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## The Ag-Bi-Pb-Sb-S-Se-Te Mineralogy of the Darwin Lead-Silver-Zinc Deposit, Southern California

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### Abstract

Analyses by electron microprobe have disclosed unexpected complexity in the mineralogy of the Ag-Bi-bearing galena ores at Darwin, yet reveal that these elements are carried predominantly in solid solution in PbS. Darwin "galena" can be divided into three groups on the basis of Ag-Bi content, mineral assemblage, and location in the mine. Ninety percent of the galena, aptly named, is free from inclusions, and contains less than 0.22 weight percent Ag; a fine-textured PbS<sub>ss</sub> typical of shallow workings contains 1.7 to 3.3 weight percent Ag and 3.9 to 7.3 weight percent Bi in solid solution and, moreover, contains several types of small exsolved laths (to ~0.25 mm long) that are enriched in Ag, Bi, and Sb; a third distinct PbS<sub>ss</sub>, containing 1.5 to 4.6 weight percent Ag and 3.8 to 10.8 weight percent Bi, occurs only as a breakdown product in a localized late sulfosalt stage of the mineralization.

At least two, and perhaps three, distinct types of sulfosalt that relate compositionally to the minerals cosalite (Pb<sub>2</sub>Bi<sub>2</sub>S<sub>5</sub>), gustavite (AgPbBi<sub>3</sub>S<sub>6</sub>), and "schirmerite" (AgPb<sub>2</sub>Bi<sub>3</sub>S<sub>7</sub>?) have exsolved from the fine-textured PbS<sub>ss</sub>, as have lesser amounts of matildite and tetradyomite. A chemically complex sulfosalt similar in structure to heyrovskýite (6Pb<sub>1-x</sub>Bi<sub>2x/3</sub>S·Bi<sub>2</sub>S<sub>3</sub>) is the predominant natural associate of the third PbS<sub>ss</sub>, and wisps of a minor, high-Te sulfosalt are typical in this association. Compositions of the heyrovskýite-like phase are variable, apparently as the result of breakdown below 250°C of a primary sulfosalt of approximate composition: Pb-41; Bi-31; Ag-7; S-10; Se-9; and Te-1 weight percent.

One-to-one coupling of Ag and Bi is approached in the two groups of PbS<sub>ss</sub> (the average atomic ratio of Bi:Ag is 1.29) but is not characteristic of the sulfosalts. Consideration of sulfosalt bonding characteristics provides an apparent explanation for this lack of one-to-one coupling between Ag and Bi, as well as for the variable ratios of Pb to Bi measured for the several exsolved sulfosalt phases. Extensive, near-ideal substitution of Se for S is typical of the various PbS<sub>ss</sub>-sulfosalt assemblages. Significant substitution of Sb for Bi is noted only in the exsolved sulfosalts found in the fine-textured PbS<sub>ss</sub>.

Because exsolved mineral phases persist in samples annealed at 350°C, ore deposition at Darwin is presumed to have occurred at higher temperatures.

### Introduction

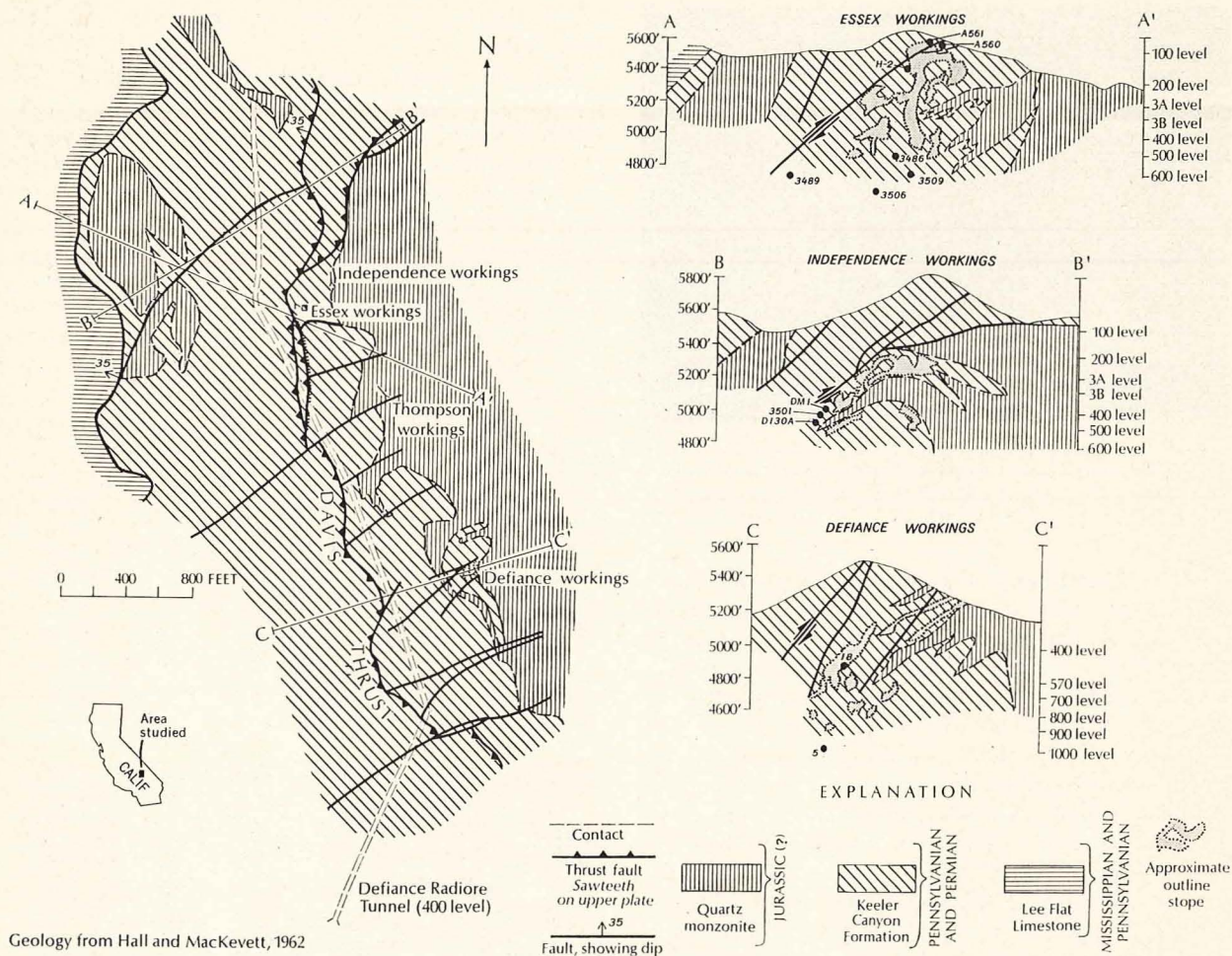
THE mineralogy of galena ores rich in silver has been the subject of many field and laboratory studies. Such ores may be placed into two groups, one characterized by the association Ag-Sb, and the other by the association Ag-Bi (e.g., Malakhov, 1969). As an example of the Ag-Sb association, we have recently published a report on the mineralogy of the Wood River, Idaho deposits (Hall and Czamanske, 1972). This study of the Ag-Bi-bearing galena ores at Darwin is part of a series of mineralogical and geochemical studies of the Darwin ores (Hall, 1971; Hall et al., 1971; and Rye et al., 1974).

Although the occurrence of Ag and Bi in galena ores is fairly well documented in terms of typical concentration levels and patterns of intramine distribution (e.g., Leutwein and Herrmann, 1954; Ontoev et al., 1960; Malakhov, 1969), the understand-

ing of the mineralogy of such ores has been complicated by the typical occurrence of minor, exsolved phases. References such as Ontoev et al. (1960, Fig. 3), Craig (1967, Table 11), and Ramdohr (1969) show that an unusual number of Ag-Bi-Pb-S minerals that have been proposed on the basis of microscopic study and bulk chemistry are now discredited.

Laboratory studies that have provided some help in understanding natural occurrence of galenas rich in Ag and Bi include those of Van Hook (1960), Wernick (1960), Craig (1967), Salanci and Moh (1970), and Hoda and Chang (in press). A useful review relating much of this experimental work to geology and paragenesis is provided by Chang and Bever (1973). However, as indicated by Craig's work (1967), phases typical of natural occurrences may form at temperatures for which laboratory equi-





Geology from Hall and MacKevett, 1962

FIG. 1. Simplified geologic map and cross sections of the Darwin mine area showing sample localities.

libration times are unreasonably long. In particular, the right triangle in the  $Ag_2S-Bi_2S_3-PbS$  ternary that is bounded by the joins  $PbS-Bi_2S_3$ ,  $PbS-AgBiS_2$ , and  $AgBiS_2-Bi_2S_3$  contains a number of natural phases that are of importance at Darwin but have not been found experimentally. The studies of Karup-Møller (1970a, 1970b, 1972, 1973a, 1973b, and 1973c) are complementary to ours in providing data for phases of similar composition.

We share the opinion of Chang and Bever (1973), who state that one promising approach for study of lead sulfosalts is through electron microprobe analyses of natural minerals. This study relates careful microprobe analyses of the sulfide minerals to the geology and geochemistry of the Darwin deposit.

### Geology and Ore Deposits

The geology of the Darwin area has been described by Hall and MacKevett (1958, 1962). The ore occurs in a sequence of upper Paleozoic sedimentary

rocks (limestones, silty and sandy limestones, shales, and siltstones) that is intruded by a biotite-hornblende, quartz monzonite stock of Jurassic (?) age—the Darwin stock. The Paleozoic rocks are altered to calc-silicate minerals within 4,000 feet of the stock. The mine area is on the west limb of an overturned and partly inverted syncline between the Darwin stock on the east and the Davis thrust fault on the west (Fig. 1).

Most of the ore is massive and occurs in veins, bedded deposits, and steep irregular replacement bodies near feeder fissures that strike  $N 50^{\circ}-70^{\circ} E$  and cut medium-grained, light-colored calc-silicate rock. The ore consists of galena, sphalerite, pyrite, and lesser amounts of chalcopyrite, pyrrhotite, magnetite, arsenopyrite, scheelite, tetrahedrite, and the here-described phases rich in Ag, Bi, Se, and Te. Gangue minerals are calcite, fluorite, host-rock calc-silicate minerals, and a little jasperoid. Four important sulfide mineral assemblages are recognized.

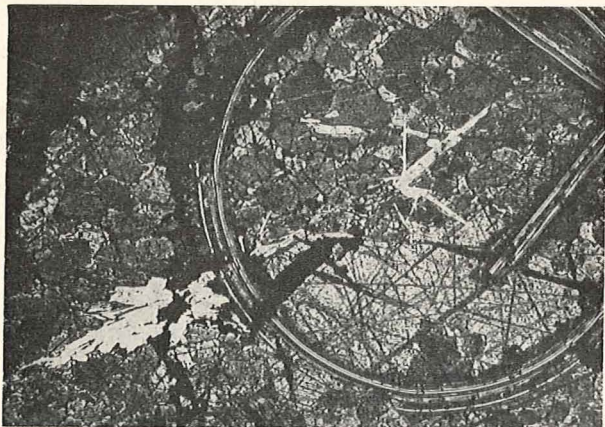


FIG. 2A. Inclusions in Group 2  $PbS_{ss}$  (specimen A561). The acicular inclusion cluster is Type I sulfosalt (cosalite?) with the central blade 0.24 mm long. Inclusions and  $PbS_{ss}$  grain texture have been enhanced by etching with HBr.

The most common is a pyrite-sphalerite-galena  $\pm$  chalcopyrite and scheelite assemblage that includes all the replacement ore in calc-silicate rock near the Darwin stock (Fig. 1). The second is a pyrite-pyrrotite-magnetite-sphalerite-galena assemblage that occurs on the footwall of the Davis thrust fault and is the greatest distance from the Darwin stock. The third is fine-grained heavy galena ore containing abundant silver, bismuth, and selenium and minor associated pyrite. This ore was most abundant near the surface in the Essex and Thompson workings and was the high-grade ore mined extensively during the early history of the district. The fourth type, which is very minor, is a late Ag-Bi-Se-Te sulfosalt assemblage. It contains a dominant silver-colored sulfosalt mineral similar to heyrovskýite, which occurs in ragged, subparallel plates in a gangue of coarse white calcite, disseminated green andradite, and pyrite cubes. This assemblage was observed only on the 400 level in the Independence workings of the Darwin mine.

#### Methods of Analysis

Although the exsolved minor phases in the Darwin galenas can be recognized in polished section by virtue of their anisotropism, their white color and hardnesses similar to that of galena make it difficult to see the overall distribution of exsolved phases. One means of quickly locating inclusions and studying their distribution in the galena is to etch the polished surfaces for four seconds with concentrated HBr. Such etched sections show the size and appearance of the inclusions and the grain size of the host galena (Fig. 2A). For recognition of minute inclusions, this etching technique is too severe, and D. C. Harris (written commun., 1975) recommends

use of  $HNO_3$  in dilutions between 1:10 and 1:5 (Fig. 2B).

Electron microprobe analyses were done on freshly polished, carbon-coated surfaces with an ARL EMX-SM microprobe using an accelerating voltage of 15 kv and a sample current of  $2 \times 10^{-8}$  amperes on benitoite. Oscilloscope-displayed secondary electron images were used to assure proper beam placement on exsolved phases. Lines analyzed and crystals used are as follows:  $AgL_{\alpha}$ ,  $BiM_{\beta}$ ,  $PbM_{\alpha}$ ,  $SK_{\alpha}$ ,  $SeL_{\alpha}$ -ADP;  $CuK_{\alpha}$ ,  $FeK_{\alpha}$ ,  $SbL_{\alpha}$ ,  $TeL_{\alpha}$ ,  $ZnK_{\alpha}$ -LiF. With the aim of obtaining analyses of great accuracy, an initial overview of phase compositions was made to allow synthesis of chemically similar standard materials. Synthetic standards ultimately employed in this study included:  $AgBiS_2$ ,  $Bi_2S_3$ ,  $Bi_2(Te_2S)$ ,  $Cu_7Fe_2Ag_3Sb_4S_{13}$ ,  $FeS$ ,  $FeS_2$ ,  $PbS$ ,  $PbSe$ ,  $PbTe$ ,  $Pb_4Ag_6Sb_6S_{16}$ ,  $2PbS \cdot AgBiS_2$ ,  $2PbSe \cdot AgBiS_2$ ,  $Sb_2S_3$ , and  $ZnS$ . These standards were synthesized by reacting high-purity elements at elevated temperatures in evacuated silica tubes. The accuracy of their compositions is based on careful weighing, known phase relations in sulfide systems, and production of material homogeneous under the microscope and in the microprobe.

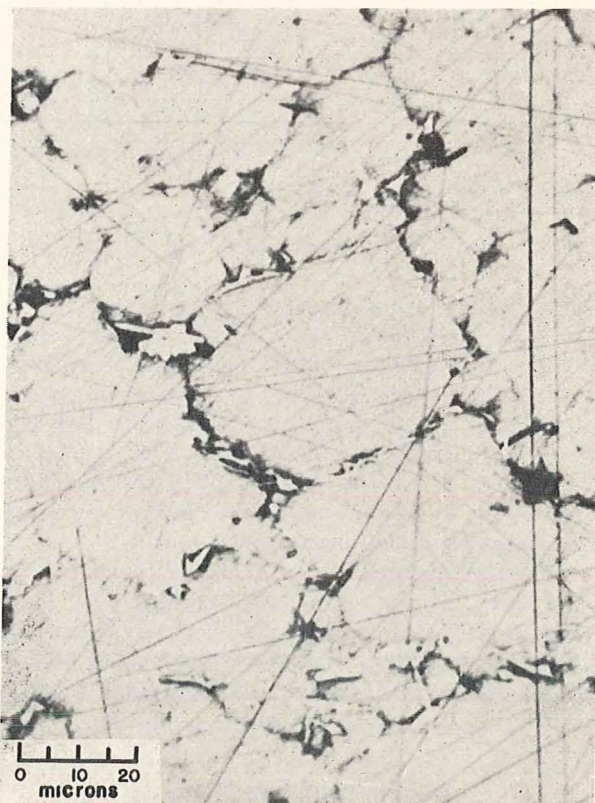


FIG. 2B. Small, unidentified sulfosalt inclusions localized along grain boundaries in Group 2  $PbS_{ss}$  (specimen H-2). Sample etched with dilute  $HNO_3$ . Photo courtesy of D. C. Harris.

After making appropriate corrections for background, calculation of analyses on the basis of direct comparison of count rates for standards and unknowns provided superior analyses for many phases. However, Pb and Bi values for an important group of phases (see Table 2) with Pb and Bi contents ranging from 20 to 40 and 30 to 49 weight percent, respectively, were uncertain because serious photon interactions between these and other elements were evident from counting ratios among the standards. Therefore, the entire mass of microprobe data was run through a comprehensive, theoretical microprobe data-reduction program, COR 2 (Henoc et al., 1973). For all elements except Bi and Pb, COR 2 returned results showing concentrations virtually identical (within 0.3 weight percent) to those calculated by direct count-rate comparisons using closely matched standards. Because of the multiplicity of good standards, it can be clearly shown that available mass absorption coefficients for the Bi- and Pb-M lines are not correct. For example, if  $2\text{PbSe}\cdot\text{AgBiS}_2$  is used as a Bi standard, COR 2 returns a value of 53.7 rather than 58.9 weight percent Bi for  $\text{Bi}_2(\text{Te}_2\text{S})$ . In our experience, COR 2 produces good values for Bi if the unknown has a Pb content similar to the standard.

Many microprobe analyses are published with no indication of standards used or data-reduction techniques. Microprobe analysis of heavy-metal sulfides is difficult. Direct count-rate comparisons with pure metal standards or end-member sulfide standards such as  $\text{Ag}_2\text{S}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{PbS}$ ,  $\text{PbSe}$ , etc., or computer-correction programs based on such standards, should be checked by analyzing some complex phases of known composition. The values presented here represent the average of the direct comparison and computer-corrected values for all elements except Bi and Pb. For these two elements reasoned compromises were made, and values for Bi and Pb in Tables 2 and 4 are less accurate than we desire. A cooperative effort between the U. S. Geological Survey and the National Bureau of Standards is underway to provide better fundamental spectrochemical data for heavy elements.

For all phases for which concentrations of Fe and Cu are not reported, the concentration of Fe is virtually nil and that of Cu is less than 0.15 weight percent. In contrast to these samples, a whole series of Cu-bearing sulfbismuthinides are discussed by Borodaev and Mozgowa (1971).

### Mineral Analyses

The Darwin "galenas" can be divided into three groups on the basis of electron microprobe analyses

(Table 1)<sup>1</sup> and optical study. These are: (1) relatively pure galena containing no exsolved phases and less than 0.22 weight percent Ag; (2)  $\text{PbS}_{\text{ss}}$  with 1.7 to 3.3 weight percent Ag and 3.9 to 7.3 weight percent Bi in solid solution and containing several exsolved sulfosalts phases enriched in Ag, Bi, and Sb; and (3)  $\text{PbS}_{\text{ss}}$  that contains Ag, Bi, and Se in amounts up to 4.6, 10.8, and 9.0 weight percent, respectively.

#### Group 1 $\text{PbS}$

Approximately 90 percent of the galena at Darwin can be classed as Group 1  $\text{PbS}$ , that is, it contains less than 0.22 weight percent Ag (i.e., about 0.6 oz Ag for each percent Pb in the ore). Most of the galena in the replacement ore of the Defiance workings and most of that in the deeper parts of the Essex, Thompson, and Independence workings is of this type. Group 1  $\text{PbS}$  is typically medium to coarse grained (grains to 12 mm on an edge) and occurs in both the pyrite-sphalerite-galena  $\pm$  chalcopyrite and scheelite assemblage and the pyrite-pyrrhotite-magnetite-sphalerite-galena assemblage.

The six examples of Group 1  $\text{PbS}$  listed in Table 1 contain Ag, Bi, Sb, and Se in amounts up to 0.22, 0.31, 0.17, and 0.43 weight percent, respectively. Atomic proportions (Table 1) give little evidence of coupled substitution involving Ag plus Bi and/or Sb, a conclusion also reached by Hall (1971) on the basis of minor-element data for bulk galena separates. No Ag-bearing inclusions could be found in these galenas, and there is good agreement between the Ag-values obtained by bulk chemical analysis and microprobe analysis.

#### Group 2 $\text{PbS}_{\text{ss}}$

Group 2  $\text{PbS}_{\text{ss}}$  is fine grained and steel textured and was most abundant in the shallow levels of the Essex and Thompson workings; samples 5, H-2, and A-561 in Table 1 are representative. The analyses show Ag contents up to 3.3 weight percent, with correspondingly high Bi content, suggesting coupled substitution. The atomic ratio (Bi + Sb):Ag averages 1.16.  $\text{PbS}_{\text{ss}}$  of this group also contains up to 2.1 weight percent Se but virtually no Sb. As expected (Van Hook, 1960), unit cell edges for Group 2  $\text{PbS}_{\text{ss}}$  are far less than for pure galena (5.91XXÅ versus 5.9359Å, Hall, 1971).

In addition to holding appreciable Ag and Bi in solid solution, Group 2  $\text{PbS}_{\text{ss}}$  is characterized by the presence of several minor exsolved phases that are complex Pb-Bi-sulfosalts (Table 2, top row and Table 3, columns 1 and 2). The exsolved phases

<sup>1</sup>Note that sample numbers used in this report correspond to those of Hall (1971), Hall et al. (1971), and Rye et al. (1974), where additional data are available.

TABLE 1. Compositions Typical of Three Groups of "Galenas" from the Darwin Ores Distinguished on the Basis of Ag-Bi and Se Contents (Weight Percentages and Atomic Proportions)

Sample No.	Group 1											
	18		A560		3486 & 3489 <sup>1</sup>		3506		3509			
Pb	86.6 ± 1.4 <sup>2</sup>	0.992	86.1	0.982	86.6	0.996	86.3	1.004	86.2	1.025		
Bi	0.11 ± 0.02	0.001	0.33	0.004	0.00	—	0.00	—	0.00	—		
Ag	0.14 ± 0.05	0.003	0.22	0.005	0.20	0.005	0.18	0.004	0.20	0.005		
Sb	0.11 ± 0.02	0.002	0.04	0.001	0.14	0.003	0.17	0.003	0.08	0.002		
		0.998		0.992		1.004		1.011		1.032		
S	13.5 ± 0.5	0.999	13.4	0.987	13.4	0.996	13.3	1.000	13.0	0.999		
Se	0.04 ± 0.02	—	0.43	0.013	0.11	0.003	0.01	—	0.03	0.001		
Te	0.04 ± 0.02	0.001	0.01	—	0.02	—	0.00	—	0.00	—		
	100.5	1.000	100.5	1.000	100.5	0.999	100.0	1.000	99.3	1.000		
$\frac{\text{Bi} + \text{Sb}^3}{\text{Ag}}$	1.00		1.00		0.60		0.75		0.40			
Group 2												
Sample No.	5		H-2		A561							
Pb	80.5 ± 1.6	0.908	73.7	0.872	75.0	0.866						
Bi	3.9 ± 0.2	0.044	7.3	0.086	7.0	0.080						
Ag	1.7 ± 0.2	0.037	3.3	0.075	3.2	0.071						
Sb	0.02 ± 0.02	—	0.01	—	0.00	—						
		0.989		1.033		1.017						
S	13.5 ± 0.5	0.984	12.2	0.932	12.6	0.940						
Se	0.45 ± 0.1	0.013	2.1	0.065	1.9	0.058						
Te	0.13 ± 0.05	0.002	0.11	0.002	0.11	0.002						
	100.2	0.999	98.7	1.000	99.8	1.000						
$\frac{\text{Bi} + \text{Sb}}{\text{Ag}}$	1.19		1.15		1.13							
Group 3												
Sample No.	D130A <sup>4</sup>		3501,1 <sup>5</sup>		3501,2 <sup>*</sup>		3501,3 <sup>*</sup>		DM1,P <sup>*</sup>		DM1,X <sub>2</sub>	
Pb	76.3 ± 1	0.915	66.2	0.770	73.6	0.871	73.6	0.891	72.0	0.838	67.4	0.809
Bi	3.8 ± 0.2	0.045	10.8	0.125	6.1	0.072	7.4	0.089	5.5	0.063	10.0	0.119
Ag	1.5 ± 0.2	0.035	4.6	0.103	2.1	0.048	2.5	0.056	2.2	0.049	4.4	0.101
Sb	0.00 ± 0.02	—	0.00	—	0.00	—	0.00	—	0.08	0.002	0.00	—
		0.995		0.998		0.991		1.036		0.952		1.029
S	9.7 ± 0.5	0.752	10.6	0.796	10.2	0.780	10.0	0.783	9.6	0.722	9.1	0.706
Se	7.6 ± 0.5	0.239	6.4	0.195	6.7	0.208	6.7	0.213	8.8	0.269	9.0	0.284
Te	0.46 ± 0.05	0.009	0.43	0.008	0.61	0.012	0.20	0.004	0.50	0.009	0.55	0.011
	99.4	1.000	99.0	0.999	99.3	1.000	100.4	1.000	98.7	1.000	100.5	1.001
$\frac{\text{Bi} + \text{Sb}}{\text{Ag}}$	1.29		1.21		1.50		1.59		1.33		1.18	

<sup>1</sup> Analyses for these samples are identical.

<sup>2</sup> Estimated errors for element pertain to entire subgroup. Also see text.

<sup>3</sup> (Bi + Sb)/(Ag) calculated on atomic basis for all tables.

<sup>4</sup> "\*" indicates analysis refers to included (i.e. minor) phase. Often cross reference between included and host phase may be made between Tables 1 and 2.

<sup>5</sup> Use of "1" refers to particular area or analyzed grain(s) within mount.

range in maximum dimension from several tenths of a millimeter (Fig. 2A) down to micron-sized grains which are concentrated along boundaries between galena grains (Fig. 2B). To avoid interference from the host phase, all microprobe analyses of

exsolved phases have been made on grains whose smallest dimension exceeds 10 microns. By comparing analyses for Group 1 PbS and Group 2 PbS<sub>ss</sub> (Table 1), it can be seen that during the process of exsolution Sb has been stripped from the host PbS<sub>ss</sub>

TABLE 2. Compositions of Complex Sulfosalts, Rich in Ag, Bi, Sb, and Se, Associated with PbS<sub>88</sub> in the Darwin Ores (Weight Percentages and Atomic Proportions)

Sample No.	Sulfosalts exsolved from Group 2 PbS <sub>88</sub>																					
	Type I (Cosalite?)		Type II				?		Type III (Gustavite?)													
	A561, C*	A561, A*	A561-D*		H-2, A*		H-2, C*		A561, E*		A561, D*		H-2, B*		H-2, D*							
Pb	40.4 ± 0.8	0.370	39.1	0.355	37.9	0.348	25.5	0.237	25.8	0.242	22.2	0.200	19.7	0.178	19.7	0.177	20.1	0.183				
Bi	30.2 ± 0.5	0.274	31.0	0.279	31.0	0.282	41.7	0.385	42.1	0.392	43.0	0.385	47.0	0.421	47.5	0.423	48.6	0.438				
Ag	2.4 ± 0.2	0.042	2.9	0.051	3.0	0.053	9.6	0.172	9.5	0.171	9.4	0.163	9.2	0.160	9.0	0.155	8.9	0.155				
Sb	7.5 ± 0.3	0.117	7.7	0.119	7.3	0.114	3.6	0.057	3.3	0.053	4.4	0.068	4.7	0.072	4.4	0.067	4.0	0.062				
		0.803		0.804		0.797		0.851		0.858		0.816		0.831		0.822		0.838				
S	16.3 ± 0.4	0.964	16.3	0.958	16.1	0.956	15.4	0.926	15.5	0.940	16.1	0.939	16.2	0.946	16.4	0.952	16.2	0.951				
Se	1.4 ± 0.2	0.034	1.7	0.040	1.7	0.041	2.9	0.071	2.3	0.057	2.5	0.059	2.2	0.052	2.0	0.047	2.0	0.048				
Te	0.19 ± 0.02	0.003	0.13	0.002	0.19	0.003	0.21	0.003	0.21	0.003	0.10	0.001	0.13	0.002	0.07	0.001	0.10	0.001				
Bi + Sb	98.4	1.001	98.8	1.000	97.2	1.000	98.9	1.000	98.7	1.000	97.7	0.999	99.1	1.000	99.1	1.000	99.9	1.000				
Ag	9.31		7.80		7.47		2.57		2.60		2.78		3.08		3.16		3.23					
Sample No.	Type IV sulfosalt associated with Group 3 PbS <sub>88</sub> (analyses listed in order of increasing Bi content)																					
	DM1, D	DM1A, B		D130A, 0		D130A, 1		3501, 4		DM1, P		DM1, X <sub>2</sub> *		DM1, X <sub>1</sub> *		3501, 2		3501, 3		3501, 1*		
Pb	39.3 ± 0.5	0.421	38.9	0.408	37.3	0.395	37.3	0.389	33.2	0.340	29.4	0.299	29.2	0.309	29.4	0.306	32.2	0.330	32.4	0.336	29.0	0.290
Bi	31.6 ± 0.6	0.335	33.9	0.353	34.6	0.363	34.8	0.360	36.5	0.371	36.9	0.372	37.5	0.394	37.8	0.390	37.9	0.385	38.3	0.394	40.1	0.397
Ag	7.3 ± 0.3	0.150	6.8	0.137	6.4	0.130	6.4	0.128	8.4	0.166	11.0	0.215	10.7	0.218	10.3	0.206	8.1	0.159	8.9	0.177	9.1	0.175
Sb	0.11 ± 0.02	0.002	0.09	0.002	0.13	0.002	0.13	0.002	0.00	—	0.08	0.001	0.14	0.002	0.10	0.002	0.00	—	0.00	—	0.00	—
		0.908		0.900		0.890		0.879		0.877		0.887		0.923		0.904		0.874		0.907		0.862
S	10.6 ± 0.5	0.733	10.9	0.739	10.9	0.746	11.4	0.768	11.9	0.788	10.9	0.717	10.2	0.698	10.6	0.713	11.8	0.781	11.5	0.770	12.4	0.801
Se	9.0 ± 0.4	0.253	9.1	0.250	8.8	0.244	8.1	0.222	7.4	0.199	10.0	0.267	10.3	0.286	10.0	0.273	7.8	0.208	8.0	0.218	7.2	0.180
Te	0.79 ± 0.05	0.014	0.64	0.011	0.59	0.010	0.59	0.010	0.75	0.013	1.00	0.016	0.95	0.016	0.87	0.015	0.64	0.011	0.71	0.012	0.64	0.010
Bi + Sb	98.7	1.000	100.3	1.000	98.7	1.000	98.7	1.000	98.2	1.000	99.3	1.000	99.0	1.000	99.1	1.001	98.4	1.000	99.8	1.000	98.4	1.000
Ag	2.25		2.59		2.81		2.83		2.23		1.73		1.82		1.90		2.42		2.23		2.27	

TABLE 3. Compositions of Matildite, Tetradymite, Tetrahedrite, and a High-Te Phase Associated with "PbS<sub>ss</sub>" in the Darwin Ores (Weight Percentages and Atomic Proportions)

Mineral Sample No.	Matildite		Tetradymite		Tetrahedrite		High-Te Phase		
	A561 (1) <sup>1</sup>		5 (4)		3506 (3)		DM1 (4) & DM1A (2) <sup>2</sup>		
Pb	3.5 ± 0.3 <sup>3</sup>	0.033 <sup>4</sup>	0.033	0.2 ± 0.1	0.001	<0.2	0.002	18.3 ± 0.5	0.853
Bi	51.7 ± 1.5		0.965	58.9 ± 1.8	1.973	0.0		46.0 ± 2	2.128
Ag	27.1 ± 1	0.980		0.1	0.001	20.4 ± 0.7	3.442	0.53 ± 0.06	0.048
Sb	0.4 ± 0.2		0.012	0.2 ± 0.1	0.011	27.1 ± 0.2	4.052	0.14 ± 0.02	0.011
		1.013	1.010		1.986				3.040
S	15.5 ± 0.5	1.886		4.6 ± 0.1	1.005	22.9 ± 0.5	13.000	4.6 ± 0.2	1.387
Se	2.3 ± 0.2	0.114		0.4 ± 0.05	0.036	0.0		8.1 ± 0.4	0.992
Te	0.02	—		35.7 ± 0.3	1.959	0.0		21.4 ± 0.4	1.621
		2.000			3.000				4.000
Cu	—			—		22.8 ± 0.4	6.522	—	
Fe	—			—		5.7 ± 0.1	1.858	—	
Zn	—			—		1.0 ± 0.2	0.278	—	
	100.5			100.1 <sup>5</sup>		100.1	12.102	99.1	

<sup>1</sup> Number of grains analyzed.<sup>2</sup> Analyses from these two specimens identical within limits of error.<sup>3</sup> Estimated error based on variation in raw count data and determinations on multiple grains.<sup>4</sup> Pb arbitrarily split 50:50 between positions.<sup>5</sup> Au = 0.00.

and concentrated in the exsolved sulfosalts (Table 2, top row). Furthermore, the Se contents are similar for virtually all Ag-Bi-Pb-Sb-S-Se phases within a given specimen of ore (compare Table 1, Group 2, Table 2, top row, and Table 3, column 1; also Table 1, Group 3 and Table 2, bottom row).

#### Group 3 PbS<sub>ss</sub>

Group 3 PbS<sub>ss</sub> is found in a late, rare ore type at Darwin, known only on the 400 level north of the Essex workings (Fig. 1). This group comprises PbS<sub>ss</sub> that has formed by breakdown of a new sulfosalt (approximate composition, in weight percent: Pb-41; Bi-31; Ag-7; S-10; Se-9; and Te-1) disseminated in a calcite-andradite-pyrite gangue. In polished sections of this ore, PbS<sub>ss</sub> has been observed both as the apparent dominant phase in sections of small, irregular sulfosalt masses (note Fig. 3A) and as irregular elongate inclusions within Type IV host. The latter occurrence is more typical, and PbS<sub>ss</sub> is actually less abundant in this ore type than the associated breakdown product, Type IV sulfosalt (see below). These findings explain the divergence from the PbS-AgBiS<sub>2</sub> join of bulk compositions for samples 3501 and DM1 (Hall, 1971, fig. 2).

This PbS<sub>ss</sub> contains Ag, Bi, Se, and Te in amounts up to 4.6, 10.8, 9.0, and 0.61 weight percent, respectively, and is free of Sb, as is Group 2 PbS<sub>ss</sub>. Cell edges of the PbS<sub>ss</sub> components of two shreds from DM1 are 5.955 and 5.971 Å (PbS = 5.9360 Å), reflecting the substantial content of Se and Te in the

PbS<sub>ss</sub> from DM1 as well as its variable content of Ag, Bi, Sb, Se, and Te. The average (Bi + Sb) : Ag ratio is 1.35, which is higher than for the previous group. The data in Tables 1, 2, 3, and 4 suggest that the Se contents of Group 3 PbS<sub>ss</sub>, as well as other phases in the late sulfosalt mineralization, simply reflect the availability of this element. In order of decreasing Se content, the ranking is DM1, D130A, and 3501.

#### Sulfosalt Types I, II, and III

Numerous inclusions are evident in Group 2 PbS<sub>ss</sub> (e.g., Figs. 2A and B). On the basis of bulk compositional data, which showed Group 2 PbS<sub>ss</sub> to extend toward AgBiS<sub>2</sub> in composition, on X-ray data, and on understanding of the system Ag-Bi-Pb-S at that time, Hall (1971) concluded that these inclusions were matildite. In fact, most of those inclusions large enough to analyze are not matildite, but apparently comprise two or three discrete sulfosalt types (Table 2, top row). Bulk compositions of "galena" separates plot close to the PbS-AgBiS<sub>2</sub> join (Hall, 1971, fig. 2) because of the near-coupled substitution, Ag<sup>+</sup> + Bi<sup>3+</sup> ⇌ 2Pb<sup>2+</sup>, in the dominant host PbS<sub>ss</sub> (Table 1, middle row) and the relatively small volume represented by the inclusions.

Those sulfosalt inclusions which we have analyzed are quite similar in appearance and typically occur as white, weakly anisotropic blades about 0.01 mm wide and up to 0.25 mm long. The color and hard-



TABLE 4. Compositions of Phases in Samples of H-2, A561, and DM1 After Annealing at 250° and 310°C for 40 Weeks (Weight Percentages and Atomic Proportions).

Sample No. and treatment	Phases present in annealed Group 2 galena												
	H-2*, 250°			H-2*, 310° <sup>1</sup> three grains				A561*, 310°					
Pb	26.7	0.248	0.393	41.7	—	44.1	0.432	43.4	0.405				
Bi	42.9	0.395	0.298	31.9	—	30.0	0.291	28.5	0.264				
Ag	9.5	0.170	0.100	5.5	—	5.2	0.098	2.4	0.043				
Sb	2.9	0.046	0.046	2.9	—	3.1	0.052	7.0	0.111				
		0.859	0.837				0.873		0.823				
S	15.7	0.943	0.938	15.4	—	14.8	0.937	16.0	0.964				
Se	2.2	0.054	0.059	2.4	—	2.3	0.059	1.4	0.034				
Te	0.21	0.003	0.003	0.20	—	0.25	0.004	0.12	0.002				
Bi + Sb	100.1	1.000	1.000	99.9	—	99.8	1.000	98.8	1.000				
Ag	2.60		3.45	3.51				8.73					

Sample No. and treatment	Components of annealed DM1																
	DM1, 250° three shreds				DM1, 250° <sup>2</sup> two hosts			DM1, 310° seven shreds				DM1, 310° four hosts					
Pb	0.710	14.8	—	19.4	0.935	41.0	0.449	0.529	11.4	—	19.6	0.942	40.5	—	42.5	0.462	
Bi	2.248	47.2	—	45.9	2.193	30.6	0.332	2.211	48.0	—	45.4	2.163	30.9	—	31.4	0.339	
Ag	0.194	2.1	—	1.9	0.176	7.4	0.156	0.286	3.2	—	3.1	0.286	0.139	—	6.2	0.130	
Sb	0.016	0.2	—	0.016	0.016	0.2	0.004	0.014	0.18	—	0.15	0.012	0.004	—	0.2	0.004	
	3.168			3.320		0.941		3.040				3.403	0.900			0.935	
S	1.334	4.3	—	4.6	1.433	10.3	0.729	1.350	4.5	—	4.6	1.429	0.759	11.0	—	10.3	0.724
Se	0.857	6.8	—	7.6	0.962	9.0	0.259	0.817	6.7	—	7.7	0.971	0.230	8.2	—	9.1	0.260
Te	1.809	23.2	—	20.5	1.605	0.68	0.012	1.833	24.3	—	20.5	1.600	0.012	0.68	—	0.90	0.016
Bi + Sb	4.000	98.4	—	100.1	4.000	99.2	1.000	4.000	98.3	—	101.1	4.000	1.001	98.3	—	100.6	1.000
Ag	11.67			12.57		2.16		7.78			7.61		2.37			2.64	

<sup>1</sup> As used in this table to indicate a range of compositions, each analysis happens to represent both an individual grain and a representative end member for each element.

<sup>2</sup> Analyses within estimated error and hence averaged.

ness of all three types are similar to those of galena. Certain peculiarities of note are that: (1) Type I often occurs as blades of complex morphology (Fig. 2A); and (2) Types II and III are more often present as larger grains (to 0.05 × 0.25 mm) that are typically more irregular in form.

Consideration of Figure 4 and the analyses at the top of Table 2 shows that: (1) these inclusions are rather closely related to the phases cosalite (Pb<sub>2</sub>Bi<sub>2</sub>S<sub>5</sub>), "schirmerite" (AgPb<sub>2</sub>Bi<sub>3</sub>S<sub>7</sub>, definition of Karup-Møller, 1973a), and gustavite (AgPbBi<sub>3</sub>S<sub>6</sub>, Karup-Møller, 1972); (2) they contain significant Sb and Se; and (3) Types II and III may not be distinct. Analyses in Table 2 generally represent the average of determinations at 6 to 8 points, typically on several blades within a small area (~2 mm<sup>2</sup>). The small size of Types I, II, and III inclusions has precluded X-ray study of these phases.

On the basis of atomic proportions (Fig. 4), Type I inclusions are thought to be related to cosalite, one of the most common Pb-Bi-sulfosalts. Although the Darwin material is impure, there is precedent for incorporation into cosalite of all elements but Sb. Substitution of Ag is indicated by analyses in Palache et al. (1944) and by more recent microprobe determinations (Klomínský et al.,

1971, and Karup-Møller, 1973b). The Ag content of the cosalite at Darwin appears to represent Ag saturation in this assemblage (see also Table 4, A561, 310°C). Ramdohr (1969) noted that cosalite from Rizbanya contains 6.57 weight percent Se. Although Sb has not been reported in cosalite, there are many examples that establish a precedent for substitution of Sb for Bi in sulfosalts (e.g., Graham, 1951; Wernick et al., 1958; Jambor and Lachance, 1968; Karup-Møller, 1972). Sb has been quantitatively concentrated in the inclusion phases of the Group 2 PbS<sub>ss</sub>, and this steel-textured ore type is characterized by a moderate high (0.3 to 0.4 weight percent) in Sb content (Hall, 1971; Table 1).

Type III inclusions have elemental proportions virtually identical to those proposed for end-member gustavite by Karup-Møller (1970a, 1972, and 1973b). The presence of Se and a somewhat greater Sb content are the only novel features of this phase at Darwin. It is interesting that gustavite, a discovery of the electron microprobe age, has now been positively identified from at least seven deposits (Karup-Møller, 1970a and 1972; Borodaev and Mozgova, 1971; and this work), whereas so many phases of long standing in the system Ag-Bi-Pb-S have been discredited.

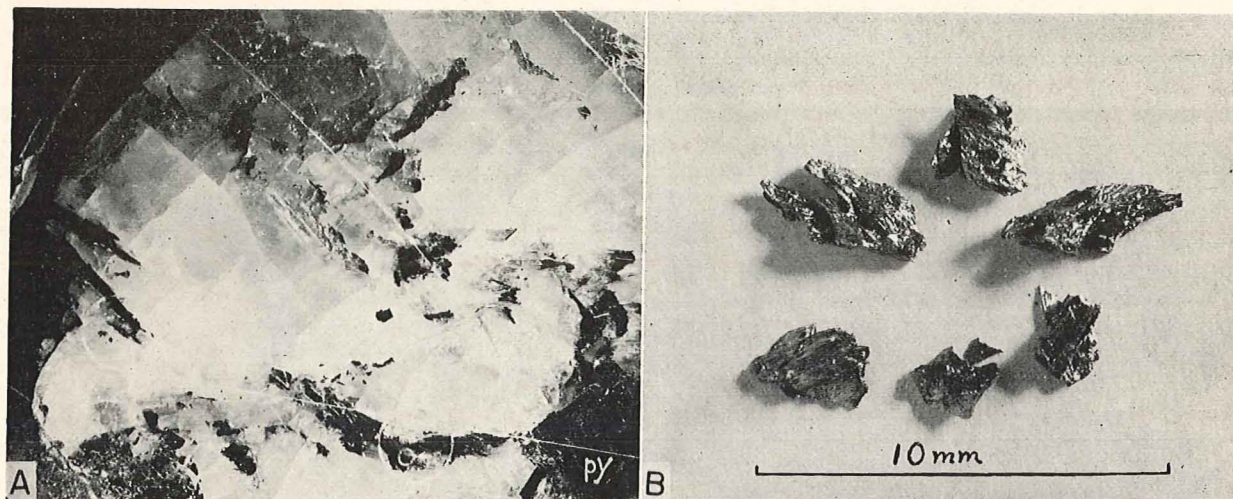


FIG. 3A. Polished surface of specimen DMI showing pyrite cube (py, lower right) and shreds of sulfosalt plunging into semitransparent carbonate gangue. Area shown approximately  $17 \times 23$  mm.

FIG. 3B. Shreds of DMI sulfosalt extracted by dissolving carbonate gangue in HCl. Note irregular outlines and striated surfaces.

Inclusions of Type II may not represent a separate phase from gustavite, an impression strengthened by the intermediate composition of A561,E. Certainly the Pb:Bi ratio is the only substantial difference between Type II, A561,E, and Type III analyses. Karup-Møller (1972) alluded to a range of compositions in gustavite laths from Old Laut, Ouray, Colorado. On the assumption that his published analyses (Karup-Møller, 1972; Table 5) are representative, this range has been plotted in Figure 4. The spread in the Old Laut compositions is roughly equivalent to that between sulfosalt inclusion Types II and III and is explained by Karup-Møller as substitution of  $2\text{Pb}^{2+} + \text{Bi}^{3+}$ . In contrast, the compositional trend established by Type II and III inclusions extends from gustavite toward  $\text{PbS}_{\text{ss}}$ , i.e., higher proportions of Ag are maintained (cf., Fig. 4). Further consideration of this matter is deferred to the discussion.

#### Type IV sulfosalt

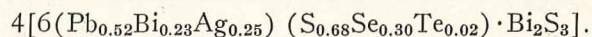
Type IV compositions are represented only in specimens from the late, sulfosalt stage of mineralization. Within the coarse calcite gangue, ragged, striated metallic shreds (Fig. 3) consists dominantly of this phase. Intergrown in patchy texture are lesser amounts of Group 3  $\text{PbS}_{\text{ss}}$  (Table 1); sparse lamellae of a high-Te phase (Table 3) are also common in specimens DMI and DMIA. Euhedral pyrite, 0.1 to 5 mm on an edge, is typically intergrown with the sulfosalt (e.g., Fig. 3A), and minor native Au and sphalerite have been found.

The color of Type IV sulfosalt is variable owing to variation in composition (Table 2, bottom row). Colors similar to galena are typical of the high-Pb,

low-Bi examples, whereas a distinct pale-yellow color is noted for more Bi-rich compositions. Type IV sulfosalt is strongly anisotropic from light gray or from pale yellow to dark yellowish gray. The anisotropism typically reveals an internal lath-like or bladed character that contrasts strongly with the external irregularity of the shreds.

X-ray study has been made of the Type IV sulfosalt by Richard C. Erd of the United States Geological Survey (Erd and Czamanske, in press). Powder data were obtained by grinding material such as that shown in Figure 3B and by gouging material from areas analyzed by electron microprobe. Single crystal data were obtained for smaller crystals dissolved from carbonate gangue. Most X-ray patterns are complicated by the presence of lines ascribed to exsolved  $\text{PbS}_{\text{ss}}$  and to the high-Te phase. The best X-ray data are for material gouged from analyzed area 3501,4 (Table 2 and Fig. 4).

Least-squares computer refinement (Appleman and Evans, 1973) of the X-ray powder diffraction data yields, in Å,  $a = 13.666(3)$ ,  $b = 30.778(5)$ ,  $c = 4.1403(5)$ , with a unit cell volume of  $1741.5(3)\text{Å}^3$ . The diffraction symbol is  $Bb^{**}$  and  $Z = 4$ . The unit cell content for analysis 3501,4 may be idealized as



For this composition  $D_{\text{calc}}$  is  $7.223\text{g/cm}^3$ ; this value compares with specific gravity values of 7.14<sub>4</sub> and 7.37<sub>0</sub> measured by Berman balance on shreds such as those of Figure 3B which are Type IV sulfosalt-galena intergrowths.

All data obtained are comparable to the unit cell parameters measured for natural and synthetic

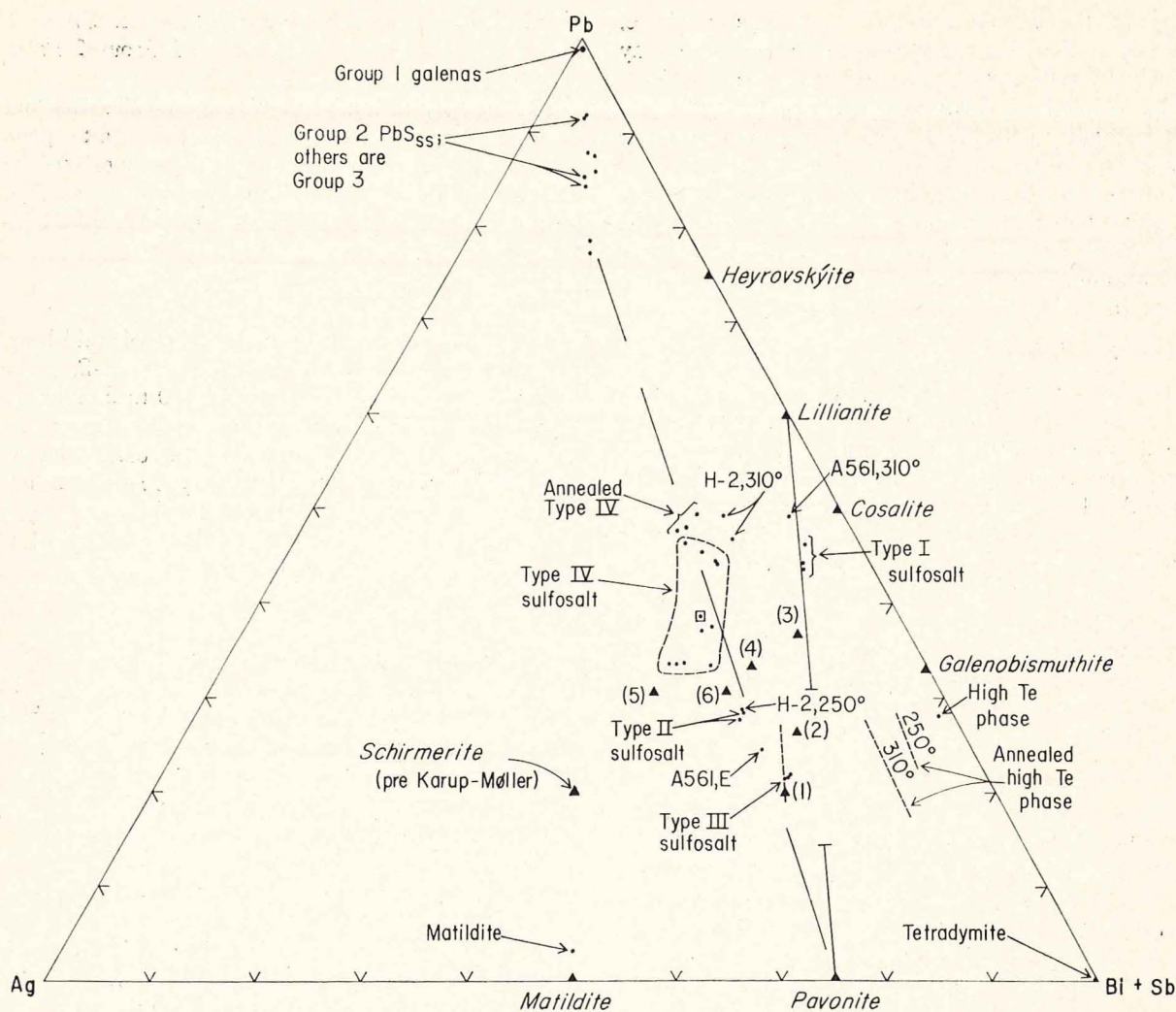


FIG. 4. Schematic ternary diagram showing atomic proportions of metals in the Darwin sulfides and sulfosalts. Proportions of S, Se, and Te are variable among the Darwin minerals, and should be checked by reference to Tables 1, 2, 3, and 4. Compositions of end members referring to locations other than Darwin are marked by triangles; names for such compositions are in italics. The phases heyrovskýite, lillianite, and galenobismuthite are located at points equivalent to the lower temperature compositional limits of phases II, III, and IV of Otto and Strunz (1968) and Salanci and Moh (1970). Compositions marked by bracketed arabic numerals refer to phases identified by Karup-Møller, as follows: (1) gustavite,  $\text{Ag}_3\text{Pb}_5\text{Bi}_5\text{S}_8$  (1972); (2) ivigtut gustavite,  $\text{Ag}_3\text{Pb}_5\text{Bi}_{11}\text{S}_{23}$  (1970a and 1973b); (3) phase X,  $\text{Ag}_2\text{Pb}_7\text{Bi}_{10}\text{S}_{23}$  (197a); (4) "schirmerite",  $\text{AgPb}_2\text{Bi}_3\text{S}_7$  (1973a); (5) M4100 and (6) 2571, "schirmerites" (1973a). Compositional ranges for annealed high-Te phase and gustavite (Karup-Møller, 1972) are indicated by short-dashed lines. The boxed analysis within the area of Type IV sulfosalt is 3501,4 (Table 2) for which X-ray data are presented. An interrupted line represents solid solution between lillianite and pavanite at 500°C as outlined by Hoda and Chang (in press).

heyrovskýite ( $6\text{Pb}_{1-x}\text{Bi}_{2x/3}\text{S} \cdot \text{Bi}_2\text{S}_3$ ) by Klomínský et al. (1971), Otto and Strunz (1968), and Salanci and Moh (1970). Craig (1967), Otto and Strunz, and Salanci and Moh have all designated this phase as Phase II. It is quite puzzling that Type IV sulfosalt is structurally similar to heyrovskýite (Phase II) but appears to be compositionally more closely related to lillianite (Phase III; see Fig. 4). We suggest that this situation is related to the effect of Ag on the sulfosalt structural elements (see later amplified discussion) rather than to the Sb, Se, and

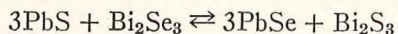
Te impurities in the Darwin, Type IV sulfosalt. The report by Karup-Møller (1970a) that gustavite and lillianite have similar unit-cell dimensions (see Fig. 4) supports this contention.

The Type IV analyses of Table 2 and consideration of Figure 4 show that there is little basis for supposing that the Type IV compositions represent anything other than a solid-solution series in which the dominant substitution is between Pb and Bi + Sb. Across the entire range of compositions there is no systematic change in content of Ag, Se, or Te

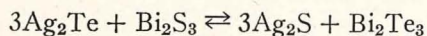
servation that they are equivalent to the high-Te phase noted in unannealed material. Because this phase occurs in both PbS<sub>ss</sub> and Type IV sulfosalt and is present when all else in the DM1 sulfosalt shreds is homogenized, it either exsolved first from the original complex sulfosalt at temperatures above 350°C or, less probably, was a primary phase. Considerable range in composition was measured for the annealed high-Te phase (Table 4), as depicted in Figure 4. On the basis of these compositions, two points seem noteworthy: (1) the high-Te phase is capable of holding more Ag in solid solution at elevated temperatures; and (2) there is the suggestion that the phase was richer in Bi at elevated temperature.

### Discussion

Figure 4 has been constructed for the metals on an atomic percentage basis. No attempt was made to distribute S, Se, and Te among Ag, Pb, and (Bi,Sb) because the data of Table 2 suggest few clearcut correlation patterns among the various elements on which such assignment might be based. Consideration of heats of formation at 25°C for binary sulfides, selenides, and tellurides in reactions such as:



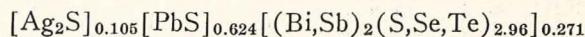
and



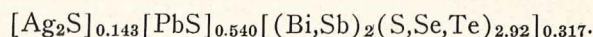
suggests the following order of affinity: (1) for Te, Bi > Pb > Ag; (2) for Se, Ag > Pb > Bi. Little apparent gain would result from more refined calculations for these reactions at elevated temperature. Rather, the calculations are mentioned simply to suggest the relative probabilities of particular bonding neighbors within the mineral structures. The presence of tetradymite and the presence and stability of the high-Te phase clearly support the indicated affinity between Bi and Te. Affinity between Ag and Se is not demonstrable, but compositional variation in the annealed high-Te phase and compositions of high-Se PbS<sub>ss</sub> require Pb-Se association.

Atomic proportions have been presented in all tables but do not give clear indications of charge balance because of the importance of metals of three different valences. Moreover, Otto and Strunz (1968) suggest that cation vacancies exist in sulfosalts of similar chemistry. However, as a check on the analyses and to gain insight into relations between phases, many analyses have been recalculated on the basis of the components [Ag<sub>2</sub>S], [PbS], and [(Bi,Sb)<sub>2</sub>(S,Se,Te)<sub>3</sub>]. The analyses calculate out well on such a basis; for example, analyses DM1A,B and 3501,3, which represent the range of Type IV

compositions, calculate respectively to



and



Overall, for the analyses of Table 2, the subscripts on (S,Se,Te), in which errors of analysis, charge-balance deficiencies, and cation vacancies are accumulated, average about  $3.00 \pm 0.05$ . The presence of the possible components Ag<sub>2</sub>(Se,Te) and/or Pb(Se,Te) does not affect this representation of charge distribution.

It is clear that *rigorous* coupling in the sense of Ag<sup>+</sup> + Bi<sup>3+</sup> substituting for 2Pb<sup>2+</sup> is not characteristic of either galena or exsolved phases at Darwin. Because this is one of the first studies to provide Ag and Bi concentrations attributable to solid solution in Pb(S,Se) and to phases interpreted to have exsolved therefrom, it is important to compare measured, theoretical, and experimental relations. It is also important to note that in studies of this type of ore, workers should ascertain whether Ag and Bi are in fact held in solid solution in PbS or are present as fine exsolution lamellae of AgBiS<sub>2</sub>. D. C. Harris (written commun., 1975), in studying ores from the Fresnillo mine, Mexico, found that gentle etching revealed (at 270× in oil) a complex, lamellar, exsolution texture of AgBiS<sub>2</sub> in galena. These lamellae are so fine and regularly distributed that routine microprobe analysis suggested that the galena carried 7.3 weight percent Ag and 13.7 weight percent Bi in solid solution. Darwin specimens H-2, A561, and DM1 have been examined with great care and show no exsolution lamellae at magnifications of 1050×. In future studies it may be possible to establish whether there are relatively fixed limits on the amount of Ag and Bi which PbS<sub>ss</sub> may hold or whether those limits will depend on the thermal history of the ore.

The maximum solubility of Ag<sub>2</sub>S in PbS is only 0.4 mole percent (Van Hook, 1960), whereas that of Bi<sub>2</sub>S<sub>3</sub> in PbS is  $10 \pm 1$  mole percent (Craig, 1967). This disparity is expectable from consideration of the bonding characteristics of these metal sulfides (e.g., Povarennykh, 1971), but for some time was not reflected in studies of sulfide and sulfosalt composition. After recognition of the mineral matildite, AgBiS<sub>2</sub>, and considering the logic of the substitution Ag<sup>+</sup> + Bi<sup>3+</sup>  $\rightleftharpoons$  2Pb<sup>2+</sup>, there was expectation that Bi:Ag ratios for phases in the system Ag-Bi-Pb-S would be constant at 1:1 (e.g., Ontoev et al., 1960). Indeed, as recently as 1967, no ternary sulfides with Bi:Ag ratios other than 1:1 were known in the system Ag<sub>2</sub>S-Bi<sub>2</sub>S<sub>3</sub>-PbS (Craig, 1967). The studies of Karup-Møller (1970a,

1970b, 1972, 1973a, and 1973b) Borodaev and Mozgowa (1971), and the present work changed that picture, and Hoda and Chang (in press) have now demonstrated extensive solid solution between lillinite and pavonite. While the suggestion by Goldschmidt (1954) that Ag and Bi may be "taken up quite independently into the galena lattice" appears to be overstated, crystal chemical considerations that explain the relative ease of formation of Pb-Bi compounds as opposed to Pb-Ag compounds provide a means of interpreting recent data on natural phases.

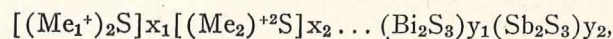
Van Hook (1960) and Hoda and Chang (in press) have engaged in the most extensive discussion of the ratios of Bi:Ag in  $\text{PbS}_{\text{ss}}$ . As indicated in figures 13 and 14 of Van Hook and confirmed by Hoda and Chang, there is natural and experimental evidence that a 1:1 ratio is not required for substitution in PbS. The PbS solid solutions at Darwin must again be considered in three groups. As expected, (Bi + Sb):Ag ratios for the low Ag-Bi galenas of Group 1 are quite variable because the solubility limits of  $\text{Ag}_2\text{S}$  and  $\text{Bi}_2\text{S}_3$  are not exceeded and Ag and Bi are incorporated as available. This study (Table 1, top row) supports that of Leutwein and Herrmann (1954) in suggesting that galenas with low contents of Ag and Bi commonly contain more Ag than Bi. Group 2  $\text{PbS}_{\text{ss}}$  has an average (Bi + Sb):Ag ratio of 1.16 (Table 1, middle row), compatible with the schematic isothermal sections of Van Hook (1960, fig. 13), which suggest that  $\text{PbS}_{\text{ss}}$  is likely to be enriched in Bi over Ag. Further relative enrichment in Bi is evidenced by Group 3  $\text{PbS}_{\text{ss}}$  in which the average (Bi + Sb):Ag ratio is 1.35 and two ratios are  $\geq 1.5$  (Table 1, bottom row).

Considering the markedly higher (Bi + Sb):Ag ratios typical of the sulfosalts phases associated with Groups 2 and 3  $\text{PbS}_{\text{ss}}$  (Table 2), it is apparent that there is some constraint within the PbS structure to approximate the 1:1 substitution. There appears to be a closer approach to 1:1 when  $\text{PbS}_{\text{ss}}$  is the dominant phase and is expelling Ag and Bi from lattice positions at temperatures above 310°C (Group 2  $\text{PbS}_{\text{ss}}$ ) than when the  $\text{PbS}_{\text{ss}}$  is itself the phase exsolved below 250°C (Group 3  $\text{PbS}_{\text{ss}}$ ). (We consider the greater abundance of Se in Group 3  $\text{PbS}_{\text{ss}}$  to be less important in determining (Bi + Sb):Ag ratio.)

Both the  $\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3-\text{PbS}$  and the  $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3-\text{PbS}$  systems (e.g., Chang and Bever, 1973; Hoda and Chang, in press; Hall and Czamanske, 1972) are characterized by numerous phases along the  $\text{PbS}-\text{Bi}_2\text{S}_3$  and  $\text{PbS}-\text{Sb}_2\text{S}_3$  joins and by a number of ternary Ag-(Bi,Sb)-Pb sulfosalts with atomic ratios of Bi:Ag and Sb:Ag greater than 1:1. In contrast,  $\text{Ag}_2\text{S}-\text{PbS}$  binary compounds are unknown, and there are no known ternary phases containing

more Ag than Bi or Sb. Finally, there is an apparent contrast between the  $\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3-\text{PbS}$  and  $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3-\text{PbS}$  systems in that numerous ternary phases of fixed composition appear typical of the Sb-bearing system, whereas both this study and those of Karup-Møller (1970a, 1972) suggest variable Pb:Bi for ternary phases in the Bi-bearing system.

The Bi:Ag ratios for the exsolved phases at Darwin, the several phases described by Karup-Møller (1970a, 1970b, 1972, 1973a, and 1973b), and those reported by Borodaev and Mozgowa (1971) indicate that 1:1 coupling is apparently far less common in nature than might have been supposed from simple considerations of charge compensation. Nowacki (1971) and Povarennykh (1971) have recently reviewed other factors involved in the control of elemental substitutions within mineral structures. Nowacki (1971) has noted that sulfosalts *sensu stricto* are of the type



and we have noted that the phases of Table 2 fit this criterion. From the atomic proportions of Table 2, the sulfosalts at Darwin can be classified according to the structural classification set forth by Nowacki (1971, Table 2) on the basis of the  $\varphi$ -value, where  $\varphi \equiv (\text{S, Se, Te})/(\text{As, Sb, Bi})$ , in terms of atoms. This ratio varies from about 2.0 for Type III (gustavite) inclusions to 3.0 for the annealed Type IV sulfosalt, which is considered representative of initial deposition. These values of  $\varphi$  correspond to Nowacki's classes II, III, and IV; most fall in Class III where  $2 < \varphi < 3$ . This class, of which cosalite is a member, comprises various types of finite groups of connected trigonal pyramids ( $\text{BiS}_3$ ) or tetrahedra ( $\text{BiS}_4$ ).

Two points are notable. First, the entire sulfosalt structural classification is based on the ratio of the anions (S, Se, Te) to the trivalent elements (As, Sb, Bi). In terms of the Darwin sulfosalts, this means that the elements Ag and Pb should be thought of as relating to a structure composed of  $\text{Bi}(\text{S, Se})_3$  pyramids. For sulfosalts, focus on charge compensation, specifically the substitution  $\text{Ag}^+ + \text{Bi}^{3+} \rightleftharpoons 2\text{Pb}^{2+}$ , draws attention from more basic aspects of structural mineral chemistry and is not required by theory, nor is it borne out by natural phase compositions.

Second, Bi may readily assume sixfold coordination, whereas As and Sb do not (Povarennykh, 1971). According to Povarennykh, the association of Pb (which forms relatively weak bonds with sulfur) with the  $\text{BiS}_3$  structural elements weakens bonds within the pyramids such that Bi assumes 6 or even 7 coordination as in the minerals cosalite and galenobismuthite. The observed variation in

Pb:Bi for ternary sulfosalts in the  $\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3-\text{PbS}$  system suggests that the two elements may be of similar coordination. Bonding characteristics and analogy with determined structures on the  $\text{PbS}-\text{Bi}_2\text{S}_3$  join also support the contention that Pb and Bi are both in sixfold coordination in these sulfosalts. If this is true, the structural similarities between Sb and Bi "analogues" will be less than supposed by Karup-Møller (1970a). Povarennykh (1971) noted that, within complex sulfides, isomorphous interchange between As and Sb is much more common than between Sb and Bi. The fact that ternary phases appear to have more fixed compositions in the  $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3-\text{PbS}$  system than in the  $\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3-\text{PbS}$  system may obtain because Sb does not assume sixfold coordination.

In contrast to the effect of Pb, association of more strongly bonding Ag with  $\text{BiS}_3$  structural pyramids will favor stabilization of the pyramids.

It seems appropriate to rationalize the phase compositions plotted in Figure 4, accepting that this is a speculative undertaking. The only experimental study that has established phases within the field bounded by  $\text{PbS}-\text{AgBiS}_2$ ,  $\text{PbS}-\text{Bi}_2\text{S}_3$ , and  $\text{AgBiS}_2-\text{Bi}_2\text{S}_3$  is that of Hoda and Chang (in press). They have demonstrated extensive, but incomplete, solid solution between lillianite ( $3\text{Pb}_{1-x}\text{Bi}_{2x/3}\text{S}\cdot\text{Bi}_2\text{S}_3$ ) and pavonite ( $\text{AgBi}_3\text{S}_5$ ). The limits of this solid solution at  $500^\circ\text{C}$  are indicated schematically on Figure 4 by the solid lines ending in cross-bars; at lower temperatures solid solution is more limited, particularly for pavonite-rich compositions. It is puzzling that the relation of gustavite to the lillianite-pavonite solid solution join is so poor. Gustavite is not only enriched in Ag relative to the join but also lies well within the miscibility gap at temperatures reasonable for ore deposition. As shown by Figure 4, most of the phases here reported relate more closely to the hypothetical join  $\text{PbS}_{88}-\text{AgBi}_3\text{S}_5$  than to the solid solution found by Hoda and Chang. Because pavonite ( $\text{AgBi}_3\text{S}_5$ ) is monoclinic ( $C2/m$ , Nuffield, 1954) over its entire stability range (Craig, 1967), it seems unlikely that significant solid solution exists between  $\text{PbS}_{88}$  and  $\text{AgBi}_3\text{S}_5$ . Yet it seems reasonable that phases of variable composition that exsolve from  $\text{PbS}_{88}$  should lie on a join involving  $\text{PbS}_{88}$ . It may be significant that none of the "primary" ternary phases with  $\text{Bi}:\text{Ag} > 1$  that have been found to date plot to the Ag-rich side of the  $\text{PbS}_{88}-\text{AgBi}_3\text{S}_5$  join. Is it possible that the Darwin Pb-sulfosalt phases have Bi:Ag ratios that are determined by an auspicious balance between the effect of Pb in promoting sixfold coordination for Bi and the contrary effect of Ag in stabilizing  $\text{BiS}_3$  pyramids? Perhaps Ag contents near those represented by the line  $\text{PbS}_{88}-\text{AgBi}_3\text{S}_5$  are the maximum for

which remaining Pb sites will be sufficient to effect sixfold coordination for Bi. Deviation from this balance, as in compositions of Type IV sulfosalt from which Group 3  $\text{PbS}_{88}$  has exsolved, might be explicable on the basis of a model in which withdrawal of major proportions of Pb, as well as Bi and Ag in relatively fixed ratio, leads to residual concentrations of Ag that exceed the most stable balance.

At least three structural types are represented along the join between  $\text{PbS}_{88}$  and  $\text{AgBi}_3\text{S}_5$  as evidenced by unit cell  $b$ -dimensions of roughly  $20\text{\AA}$  (gustavite),  $30\text{\AA}$  (Type IV sulfosalt), and  $44\text{\AA}$  ("schirmerite"). Both the Type IV sulfosalt at Darwin and gustavite have been shown to be variable in Pb:Bi ratio. It is intriguing that primary Type IV sulfosalt apparently evolves toward more Bi-rich compositions whereas deviations from gustavite stoichiometry are toward more Pb-rich compositions (Fig. 4); for compositions between that of gustavite and primary, Type IV sulfosalt,  $\varphi$  will fall between 2 and 3 and only one basic sulfosalt structural type is represented. Analyses available to date support Karup-Møller's suggestion (1970a, 1972) that  $\text{AgPbBi}_3\text{S}_6$  may be an end member. In terms of sulfosalt structure, this composition is significant in that more Bi-rich compositions would lead to values of  $\varphi < 2$ , and another distinct structural type. At this writing, it is not clear how many well-defined phases exist along the  $\text{PbS}_{88}-\text{AgBi}_3\text{S}_5$  join or within the compositional space defined by Figure 4 ( $\text{Ag}_2\text{S}-\text{PbS}-\text{Bi}_2\text{S}_3$ ).

It is unfortunate that the name "schirmerite", long associated with a composition on the  $\text{PbS}-\text{AgBiS}_2$  join, has been ascribed by Karup-Møller (1973a) to a phase of much different composition. [Karup-Møller's seeming ambivalence in ascribing the name gustavite to the formula  $\text{Ag}_3\text{Pb}_5\text{Bi}_{11}\text{S}_{24}$  as well as to  $\text{AgPbBi}_3\text{S}_6$  is also disconcerting (Karup-Møller, 1970a, 1972)]. More fundamental is the fact that in an apparent effort to reduce formula complexity Karup-Møller has, in our estimation, obscured the data. Shown in Figure 4 as points (5) and (6), his data for these two "schirmerites" plot just off the limits of the Type IV field, with 2571 [(6)] quite near in composition to Type II and close to the line drawn between  $\text{PbS}_{88}$  and  $\text{AgBi}_3\text{S}_5$ . Moreover, the geologic occurrence of the two phases might be suspected from the compositions on the basis of previous arguments; 2571 occurs as laths in quartz and presumably represents a freely determined stoichiometry, whereas M4100 [(5)] occurs in an interpreted decomposition assemblage and may be an example of excess residual Ag concentration as we have discussed for Ag-rich examples of Type IV sulfosalt. (Note that Karup-Møller has determined structural parameters that distinguish

his "schirmerites" from the Darwin Type IV sulfosalt.)

The minor phase at Darwin that does not relate to the hypothetical  $PbS_{ss}$ - $AgBi_3S_5$  join of Figure 4 is Type I sulfosalt (and the similar phase in A561 annealed at 310°C). Because cosalite is a common phase, is typically impure, and has metal ratios approximately equivalent to Type I sulfosalt, we suggest that Type I material is cosalite. [Craig (1967) mentions the possibility that cosalite may not be a phase in the pure Bi-Pb-S system.] The establishment of extensive solid solution between lillianite (Phase III) and pavonite ( $AgBi_3S_5$ ) by Hoda and Chang (in press) raises the possibility that Type I inclusions are more closely related to lillianite than cosalite. We have no way of deciding between these two alternatives but prefer the former. Moreover, we question the composition of Phase X (Karup-Møller, 1970a) and its postulated relation to the lillianite solid-solution series (Hoda and Chang, in press). While we see no reason that this composition may not be valid, the profiles shown by Karup-Møller as figure 19 clearly are consistent with the possibility that he has ascribed low Pb, as well as high Ag and Bi values, to this phase. In our opinion, the actual composition of this phase must relate more closely to cosalite (our Type I inclusions) than his analyses suggest, and his ascribed formula is in doubt.

The analyses of Tables 1, 2, and 4 are a remarkable demonstration of the free substitution of Se for S, and the distribution of phase compositions in Figure 4 suggests that the substitution may have little effect on phase relations. Wernick (1960) confirmed the near ideality of the  $PbS$ - $PbSe$  and  $AgBiSe_2$ - $AgBi_3S_5$  solid-solution series. It is thus rather surprising but not inexplicable that Darwin  $PbS_{ss}$  with up to 28 mole percent Se substituting for S plots according to relations described by Van Hook (1960) for the system  $Ag_2S$ - $Bi_2S_3$ - $PbS$ . More noteworthy is the fact that for samples such as H-2 and A561, similar contents of Se are found in coexisting  $PbS_{ss}$ , matildite, Type I, Type II, and Type III sulfosalts. Specimens 3501 and DM1 differ slightly in bulk Se content (Hall, 1971), and this fact is reflected in the Se composition of each of their constituent phases. Data for the phases in DM1 are of particular interest because they demonstrate that Se is actually more uniformly distributed among the various phases than S, i.e., the high-Te phase (Tables 3 and 4) contains roughly equivalent Se but only one-half the S of the other phases. One may consider a model in which an anion framework was established on crystallization, exsolution was dominated by movement of metal ions, and the

smaller  $S^{2-}$  ion (1.74Å) was more mobile than the  $Se^{2-}$  ion (1.91Å).

$Te^{2-}$  (2.11Å) does not readily substitute for Se or S. Wernick et al. (1958) show that  $AgBiSe_2$ - $AgBiTe_2$  is non-ideal below 428°C and that  $AgBiTe_2$  does not even exist stably at room temperature. Formation of tetradyomite (specimen 5) and exsolution of a high-Te phase (specimen DM1) are thus consistent with expectation.

Povarennykh (1971) indicates that although  $Sb_2S_3$  and  $Bi_2S_3$  are isostructural and show complete solid solution (Springer and Laflamme, 1971), isomorphic replacement between the two metals in complex sulfides is limited. Our data agree with those of others (e.g., Jambor and Lachance, 1968; Karup-Møller, 1972) in showing that limited substitution of Sb for Bi is commonplace. The data support other arguments by Povarennykh in showing virtually complete removal of Sb (down to 0.02 weight percent) from  $PbS_{ss}$ , which is dominated by sixfold coordination, to the sulfosalt structure where three- and fourfold coordination is possible. In contrast, up to 7 weight percent Bi remains in the  $PbS_{ss}$ . Garvin (1973) has shown that the solubility of  $Sb_2S_3$  in  $PbS$  is slightly less than 2 mole percent at 400°C, well above the bulk Sb content of the Group 2  $PbS_{ss}$  ores (Hall, 1971). Therefore, exsolution of Sb-enriched phases at Darwin was not dependent on Sb saturation in the host; Sb simply sought the preferred structure.

Experimental studies by Van Hook (1960) and Craig (1967) gave no indication of phases within the  $Ag_2S$ - $S$ - $Bi_2S_3$ - $PbS$  ternary, and the study of Hoda and Chang (in press) does not help appreciably in understanding the Darwin mineralogy. Craig and Barton (1973) note that "relatively small changes in temperature, pressure, and composition might rather strongly modify the configuration of sulfosalt fields in phase diagrams." Two factors may be involved in the understanding of why the complex ternary phases now reported (Fig. 4) were not observed experimentally. In our opinion, the most important consideration is that these ternary phases have demonstrably formed at low temperatures at Darwin (Hall et al., 1971; Rye et al., 1974; and this study) and may be presumed to have low stability temperatures. Complex phases are often difficult to synthesize at low temperatures. Although 400°C would not appear to qualify as "low temperature", Craig (1967) failed to synthesize cosalite, even though he estimated its upper stability limit at 425°C from experiments with natural material. (For a general discussion of this problem, see Goldsmith, 1953.) Another factor, however, is the possibility that the elements Se and Sb, foreign to the  $Ag_2S$ - $Bi_2S_3$ - $PbS$  system studied by Van Hook and Craig,

may have stabilized the complex phases. The existence of Se-free examples of some of these phases (e.g., Karup-Møller, 1970a, 1970b, 1972, 1973a; Borodaev and Mozgowa, 1971) and the near ideality of S-Se substitution makes us favor the theory that these phases are actually proper to the system  $\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3-\text{PbS}$  at low temperature.

Hall (1971) had ample indication from his bulk galena analyses that Sb-content shows no relation to Ag values for the Darwin ores. Our analyses of individual phases also show that Sb and Ag are not coupled in any mineral phase. On the other hand, Hall was clearly justified in relating high Se with high bulk Ag and Bi, but microprobe analyses show that there is no mineralogic basis for this correlation. Because the dominant exsolution phases in the intermediate-stage galenas contain, on the average, about 7 weight percent Ag whereas matildite contains 28 weight percent Ag, we conclude that only about 5 percent rather than 20 percent (Hall, 1971) of the Ag and Bi present in these ores has actually exsolved from galena.

#### Conditions of Deposition

Three totally independent means of estimating temperature have been applied to the Darwin ores with only fair agreement. Hall et al. (1971) estimated temperatures of ore formation by measuring the distribution of Cd and Mn between coexisting galena and sphalerite. Average temperatures of  $377^\circ \pm 32^\circ\text{C}$  and  $416^\circ \pm 20^\circ\text{C}$  were calculated from the distribution constants of Mn and Cd, respectively. Rye et al. (1974) estimated the temperature of sulfide ore deposition at  $325^\circ \pm 55^\circ\text{C}$  on the basis of sulfur isotope fractionation between sphalerite and galena. Both studies were restricted to the dominant Group 1 PbS assemblages pyrite-sphalerite-galena  $\pm$  chalcopyrite and scheelite, and pyrite-pyrrhotite-magnetite-sphalerite-galena because sphalerite is minor in association with Group 2 and 3  $\text{PbS}_{\text{ss}}$ .

The annealing studies reported in this work suggest that the ores were deposited above  $350^\circ\text{C}$  because minor exsolved phases are present at that temperature and are dissolved in their hosts at  $400^\circ\text{C}$ . Annealing studies on the Ag-Sb-rich galena ores from Wood River, Idaho (Hall and Czamanske, 1972) showed that those ores also were deposited at temperatures above  $350^\circ\text{C}$ . The geologic environment and the mineralogy at Darwin suggest higher temperatures than those prevailing at Wood River. Malakhov (1969) and Chang and Bever (1973) have noted that sulphbismuthinides are typical of higher temperature deposits than sulphantimonides. At present we cannot satisfactorily explain the discrepancies between the various geothermometers applied to these ores and assume that

they may result partly from different degrees of re-equilibration. We wish to emphasize that careful annealing studies on exsolved mineral phases can be quite useful as another geothermometer.

Speculative arguments can be presented to explain the chonology of deposition of the distinctive mineral assemblages at Darwin. Evidence from annealing suggests that Group 1 PbS, Group 2  $\text{PbS}_{\text{ss}}$ , and Type IV sulfosalt all were formed above  $350^\circ\text{C}$  and may well have formed over a quite restricted temperature range. As noted, the low-Ag Group 1 PbS that predominates at Darwin is found in two characteristic mineral assemblages as low-grade to massive heavy replacement ore in a calc-silicate gangue. These ores are found deep in the mine, and they presumably were the earliest and highest temperature ores.

The ores in which Group 2  $\text{PbS}_{\text{ss}}$  is found are fine textured and typically massive. They are found in the upper areas of the mine and occur characteristically in podlike or veinlike masses with sharp boundaries. In some near-surface workings, assemblages bearing Group 1 PbS and Group 2  $\text{PbS}_{\text{ss}}$  are in close association. At sample locality A560 both galenas are represented. The specimen reported upon here is a low-Ag, inclusion-free galena, whereas that prepared for analysis by Hall from the same locality (Hall, 1971; Table 1) contained 2.47 weight percent Ag (no doubt the Ag-rich A560 is similar in detail to sample A561 of this report). The fine, steely or massive texture of the Group 2  $\text{PbS}_{\text{ss}}$  ores and their occurrence in veins and small pods at shallow depth suggest that, compared with Group 1 PbS ores, these ores have been precipitated more rapidly in relatively low pressure environments. Little silicate or carbonate gangue is associated with this ore.

Chang and Bever (1973) have reaffirmed the notion that ". . . through passing time and decreasing temperature . . . the crystallization sequence is generally from high lead sulfide-low trivalent metal sulfide content to low lead sulfide-high trivalent metal sulfide content." The chemical hiatus in  $\text{PbS}_{\text{ss}}$  composition between Group 1 PbS and Group 2  $\text{PbS}_{\text{ss}}$  (Table 1) would thus classically be related to evolution of the system in time and temperature. We cannot exclude the possibility that spatial relations and the effect of lower pressures on fluid chemistry and mixing were of equal or greater importance.

In our experience, the exotic sulfosalt assemblages in ores of the Darwin type are spatially marginal to more typical, heavy galena-sphalerite ores. The sulfosalt mineralization is very restricted within the Darwin mine and is the only mineralization associated with predominantly carbonate gangue. This



mineralization at Darwin can be readily interpreted as the culmination of the Ag, Bi, Se-enrichment that set Group 2 PbS<sub>ss</sub> apart from Group 1 PbS. The Darwin example is the first for which three distinct stages of enrichment have been clearly demonstrated. The ultimate reason for deposition of increasingly Ag-Bi-rich ores at shallow depths has not been determined by us at Darwin.

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