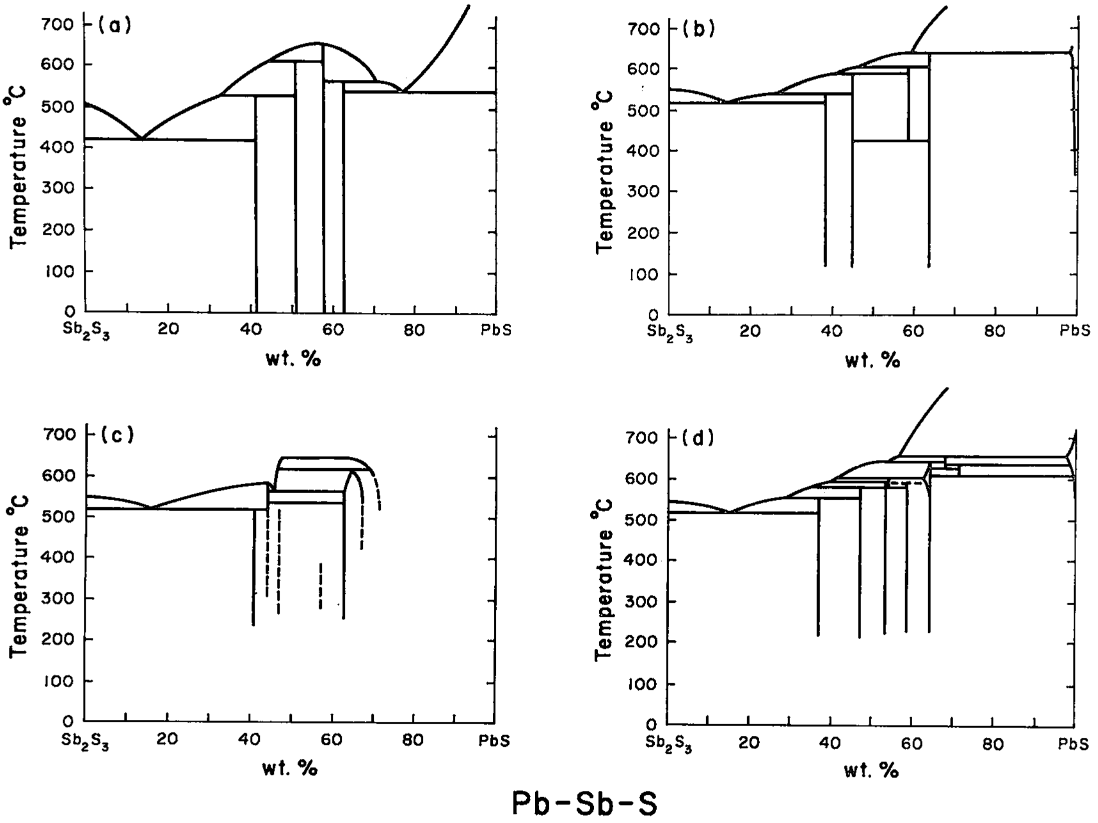

FIG. 1. The system Sb_2S_3-PbS as presented by: (a) Iitsuka (1919), phases are: $PbSb_2S_4$, $Pb_3Sb_4S_9$, $Pb_2Sb_2S_5$, $Pb_5Sb_4S_{11}$. (b) Garvin (1973), phases are: $Pb_6Sb_{14}S_{27}$, $Pb_7Sb_{12}S_{25}$, $Pb_5Sb_4S_{11}$. $Pb_2Sb_2S_5$, (c) Drafall & Koucky (1969), phases are: $PbSb_2S_4$, $Pb_7Sb_{12}S_{25}$, $Pb_5Sb_8S_{17}$, $Pb_2Sb_2S_5$, $Pb_5Sb_4S_{11}$. (d) Kitakaze (1968) phases are: $Pb_4Sb_{22}S_{37}$, $Pb_9Sb_{14}S_{30}$, $Pb_8Sb_{10}S_{23}$, $Pb_5Sb_6S_{11}$, $Pb_2Sb_2S_5$, $Pb_5Sb_4S_{11}$, $Pb_3Sb_2S_6$, $Pb_{10}Sb_6S_{19}$.

EXPERIMENTAL RESULTS AND DISCUSSION

All reported phases within the Pb-Sb-S system lie along the PbS-Sb_2S_3 join. The present study has revealed the presence of five compounds along this join above 400°C; three of these correspond to known minerals (boulangerite, robinsonite, zinckenite). The relationships established are illustrated in Figure 2. All phases are present on the liquidus where each phase melts incongruently to the next more PbS-rich phase and an Sb_2S_3-enriched liquid. The known invariant points of the Pb-Sb-S system are tabulated in Table 2.

The two phases which do not correspond to minerals have stability fields restricted to temperatures near the liquidus. They are designated as Phases I and II. Phase I exists between 610 ± 10°C and 642 ±2°C and Phase II exists between 450 ± 25°C and 603 ± 3°C. The x-ray powder diffraction data for phase I is given in Table 3.

Phase I composition is indicated by microprobe analysis to be 75 mole % PbS corresponding to $3PbS . Sb_2S_3$. Megascopically and microscopically, it closely resembles the other lead sulphantimonides. It is a brilliant metallic grey, grows as acicular or lath-like crystals (Fig. 3), is weakly bireflectant, and has moderate anisotropism.

Galena in equilibrium with Phase I and boulangerite in the temperature range 600-640°C contains 2.9 ± 0.3% Sb_2S_3 in solid solution as indicated by probe analysis, and possess an a of 5.929 ± 0.002Å, somewhat smaller than the a reported for pure PbS (5.936Å; Swanson & Fuyat 1953).

Microprobe analyses indicate that the composition of phase II is 60 mole % PbS which corresponds to $3PbS \cdot 2Sb_2S_3$. Phase II crystallizes in masses of radiating and interpenetrating acicular to lath-like crystals with cross sections up to ~100μm and lengths up to 5 mm. Megascopically, it, like many lead sulphantimonides,

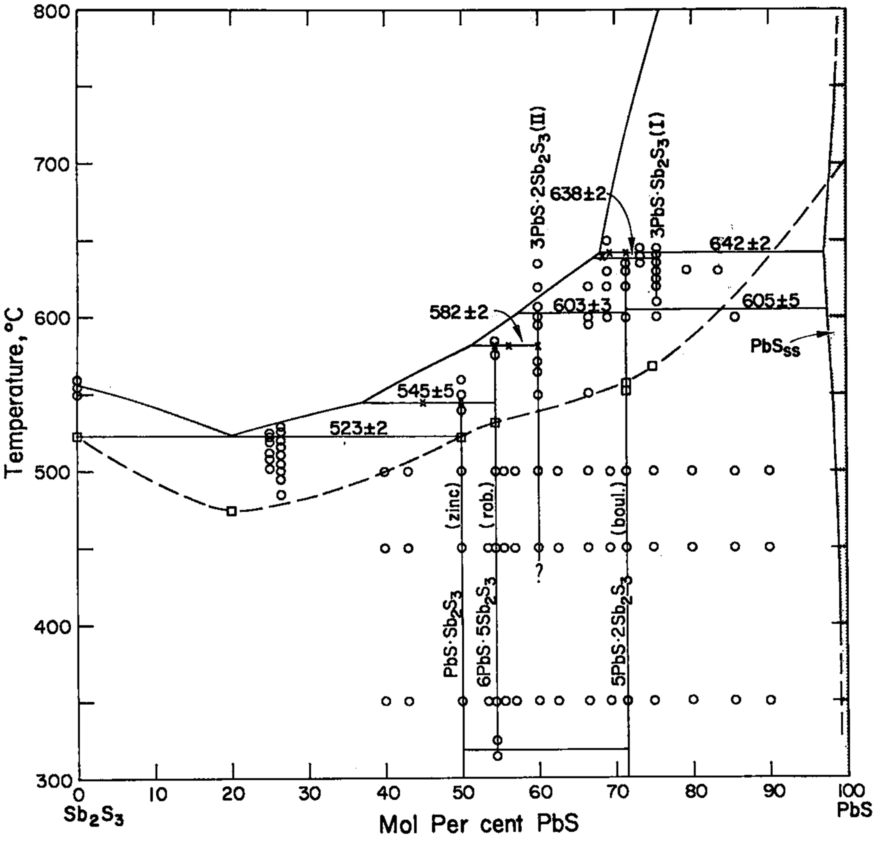

FIG. 2. Phase relations on the PbS-Sb_2S_3 join. Silica tube runs are indicated by open circles and D.T.A. maxima are indicated by X's. Open squares are D.T.A. maxima when there was an excess of sulphur.

closely resembles stibnite; crystals have a brilliant gray metallic luster. In reflected light this phase takes a fine polish, is slightly softer than PbS, is weakly bireflectant, and exhibits moderate anisotropism (tan to blue). Wang (1973) has recently determined the crystal structure of this phase as orthorhombic, $a = 19.80$, $b = 11.40$, $c = 4.04$Å, space group D_{2h}^{16}.

TABLE 2. SELECTED INVARIANT POINTS IN THE Pb-Sb-S SYSTEM (vapor present in all assemblages)

Low temp. assemblage	High temp. assemb.	T°C.	Source of Data
galena+Pb-liq	2-melts	1041	Kullerud (1969)
galena+S-liq	2-melts	800	Kullerud (1969)
phase I	galena+melt	642±2	This study
boulangerite	phase I+melt	638±2	This study
antimony	melt	630.5	Hansen & Anderko (1958)
galena+antimony	melt	622±3	This study
antimony+Sb_2S_3-rich melt	Sb-rich melt	615	Barton (1971)
boulangerite+galena	phase I	605±5	This study
antimony+Sb_2S_3-rich (Pb containing) melt			
phase II	melt+boulangerite	603±3	This study
robinsonite	phase II+melt	582±2	This study
stibnite	melt	556±5	Barton (1971)
zinckenite	robinsonite+melt	545±5	This study
stibnite+zinckenite	melt	523±3	This study
stibnite+antimony	melt	518±5	Barton (1971)
stibnite+S-liq	melt	496±5	Barton (1971)
stibnite+zinckenite+antimony	melt	480±5	This study
stibnite+zinckenite+S-liq	melt	474±3	This study
robinsonite+boulangerite	phase II	~425	This study
lead	melt	327	Hansen & Anderko (1958)
lead+galena	melt	326	Kullerud (1969)
lead+antimony	melt	252	Hansen & Anderko (1958)
lead+antimony+galena	melt	240	This study

Boulangerite, $Pb_5Sb_4S_{11}$, has a maximum stability of 638 ± 2°C, above which it melts incongruently to Phase I and a Sb_2S_3-enriched liquid.

Robinsonite composition, variously reported as $7PbS \cdot 6Sb_2S_3$ and $6PbS \cdot 5Sb_2S_3$, has been found to correspond to the latter value. Its maximum thermal stability in the presence of vapor is 582 ± 2°C above which it melts incongruently to form Phase II and a Sb_2S_3-enriched liquid. Limited experimentation indicates that robinsonite decomposes below 318°C to form zinckenite and boulangerite.

Zinckenite has been synthesized on its reported composition of $PbS \cdot Sb_2S_3$. Its maximum thermal stability in the presence of vapor is 545 ± 5°C. Zinckenite melts incongruently to robinsonite and a Sb_2S_3-enriched liquid.

TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR PHASE I, $3PbS.Sb_2S_3$

d(Å)	I	d(Å)	I
4.62	1	2.82	1
4.23	1	2.77	6
4.08	1/2	2.39	1/2
3.87	1	2.31	1/2
3.80	1	2.13	2
3.74	2	2.09	3
3.69	10	2.06	2
3.41	5	2.05	2
3.33	4	1.88	1/2
3.27	6	1.85	1/2
3.24	2	1.80	2
3.06	7	1.78	4
2.96	5	1.76	1
2.92	3	1.74	1
		1.71	1/2

FIG. 3. Acicular crystals of Phase I grown at 620°C. Crystals are approximately 2 mm long.

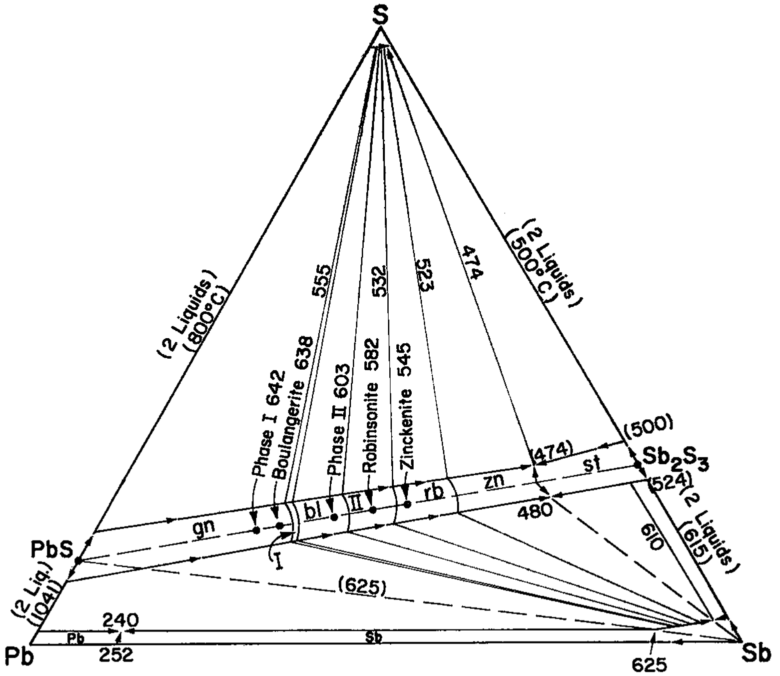

FIG. 4. Polythermal diagram of the Pb-Sb-S system : equilibrium vapor present throughout.

TERNARY RELATIONS

Ternary relations in the Pb-Sb-S system were examined in a limited manner to ascertain the nature of stable assemblages. A polythermal liquidus diagram of the Pb-Sb-S system is shown in Figure 4; this figure is based on the silica tube data and D.T.A. data shown in Figure 2.

At temperatures above 1041°C (Fig. 5) the system is spanned by two two-liquid fields (one metal-rich and one sulphur-rich) and a central sulphide-rich liquid field. The sulphide-rich member of the metal-rich two-liquid field withdraws from the Pb-PbS join into the ternary system below 1041°C. Between 1041°C and 630°C (Fig. 6), the melting point of antimony, the sulphide-liquid of this two-liquid field retreats toward the Sb-S join. Tie lines are established between galena and antimony below 622 ± 3°C. Below 615°C the Sb-Sb_2S_3 end member of the metal-rich liquid field withdraws to the ternary system. The nearly pure antimony-liquid member of the remaining metal-rich two-liquid field decomposes in a ternary monotectic at 610 ± 3°C. Stable tie lines are formed between antimony and the intermediate phases of the PbS-Sb_2S_3 join at temperatures between 622° and 480°C, the ternary eutectic among zinckenite, stibnite, and antimony. A nearly pure metal liquid remains along the Pb-Sb join; it is reduced in size and withdraws from the Pb-Sb join at a eutectic at 252°C. A ternary eutectic involving lead, antimony and galena occurs at a composition of about Pb:Sb:S = 88:11:1 (wt %) at 240 ± 3°C.

In the sulphur-rich portion of the system the two-liquid field which spans the system above 800°C consists of a nearly pure S-liquid and a sulphide-rich liquid. Below this temperature the

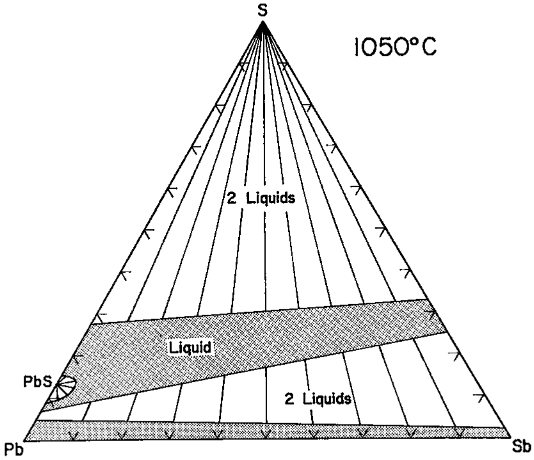

FIG. 5. Isothermal diagram of the Pb-Sb-S system at 1050°C in the presence of an equilibrium vapor.

sulphide-rich liquid withdraws from the Pb-S join into the ternary system. As the sulphide-rich liquid retreats toward the Sb-S join, tie lines are established between S-liquid and boulangerite at 655°C, between S-liquid and robinsonite at 534°C, and between S-liquid and zinckenite at 524°C. Below 496 ± 5°C the two-liquid field withdraws from the Sb-S join into the ternary system (Fig. 7). At 474 ± 3°C the sulphide-rich liquid member of the two-liquid field decomposes to zinckenite-stibnite and S-rich liquid.

PHASES NOT ENCOUNTERED IN THIS STUDY

Previous studies of naturally occurring lead antimonides (*i.e.* Jambor 1969) and of their synthetic analogs have revealed several phases not encountered during the present study (see Table 1 and tables 1 and 2 of Garvin 1973). Some of these phases have been shown to contain other necessary elements (*i.e.*, jamesonite) while others have been discredited as identical with previously described minerals (*i.e.*, yenerite = boulangerite). We have been unable to verify the previously synthesized phases: I and II of Robinson (1948), and I and F of Kitakaze (1968) even though our experiments were in the same temperature range. We have not synthesized analogs to the mineral species: semseyite, heteromorphite, dadsonite, plagionite, launayite, tintinaite and fuloppite; it appears that these minerals become stable at temperatures lower than those of this study.

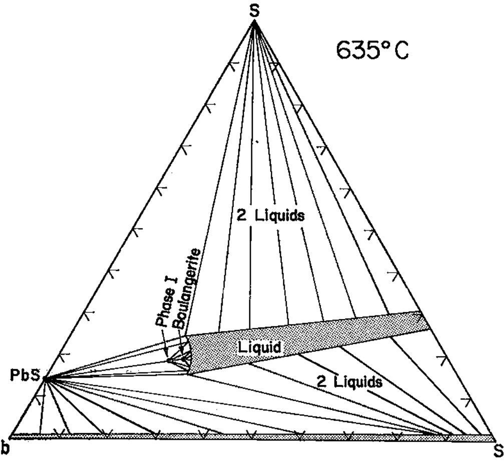

FIG. 6. Isothermal diagram of the Pb-Sb-S system at 635°C in the presence of an equilibrium vapor.

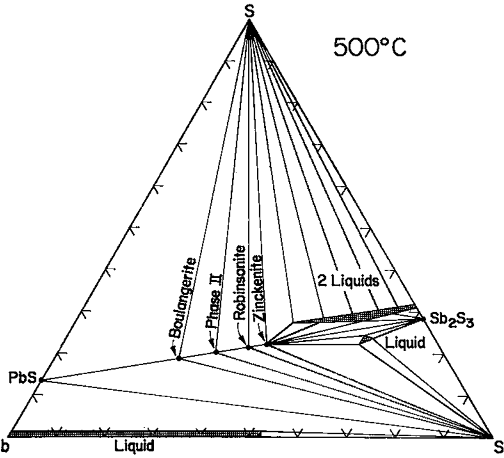

FIG. 7. Isothermal diagram of the Pb-Sb-S system at 500°C in the presence of an equilibrium vapor.

THERMOCHEMICAL CONSIDERATIONS

Although the present study has been primarily concerned with the basic phase relations of the Pb-Sb-S system, sufficient information exists to permit at least first approximations of the thermochemical functions of the lead sulphantimonides. Craig & Lees (1972) used the H_2/H_2S gas ratio data of Schenck *et al.* (1939) to calculate the free energies of formation of the lead sulphantimonides from PbS and SB_2S_3 at 400°C (boulangerite $Pb_5Sb_4S_{11}$, −311 cal/eq, −6842 cal/mol; robinsonite $Pb_6Sb_{10}S_{21}$ − 302 cal/eq, −12683 cal/mol; zinckenite $PbSb_2S_4$, −278 cal/eq, −2224 cal/mol).

We have estimated the entropies of the sulphosalt phases by summing the entropies of the end member sulphides and the appropriate entropy of reaction (*i.e.* assuming ideal reaction with $\triangle H = 0$). If we further assume that the $\triangle S$ and $\triangle H$ are temperature-independent we may formulate first approximation temperature-dependent free energy equations (Table 4a). We have then extrapolated these equations to 25°C (298°K) in order to approximate thermochemical functions. Sulphidation equations for the formation of the lead sulphantimonides (Table 4b) have been calculated in the manner described by Craig & Barton (1973). The sulphidation curves for boulangerite, robinsonite and zinckenite are plotted as curves 1, 2, 3 respectively on Figure 8. The sulphidation curves for lead and antimony and for the iron sulphides are plotted for comparison. When the low temperature stability of additional phases along the PbS-Sb_2S_3 join is demonstrated, there will likely be some slight modification of the values given in Table 4b. In any event, these values should be viewed as first approximations which are subject to correction as sufficient data become available.

The most significant point to be noted from the thermochemical data is that the stabilizing

TABLE 4. THERMOCHEMICAL APPROXIMATIONS AND SULFIDATION REACTIONS FOR THE LEAD SULFANTIMONIDES

4(a) *Thermochemical approximations for the lead sulfantimonides*

Phase	Sulphur as Rhombic S			Sulphur as S_2 Gas		
	ΔH°_{298}	ΔG°_{298}	S_{298}	ΔH°_{298}	ΔG°_{298}	$\Delta G^\circ T$ (per formula unit)
Boulangerite, $Pb_5Sb_4S_{11}$	-183130	-190074	206.4	-353740	-295234	-353740 + 196.3T
Robinsonite, $Pb_6Sb_{10}S_{21}$	-314955	-325074	367.4	-640665	-525834	-640665 + 385.3T
Zinckenite, $PbSb_2S_4$	- 58595	- 60316	68.7	-120635	- 98556	-120635 + 74.1T

4(b) *Sulfidation reactions for the lead sulfantimonides*

Phase	Reaction	G_T=	T,°C range
Phase I, $Pb_3Sb_2S_6$	$PbS+Sb+S_2 = Pb_3Sb_2S_6$	-55430 + 36.5T	610-625
Boulangerite, $Pb_5Sb_4S_{11}$	$5/3PbS+4/3Sb+Sb = 1/3Pb_5Sb_4S_{11}$	-55430 + 36.7T	25-610
Phase II, $Pb_3Sb_4S_9$	$1/2Pb_5Sb_4S_{11}+4/3Sb+S_2 = 5/6Pb_3Sb_4S_9$	-55430 + 38.3T	425-603
Robinsonite, $Pb_6Sb_{10}S_{25}$	$12/39Pb_5Sb_4S_{11}+4/3Sb+S_2 = 10/39Pb_6Sb_{10}S_{21}$	-55430 + 38.4T	25-425
Zinckenite, $PbSb_2S_4$	$2/3Pb_6Sb_{10}S_{21}+4/3Sb+S_2 = 4PbSb_2S_4$	-55430 + 39.5T	25-545

free energies for the lead sulphantimonides are quite small. Hence metastability of individual phases or of assemblages is not surprising.

SIGNIFICANCE OF THE PHASE RELATIONS

Lead sulphantimonides are widespread as minor constituents in mineralized areas. Cation substitution, Ag and Cu for Pb, and Bi and As for Sb, is very extensive in natural lead sulphantimonides (e.g. the Madoc deposit; Jambor 1967); consequently, direct application of the phase equilibria and invariant points presented here (summarized in Table 2) is possible only for assemblages of phases defined in this system. The invariant points listed in Table 2 may be used as fixed point geothermometers to place limits on the thermal conditions of mineralization. High temperature phases, I and II, have not been observed as mineral species. However, the presence of these phases at the time of mineralization may be suggested by the intimate intergrowths of the lead sulphantimonides, textures reminiscent of the breakdown of pre-existing phases. Preservation of robinsonite, which

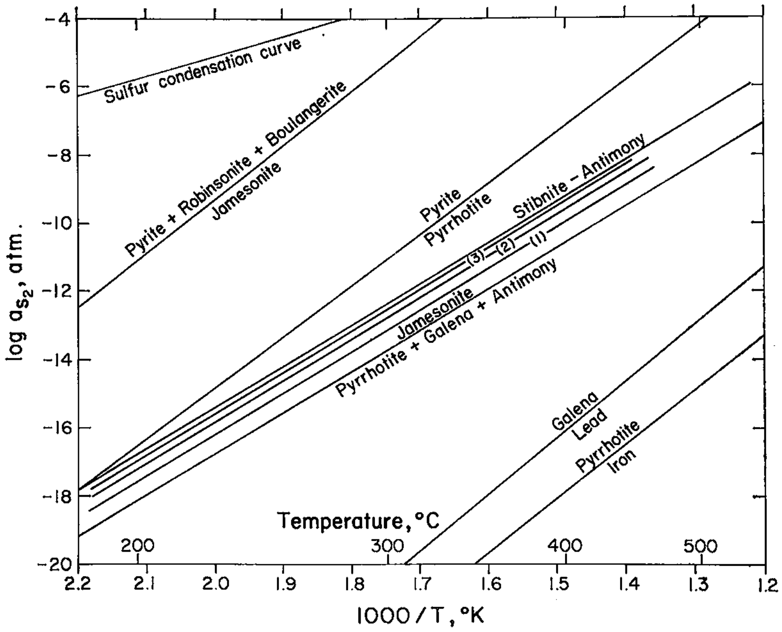

FIG. 8. Log aS_2-1000/T plot of the sulphidation curves of the lead sulphantimonides. The numbered curves are:

(1) $5/3PbS + 4/3Sb + S_2 = 1/3Pb_5Sb_4S_{11}$
(2) $12/39Pb_5Sb_4S_{11} + 4/3Sb + S_2 = 10/39Pb_6Sb_{10}S_{21}$
(3) $2/3Pb_6Sb_{10}S_{21} + 4/3Sb + S_2 = 4PbSb_2S_4$.

appears to break down below 318°C, as a mineral is a perplexing problem; natural robinsonites may be stabilized by small amounts of impurities. Understanding of the phase equilibria of the chemically complex natural lead sulphantimonides will require investigation of larger chemical systems. The relations presented here provide at least a first step toward that end.

The lead sulphantimonides frequently occur with the more common sulphides of iron, copper, *etc*. The presence of the other elements may result in formation of more complex sulphosalts if conditions of temperature and sulphur activity are appropriate. For example, the presence of iron at the time of lead sulphantimonide formation will lead to deposition of jamesonite if the sulphur activity lies within the limits defined by the jamesonite curves in Figure 8. On the other hand, if the sulphur activity is too low or too high, jamesonite will not form, instead iron sulphides will coexist with lead- and antimony-containing phases. Similar curves can be calculated for the effects of other elements (see Craig & Barton 1973).

Acknowledgement

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References

Barton, P.B., (1970) : Sulfide petrology. *Mineral. Soc. Amer. Spec. Pap.* **3,** B.A. Morgan *ed*., 187-198.

Barton, P.B. (1971) : The Fe-Sb-S system. *Econ. Geol.* **66,** 121-132.

Craig, J.R. & Barton, P.B. (1973) : Thermochemical approximations for sulfosalts. *Econ. Geol.* **68,** 493-506.

———— & Lees, W.R. (1972) : Thermochemical data for sulfosalt ore minerals: Formation from simple sulfides. *Econ. Geol.* **67,** 373-377.

Drafall, L.E. & Koucky, F.L. (1969) : Differential thermal analysis of the lead sulfantimonides. *Geol. Soc. Amer. Program Abs.* 270-271.

Elliot, R.P. (1965) : *Constitution of Binary Alloys: First Supplement.* McGraw-Hill, New York.

Garvin, P.L. (1973) : Phase relations in the Pb-Sb-S system. *N. Jb. Mineral. Abh.* **118,** 235-267.

Hansen, M. & Anderko, K. (1958) : *Constitution of Binary Alloys.* McGraw Hill, New York.

Harris, D.C. Jambor, J.L., Lachance, G.R. & Thorpe, R.I. (1968) : Tintinaite, the antimony analogue of kobellite. *Can. Mineral.* **9,** 371-382.

Iitsuka, D. (1919) : Metallographic enquiry into the antimony sulphide-lead-sulphide system. *Kyoto Imp. Univ., Coll. Sci. Mem.* **4**(2), 61-64.

Jaeger, F.M. & Van Klooster, H.S. (1912) : Studien uber naturliche und Kunstliche Sulfantimonite und Sulfarsenite. *Zeit. Anorg. Chemie* **78,** 245-269.

Jambor, J.L. (1967, 1968) : New lead sulfantimonides from Madoc, Ontario. *Canad. Min.* **9,** 7-24; 191-213; 505-521.

———— (1969) : Dadsonite (minerals Q and QM), a new lead sulphantimonide. *Mineral. Mag.* **37,** 437-441.

———— (1969) : Sulphosalts of the plagionite group. *Mineral. Mag.* **37,** 442-446.

Kitikaze, A. (1968) : The PbS-Sb_2S_3 system. *Unpub. M.S. Thesis*, Yamaguchi Univ. (in Japanese).

Kullerud, G. (1969) : The lead-sulfur system. *Amer. Jour. Sci.* **267-A,** 233-256.

Robinson, S.C. (1948) : Synthesis of lead sulphantimonides. *Econ. Geol.* **43,** 293-312.

Salanchi, B. & Moh, G. (1970) : The pseudobinary join galena-antimonite, PbS-Sb_2S_3. *N. Jb. Mineral. Mh.* **11,** 524-528.

Schenck, R., Hoffman, I., Knepper, W. & Vogler, H. (1939) : Gleichkewichstudien uber erzbildende Sulfide: I. *Zeit. Anorg. Allg. Chemie* **240,** 173-197.

Shunk, F.A. (1969) : *Constitution of Binary Alloys: Second Supplement.* McGraw-Hill, New York.

Swanson, H.E. & Fuyat, F.K. (1953) : Standard *x*-ray diffraction powder patterns. *U. S. Natl. Bur. Stds. Circ.* **539,** 2, 18-19.

Wang, N. (1973) : A study of the phases on the pseudobinary join PbS-Sb_2S_2. *N. Jb. Mineral. Mh.* **2,** 79-81.

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