THE AMERICAN MINERALOGIST
JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 50 MARCH–APRIL, 1965 Nos. 3 and 4

RECENT ADVANCES IN SULFIDE MINERALOGY

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Today it is my privilege, as a result of the honor you have bestowed upon me in electing me as your president, to address you on some mineralogical subject which I have explored. While my detailed mineralogical studies have become more scattered in recent years due to an increasing preoccupation with teaching and administration, I am attempting here to review the recent developments in the study of the sulfosalt minerals and to discuss the problems of their classification and relation to the more numerous and better known sulfide minerals. Some twenty years ago (Berry, 1943) I proposed a systematic arrangement on the basis of cell dimensions at a time when very little was known about the detailed atomic arrangement of the sulfosalts. This work showed the recurrence of certain lattice dimensions but did not suggest a useful basis for classification. Several small groups of structurally related minerals were apparent but a number of minerals stood alone.

In "The Peacock Atlas" of *x*-ray powder data for the ore minerals (Berry and Thompson, 1962) the marked crystallographic similarities between sphalerite, tetrahedrite, colusite, germanite and sulvanite resulted in their grouping in the sulfides. It also appeared reasonable to group teallite with herzenbergite in the sulfides rather than separating them as in Dana's System, volume 1 (Palache *et al.*, 1944).

Following a structural study of some of the complex lead sulfosalts which had not been attempted before, Hellner (1958) proposed a classification which ignores the classical distinction between sulfides and sulfosalts. He showed that many sulfide structures can be derived from close packing of sulfur with metals in tetrahedral (as in sphalerite) and/or octahedral holes (as in galena). This led to three main groups (I—metals in tetrahedral sites; II—metals in both tetrahedral and octahedral sites; III—metals in octahedral sites) and two additional groups (IV—in which parts of the structures have close packed sulfur with metals in tetrahedral and/or octahedral sites and V—those structures which do not fit the classification). Each of the groups I–IV can also be subdivided on the basis of the type of close packing of sulfur—hexagonal, cubic or any other type of close packing. Most of the complex sulfosalts fall in group IV, a few in III, and tetrahedrite, enargite and others in I. It was further proposed that the minerals should be also subdivided on the total metals to sulfur ratio. In this subdivision a large proportion have a ratio of 0.9 to 1. In general all sulfosalts with metals in tetrahedral holes have ratios from 1.33 to 0.9 while those with metals in octahedral holes have ratios from 1 to 0.8. Most of the complex sulfosalts (in group IV with only parts of structures close packed) have ratios from 1 to 0.5.

In view of the complexity of this classification it seemed desirable to reexamine the basis for distinguishing between the sulfide and sulfosalt classes as defined in Dana's System in the light of the latest knowledge on the structures of these minerals. In Dana, sulfides include A_mX_n compounds where A is one or more metals or semi-metals while X may be S, Se, Te, As, Sb or Bi. Sulfosalts on the other hand are "multiple" sulfides $A_mB_nX_p$ in which A is one or more metals, B a semi-metal and X is S or very rarely Se. Most of the metals and semi-metals found in sulfosalts are also found in simple sulfides. However, in sulfosalts lead and silver are the commonest metals, copper and iron are less common while mercury, thallium and manganese are rare. Sulfosalts always include arsenic, antimony, bismuth, rarely germanium, tin or vanadium. Tellurium has been reported in colusite and tetrahedrite ("goldfieldite"), selenium has been noted in polybasite substituting for sulfur (Harris *et al.* 1965).

During the early years of crystal structure studies only a few sulfosalts were subjected to analysis, for pyrargyrite and proustite (Harker, 1936), tetrahedrite and tennantite (Pauling and Neumann, 1934), enargite (Pauling and Weinbaum, 1934) chalcostibite (Hofmann, 1933) the general aspect of the structure and atomic parameters were found. In the past twelve years several laboratories have attempted structural analysis of these minerals using modern methods. New structural data have been published for about 18 sulfosalt minerals. For most, atomic positions and interatomic distances are given, for some only a general view of the structural arrangement is described. For only 8 sulfosalts, including a restudy of tetrahedrite, have the atomic positions been refined to a discrepancy factor R of less than 20 per cent, five are antimony compounds, one arsenic and one bismuth. In addition two sulfides, orpiment and stibnite, which are of particular interest in our present discussion have been refined to an R factor of less than 20.

From this survey, I find that we know a good deal less about the detailed structure of the sulfosalts than I had expected. There are still many interesting minerals to study and a great deal of information is still lacking. Hellner has shown that a number of the complex sulfosalts have small portions in which sulfur is essentially in cubic close packing with the metals occupying octahedral sites. Between these portions there are irregularities resulting from seven- or eight-fold coordination of lead-sulfur.

In the following section the interatomic distances and coordination features found for metal—sulfur in the sulfides and sulfosalts are compared with those for "semi-metal—sulfur."

METALS

Lead. Lead occurs in galena in six-fold coordination with sulfur at an interatomic distance of 2.965 Å. Lead, the commonest heavy metal in sulfosalts, is reported to occur in five-, six-, seven-, eight- or nine-fold coordination with sulfur at average distances ranging from 2.66 in five-fold to 3.20 in eight-fold and 3.17 in nine (Table 1). The value 2.66, an average of five values 2.27 to 3.02 reported in gratonite (Rosch, 1963), is unexpectedly low although the *R* factor given for the final refinement is 19.9%. Average values for Pb-S from other refined structures with *R* factors (about 21% or less) range from 3.04 to 3.17 with six to nine-fold co-

TABLE 1. AVERAGE LEAD-SULFUR DISTANCES (Å)

Mineral	Coordination Number				
	5	6	7	8	9
galena		2.965			
gratonite	2.66	3.14			
sartorite					3.17
seligmannite				3.17	
				3.15	
rathite I		2.95–3.10			
rathite III		2.8–3.0			2.95–3.3
hutchinsonite (Tl,Pb)$_{I}$			3.08		
(Tl,Pb)$_{II}$			3.25		
freieslebenite		2.97			
jamesonite			3.04	3.09	
bournonite				3.18	
				3.20	
meneghinite			3.05		
			3.06		
meneghinite (Pb+Sb)		2.97 (2)			
meneghinite (Pb $\frac{1}{4}$+Sb $\frac{3}{4}$)		2.92			
galenobismutite				3.12	
cosalite		2.92		3.11	
		2.82		3.15	
aikinite (Pb+Bi)			3.00		
			2.99		

ordination. Nine-fold coordination has been found in sartorite (pseudo-cell refined to an *R* factor of 21%, Nowacki *et al.*, 1961). The six chemical bonds (the six shortest lead-sulfur distances) average 3.03 for the refined sulfosalt structures. The additional bonds in seven-, eight- and nine-fold coordination range from 3.21 to 3.76. The Pb-S_6 polyhedron is a regular octahedron in galena. In the sulfosalts which have lower symmetry, the much larger number of atoms are often located in general positions in the space group, and the polyhedra are very irregular in shape.

In the lead-sulfur polyhedra found in sulfosalts the interatomic distances are usually unlike. The octahedron formed by the six shortest bonds are very irregular in structures where there are seven, eight or nine lead-sulfur distances of moderate length. The six shortest bonds have an average length close to that in galena. In jamesonite (with $R=16.6\%$, Niizeki and Buerger, 1957) Pb-S_7 has six lengths 2.85 to 3.08 with the seventh at 3.58, and Pb-S_8 has six lengths 2.91 to 3.13 with others at 3.29 and 3.39. In many cases one cannot distinguish six particular bonds as the "chemical bonds" on the basis of length. In galenobismutite (with *R* 10%, Iitaka and Nowacki, 1962) Pb-S_8 has six lengths 2.85 to 3.21 with the other two at 3.21 and 3.76.

Iron. Iron occurs in sulfides with four-fold or six-fold coordination (Table 2). In the recently described mineral greigite (Skinner *et al.*, 1964) the four-fold iron-sulfur distance is 2.148 Å, in chalcopyrite and cubanite the distance is 2.28 and 2.25 (average) respectively. In greigite and low temperature hexagonal FeS the six-fold iron-sulfur distance is 2.466 and 2.50 (average) respectively. In sulfosalts iron is a major constituent in berthierite (Buerger and Hahn, 1955) and jamesonite where it is found in six-fold coordination with iron-sulfur distances: 2.45 to 2.65 (berthierite) and 2.36 to 2.66 (jamesonite) averaging 2.53 in both cases. The polyhedron is close to a regular octahedron and similar to that found in sulfides. Iron is also found substituting for copper in tetrahedrites where it is in four-fold coordination with sulfur (Cu-S, 2.25 and 2.34).

TABLE 2. AVERAGE IRON-SULFUR DISTANCES (Å)

	Tetrahedral	Octahedral
Greigite	2.148 (4)	2.466 (6)
Chalcopyrite	2.28 (4)	
Cubanite	2.25 (4)	
Berthierite		2.53 (6)
Jamesonite		2.53 (6)

TABLE 3. AVERAGE COPPER-SULFUR DISTANCES (Å)

	Planar	Tetrahedral
Covellite	2.19 (3)	2.31 (4)
Cubanite		2.31 (4)
Chalcopyrite		2.28 (4)
Stromeyerite	2.28 (3)	
Enargite		2.32 (4)
Tennantite	2.25 (3)	2.28 (4)
Seligmannite		2.36 (4)
Tetrahedrite	2.25 (3)	2.343 (4)
Chalcostibite		2.42 (4)
Bournonite		2.44 (4)
Aikinite		2.33 (4)

Refinement of the tetrahedrite structure (carried out on nearly pure $Cu_{12}Sb_4S_{13}$) has not revealed whether iron favours one of the two copper sites. The metal-sulfur distance here is close to that found for tetrahedral iron-sulfur in sulfides.

Copper. In sulfides copper occurs in three-fold and four-fold coordination with distances of 2.19 Å to 2.28 and 2.28 to 2.31 (averages) respectively (Table 3), it also occurs in digenite in six-fold coordination with Cu-S about 2.77. Copper is the major metal constituent in chalcostibite, tetrahedrite, enargite, and seligmannite, bournonite, aikinite, it is a minor constituent in meneghinite, of these only tetrahedrite (Wuensch, 1963) has been refined to a low R factor (5%), with Cu-S_3 (planar) 2.25 and Cu-S_4 (tetrahedral) 2.343 similar to the values found in chalcocite, stromeyerite, chalcopyrite, covellite, cubanite and enargite. In chalcostibite there are two short Cu-S_4 (tetrahedral) distances and two longer averaging 2.42. In seligmannite, bournonite ($R=30\%$, Leineweber, 1956) and aikinite there are three short Cu-S_4 (tetrahedral) distances (2.25 to 2.41) and one longer (2.40 to 2.76) averaging 2.36, 2.44 and 2.33 respectively. In meneghinite the copper atom has not been located in the structure refinement by Euler and Hellner (1960). Electron probe study by Fredriksson and Anderson (1964) shows that Cu is a real constituent of meneghinite. The tetrahedral Cu-S distances are similar to those found in sulfides.

Silver. Knowles (1964) has recently refined the structure of miargyrite ($R=13\%$), in it silver is coordinated to two sulfur atoms at 2.41 Å or to three sulfur atoms at 2.51 (Table 4). Both silver positions approximate six-fold coordination with average distances 2.98 and 2.87. The first corresponds to that reported by Harker (1936) in pyrargyrite and proust-

TABLE 4. AVERAGE SILVER-SULFUR DISTANCES (Å)

Stromeyerite	2.40 (2)		
Proustite	2.40 (2)		
Pyrargyrite	2.40 (2)		
Miargyrite	2.41 (2)	or	2.98 (6)
	2.51 (3)	or	2.87 (6)
Freieslebenite	2.95 (6)		

ite and by Frueh (1956) in stromeyerite. In freieslebenite, Hellner (1957) reports silver in six-fold coordination with distances ranging from 2.7 to 3.33 (average 2.95). This average distance falls between those found for antimony (2.77, 2.86, 2.93, averages for six-fold) and lead (2.97 for six-fold). The minimum distance also falls between that for antimony (2.41) and for lead (2.86). The *R*-factor for the freieslebenite structure ranges from 31% to 41% in the zones [010], [100] and [001]. Further refinement should improve the *R* factors if this structural scheme is correct.

Mercury. Mercury occurs as a major constituent only in livingstonite which has been refined to an *R* factor of 13% by Niizeki and Buerger (1957). Here mercury is in six-fold coordination with average distances of 3.01 Å and 3.03 corresponding closely to the distances in cinnabar (2.92) (Table 5). Livingstonite is unique as the only example of a sulfosalt with close bonding of pairs of sulfur atoms (2.07) as found in pyrite.

Arsenic, Antimony and Bismuth

Most of the typical sulfosalts contain one of these elements. In a few cases there is evidence of solid solution between sulfarsenites and sulfantimonites (tetrahedrite, polybasite, enargite, bournonite, jordanite and ruby-silver groups). Kobellite and aramayoite contain both antimony and bismuth.

Germanium, tin and vanadium form minerals with copper or silver which have been classified with the sulfosalts.

Sulfarsenites. The structure of orpiment has been refined to an *R* factor of 18% by Morimoto (1954). Arsenic is bonded to three sulfur atoms at

TABLE 5. AVERAGE MERCURY-SULFUR DISTANCES (Å)

Cinnabar	2.36 (2)	or	2.92 (6)
Metacinnabar	2.53 (4)		
Livingstonite	2.33 (2)	or	3.01 (6)
	2.37 (2)		3.03 (6)

distances of 2.21 Å to 2.28 (2.24 average) and 2.23 to 2.26 (2.25 average). The next closest sulfur atoms are at 3.13 or 3.16 (Table 6). Similar distances are reported in proustite (2.25), and tennantite (2.21) although these structures have not been refined. Among the complex lead sulfarsenites the values for gratonite (2.39 and 2.59 averages) are substantially higher. In sartorite and baumhauerite the three shortest As-S distances average, 2.46, 2.52 and 2.55, each arsenic has two other sulfurs at about 2.9, rathite has similar As-S distances. The *R* factors for gratonite and sartorite are given as 20 and 21% respectively. In seligmannite (no *R* factor given) each arsenic has three close sulfur neighbors at 2.29 or 2.50 (average) and three additional neighbors at 3.40 to 3.99. In enargite arsenic is tetrahedrally bonded to four sulfurs at 2.21 to 2.24 (Pauling and Weinbaum, 1934). In lorandite, refined to *R* (*h*0*l*) 10% and *R* (*hk*0) 18% (Zemann and Zemann, 1959) the three shortest As-S distances average 2.23 and 2.33 and in hutchinsonite (Takéuchi *et al.*, 1964) the three shortest As-S distances average 2.28 and 2.34.

The data at hand indicate that arsenic bonds closely with three sulfur neighbors in both the sulfides and sulfosalts. In some complex sulfosalts two or three additional sulfurs are present at significantly greater distances.

TABLE 6. ARSENIC-SULFUR INTERATOMIC DISTANCES (Å)

	Shortest Distance	Second and Third Distance	Fourth and Fifth Distance	Others
Orpiment[1]	2.21	2.22, 2.28	3.16, 3.44	4.00, 4.22
	2.23	2.26 (2)	3.13, 3.56	4.24, 4.50
Tennantite	2.21	2.21 (2)		
Proustite	2.25	2.25 (2)		
Enargite	2.21	2.21, 2.24	2.24	
Gratonite[1]	2.39	2.39 (2)		
	2.18	2.80 (2)		
Seligmannite	2.16	2.36 (2)	3.65, 3.99	3.99
	2.37	2.37, 2.77	3.40, 3.54	3.54
Sartorite[1]	2.12	2.63 (2)	2.92 (2)	
	2.38	2.59 (2)	2.89 (2)	
Baumhauerite	2.2	2.55 (2)	2.85, 2.95	
Rathite I	2.15	2.6	~ 3 (3)	
Rathite III	2.1	2.6	~ 3 (2)	
Lorandite[1]	2.05	2.25, 2.39		
	2.15	2.16, 2.35		
Hutchinsonite[1]	2.25	? , 2.40		
	2.24	? , 2.34		

[1] Refined to $R=21\%$ or less.

Sulfantimonites. Antimony is a major constituent of nearly half of the known sulfosalts; and sulfantimonites are of more widespread occurrence than compounds of arsenic or bismuth.

The structure of stibnite has been refined to an R factor of 11% by Scavnicar (1960). One antimony atom has three close sulfur neighbors at 2.57(2) and 2.58 Å forming a trigonal pyramid with Sb at the vertex. One S-S (3.84) edge of the base is parallel to c and these sulfurs are shared between Sb-S_3 pyramids forming a chain. The second antimony atom has five close sulfur neighbors at 2.49, 2.62(2) and 2.82(2). The five sulfurs form a square pyramid with antimony near the centre of the base, the vertex sulfur is the closest to antimony. Two shorter edges (3.84) of the nearly square base are parallel to c, the two longer edges (4.02) are shared with adjacent pyramids forming a chain. Two such chains related by the two fold screw-axis are connected by sharing lateral, S-S (3.55) edges of the pyramids. This double square-pyramid chain $(Sb_2S_4)_n$ is linked to two trigonal chains by sharing corner S atoms to form a ribbon-like polymer $(Sb_4S_6)_n$ roughly parallel to (010), almost equal to a in width, and extending indefinitely along c. The ribbons are linked along their edges by longer Sb-S bonds (3.20) from the first type of antimony atom to form sheets parallel to (010). The sheets are linked by still longer Sb-S bonds (3.33 and 3.60) which are roughly parallel to b. These bonds, however, are shorter than the sum of the van der Waals radii for Sb and S (4.05).

The berthierite structure, (Buerger and Hahn, 1955, Fig. 13) displays similar square pyramids Sb-S_5 with Sb-S distances of 2.48, 2.58(2) and two of 2.93. These square pyramids also form a $(Sb_2S_4)_n$ chain parallel to c. As in stibnite antimony is near the centre of the base, at 2.48 from the vertex sulfur and displaced slightly outside the S_5 pyramid. The dimensions of the square base are $3.76 = c$, and 3.83, parallel to (001) and shared with adjacent pyramids. There are two such chains to a unit cell. The second antimony atom occurs in Sb-S_3 pyramids with the Sb-S distances of 2.43 and 2.48(2) with one base edge (S-S = 3.76) parallel to c, sharing corner sulfurs to form a $(SbS_2)_n$ chain, with four chains to one unit cell. The single chains $(SbS_2)_n$ are linked by four chains of Fe-S_6 octahedra to the double chains $(Sb_2S_4)_n$. Three of the Fe-S_6 sulfurs are shared with the single chains, and the other three with the double chains, the latter by sharing S-S edges. There are longer Sb-S bonds 3.24(2), 3.47, 3.56(2), 3.63 between the single and double chains, but they do not clearly suggest a cleavage direction.

In jamesonite, refined by Niizeki and Buerger (1957) to an R factor of 16.6%, there are three distinct antimony positions in the structure, the

Sb-S distances are shown in Table 7. In each case antimony and the three closest sulfurs form a trigonal pyramid group but none of the pyramid edges are parallel to *c*. If the five closest sulfurs are considered, each SbS_5 group again takes the form of a square pyramid with antimony close to but slightly outside of the square base. The apex sulfur atom to antimony distance is again the shortest. The square pyramids are less regular, and a few of the distances are longer than those in stibnite or berthierite. Two edges of the square base of each pyramid are parallel to *c* (4.03 Å), the other two are roughly perpendicular to *c* with lengths about 3.80, 3.90, 3.99. The three SbS_5 pyramids are linked in a row (Sb_3S_7) nearly parallel to (120) by sharing the S-S edges parallel to *c*. In jamesonite, in contrast to berthierite and stibnite, the longer edges of the square pyramid base are parallel to *c*, the shortest Sb-S bonds are nearly parallel to (001) and the next two shortest in each pyramid are inclined to (001) at an angle of about 40°. Each $(Sb_3S_7)_n$ group shares two sulfurs at one end with FeS_6 octahedra and five sulfurs with PbS_{6-8} polyhedra. Two

TABLE 7. ANTIMONY-SULFUR INTERATOMIC DISTANCES (Å)

	Shortest Distance	Next Two Distances	Fourth and Fifth Distances	Others
Stibnite[2]	2.57	2.57, 2.58	3.15 (2)	3.60
	2.49	2.68 (2)	2.82 (2)	3.33
Berthierite[2]	2.48	2.58 (2)	2.93 (2)	3.56 (2), 3.63
	2.43	2.48 (2)	3.24 (2)	3.47
Jamesonite[2]	2.41	2.52, 2.67[1]	2.82, 2.90	3.29, 4.08
	2.43	2.56 (2)[1]	3.04, 3.07	3.51, 4.29
	2.44	2.56, 2.81	2.94, 3.18	3.57[1], 4.40
Chalcostibite	2.44	2.52 (2)	3.11 (2)	3.66
Livingstonite[2]	2.49	2.54, 2.70	2.94, 2.95	3.57, 3.75
	2.44	2.47, 2.52	3.11, 3.15	3.25, 3.62
	2.47	2.55, 2.62	2.95, 2.96	3.51, 3.86
	2.54	2.59, 2.66	2.88, 2.98	3.24, 3.63
Bournonite	2.58	2.70 (2)	3.21, 3.58	3.58, 3.78 (2)
	2.69	2.69, 2.86	3.37 (2)	3.47, 3.88 (2)
Tetrahedrite[2]	2.436	2.436 (2)	4.03 (2)	4.03 (4)
Miargyrite[2]	2.53	2.58 (2)	3.14, 3.25	3.28
	2.48	2.49, 2.54	3.26, 3.29	3.34
Freieslebenite	2.46	2.54, 2.72	2.94, 2.94	3.45
Pyrargyrite	2.43	2.43 (2)		

[1] Tabulated values, slightly different values are given on Figure 19.

[2] Refined to *R* factor to 16% or less.

$(Sb_3S_7)_n$ groups occur base to base linked by long Sb-S bonds (3.29 to 4.40). These weak bonds, across a plane parallel to (120), are consistent with a prismatic cleavage and the weaker bonds parallel to *c* explain the (001) cleavage.

In chalcostibite, livingstonite, freieslebenite, bournonite, and miargyrite the three shortest Sb-S distances outline similar trigonal pyramids. In the first two of these there is clear indication of SbS_5 square pyramids similar to stibnite and berthierite. In tetrahedrite and pyrargyrite the SbS_3 pyramids have trigonal symmetry with Sb-S bonds of 2.436 and 2.43 respectively. In bournonite there is no indication of the square pyramid configuration without including substantially longer Sb-S distances.

As with arsenic, the bonding of antimony to sulfur is very similar in the simple sulfide, stibnite, and in the sulfosalts but differs markedly from that of the metals with which it is associated. The contrast between the $Sb\text{-}S_3$ distances and the next two or more Sb-S distances is less marked than in arsenides. In meneghinite (Euler and Hellner, 1960), two of the metal positions are occupied by both lead and antimony atoms.

Sulfobismuthites. Bismuthinite is very similar in morphology and lattice dimensions to stibnite, and Hofmann (1933b) states that it has a similar structure. The structure has not been refined, and the atomic parameters are not known. Hofmann (1933a) also states that emplectite is isostructural with chalcostibite but the atomic parameters or interatomic distances were not determined. The structures of aikinite (Wickman, 1953), cosalite (Weitz and Hellner, 1960), and galenobismutite (Iitaka and Nowacki, 1962) have been solved in recent years. The latter, refined to an *R* factor of about 10%, shows bismuth in six- and seven-fold coordination with sulfulr. In the six-fold position three distances are 2.63 Å and 2.73(2), the other three are 2.99(2) and 3.12. In the

TABLE 8. BISMUTH-SULFUR INTERATOMIC DISTANCES (Å)

	Shortest Distance	Second and Third	Fourth and Fifth	Others
Galenobismutite	2.63	2.73 (2)	2.99 (2)	3.12, 3.63
($R=10\%$)	2.78	2.78, 2.79	3.00, 3.02	3.02, 3.10
Cosalite	2.62	2.83 (2)	2.85 (2)	3.25
($R=25\%$)	2.64	2.72 (2)	2.94 (2)	3.05
	2.62	2.85 (2)	3.04 (2)	3.44
	2.54	2.66 (2)	3.04 (2)	3.31
Aikinite	2.84	2.87 (2)	2.99 (2)	3.12, 3.35
(Pb or Bi)	2.88	2.88, 2.93	2.93, 2.98	3.16 (2)

seven-fold position three Bi-S distances are 2.78(2) and 2.79, the other four range from 3.00 to 3.10. In both cases the Bi-S_3 distances are less than most Pb-S distances and the Bi-S_6 distances give a lower average than most Pb-S_6 distances.

In cosalite (R factor 25%) the bismuth-sulfur distances range from 2.54 to 2.85 for Bi-S_3 and to 3.44 for Bi-S_6, with averages for Bi-S_6 from 2.84 to 2.97. The shortest distances are less than most Pb-S distances and less than the shortest Pb-S distances in cosalite, however, the average Bi-S_6 distances are not distinguishable from the two Pb-S_6 average distances in cosalite (2.82 and 2.92). This indicates some uncertainty in the identification of some of the metal positions in cosalite. The structure analysis of aikinite identifies the copper positions but does not distinguish between lead and bismuth. The two latter positions are seven-fold with M-S_7 distances of 2.84 to 3.35 with averages of 2.99 and 3.00.

In sulfobismuthites short metal-sulfur distances have been used to distinguish between lead and bismuth. The coordination of bismuth to three sulfur neighbors compared with the next three sulfur atoms is not as distinct as in the arsenic and antimony compounds. It would be interesting to compare these structures with bismuthinite and emplectite where the bismuth positions may be identified with certainty.

CONCLUSIONS

Iron, copper, silver and mercury occur in sulfide and sulfosalt minerals with very similar coordination with sulfur. In sulfosalts iron is found mainly in six-fold coordination but probably substitutes for four-fold copper in tetrahedrites.

Lead occurs in six-fold coordination with sulfur in galena but is found in five- to nine-fold in sulfosalts, although mainly in six- or eight-fold coordination. The lead-sulfur distances for six-fold are similar in galena and sulfosalts. In seven, eight and nine-fold the average lead-sulfur distances are larger than in six-fold by three to eight per cent.

In both sulfides and sulfosalts, arsenic, antimony and bismuth each form trigonal pyramids with their three closest sulfur neighbors. In some arsenic sulfosalts other sulfurs occur at substantially greater distances, except in enargite where tetrahedral coordination occurs.

Antimony-sulfur trigonal pyramids form single chains by sharing corner atoms in stibnite and berthierite. Some antimony atoms, with three close sulfur neighbors (2.41 to 2.8) and two others at 2.82 to 2.98, form square pyramids which form double chains by sharing edges. Various $(Sb_xS_y)_n$ polymers occur which are cross linked by lead or iron polyhedra or by longer Sb-S bonds. Bismuth has three close sulfur neighbors at distances distinctly less than those for lead-sulfur and three additional sulfurs at distances of 3.0 to 3.3 approximately six-fold coordination similar to that found for lead.

In all sulfosalts for which structural data is available the metal to sulfur bonding is distinctly different from the arsenic, antimony or bismuth to sulfur bonding. In bismuth compounds this distinction is less marked. Complex polymers analogous to those in oxygen salts are present in some sulfosalts. The latest structural studies support the classical distinction between sulfides and sulfosalts although there are close similarities between some members of the two classes. These studies show that galenobismutite and berthierite are not isostructural as might have been thought from the similarities in formula and lattice dimensions. Further structural refinements are required to confirm the isostructural character of proustite-pyrargyrite, tennantite-tetrahedrite, chalcostibite-emplectite and others.

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