THE Pb–Bi–Ag–Cu–(Hg) CHEMISTRY OF GALENA AND SOME ASSOCIATED SULFOSALTS: A REVIEW AND SOME NEW DATA FROM COLORADO, CALIFORNIA AND PENNSYLVANIA

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ABSTRACT

Galena, associated with Pb–Bi–Ag sulfosalts and simple sulfides, contains varied amounts of Ag and Bi in the Dandy vein system, Idarado mine, Ouray, Colorado; the Jackass mine, Darwin District, California; and the Leadville district, Colorado. Silver- and bismuth-bearing galena associated with minor amounts of pyrite, chalcopyrite and sphalerite occur at the Pequea mine, Lancaster County, Pennsylvania. Ag and Bi contents in the Dandy suite of galena range from about 1.4 to 3.4 and 2.5 to 6.5 wt.% respectively, and are comparable or lower in galena from the other localities. Exsolved matildite is present in galena from the Dandy, Jackass and Leadville localities. The presence in significant amounts of both Ag and Bi in a Pb-rich sulfide system is necessary for formation of PbS_{ss} (galena solid-solution). If Ag (especially) and Bi (to a lesser extent) are absent, the galena formed will be essentially pure PbS. Some minor Sb may substitute for Bi. Compositional data for all of the galena samples are in agreement with a previously proposed linear relationship between a and Ag–Bi(Sb) content. Matildite and seven additional Pb–Bi–Ag–Cu sulfosalts have been identified from the Dandy vein system, based on electron-microprobe analyses and some X-ray powder-diffraction data. The sulfosalts include gustavite$_{65}$lillianite$_{35}$, nonstoichiometric aikinite and friedrichite, heyrovskyite and one Ag-bearing Pb–Bi sulfosalt with $N_{chem} = 8.4$, which may be eskimoite(?) or heyrovskyite$_{ss}$. A Cu–Ag–Pb–Bi sulfosalt with $N_{chem} = 7.25$, which may be the Cu-dominant analogue of eskimoite(?), Cu-substituted heyrovskyite$_{ss}$ or a new Pb–Bi–Cu–Ag sulfosalt, also is present. An unidentified Bi–Pb–Ag sulfosalt with $N_{chem} = 6.06$ and a composition close to vikingite also was found. Eskimoite(?) or Ag-bearing heyrovskyite(?) with $N_{chem} = 8.19$ also was identified in high-grade silver ore from the Jackass mine. The sample from Leadville contains major amounts of galena and matildite along with minor amounts of hessite and "tellurian canfieldite", $Ag_8SnS_4Te_2$, as well as very sparse aikinite and two unidentified Cu–Pb–Bi–Ag sulfosalts, one of which may be Cu- and Bi-substituted galena. An Sb-bearing Bi–Pb–Ag sulfosalt, most likely ourayite (Our$_{73}$) was identified from the Wombat mine, Montezuma district, Colorado. Multiple stages of mineralization, some possibly involving reheating cycles, are known to have occurred at four of these five localities and are believed responsible for the formation of multiple galena solid-solutions (PbS_{ss}) as well as the complex Pb–Bi–Ag–Cu sulfosalt assemblages.

Keywords: galena, PbS_{ss}, Pb–Bi–Ag–Cu sulfosalts, California, Colorado, Pennsylvania.

SOMMAIRE

La galène associée aux sulfosels de Pb–Bi–Ag et aux sulfures simples dans les indices minéralisés 1) de Dandy à la mine Idarado, à Ouray, au Colorado, 2) de la mine Jackass, camp minier de Darwin, en Californie, et 3) du camp minier de Leadville, au Colorado, contient des quantités variables de Ag et de Bi. De plus, nous trouvons la galène ainsi enrichie associée à des quantités accessoires de sulfures enrichis en plomb est nécessaire à la formation de la phase PbS_{ss}. Là où l'argent et, à un degré moindre, le bismuth, font défaut, la galène possède une composition stoechiométrique. Le Sb peut remplacer le Bi en quantités limitées. Les données confirment la relation linéaire proposée antérieurement entre a et teneur en Ag + Bi(Sb). Nous avons identifié la matildite et sept sulfosels de Pb–Bi–Ag–Cu dans le système minéralisé de Dandy au moyen d'analyses obtenues à la microsonde électronique et de données diffractométriques (méthode des poudres): gustavite$_{65}$lillianite$_{35}$, aikinite ou friedrichite (ou un mélange) non-stoechiométrique, heyrovskyite, et un sulfosel de Pb–Bi argentifère possédant $N_{chim} = 8.4$, qui pourrait être soit eskimoïte(?), soit heyrovskyite$_{ss}$. Un sulfosel de Cu–Ag–Pb–Bi ayant $N_{chim} = 7.25$, qui pourrait correspondre à une eskimoïte(?) à dominance de Cu, une heyrovskyite$_{ss}$ cuprifère ou un sulfosel nouveau de Pb–Bi–Cu–Ag, et un sulfosel non-identifié ($N_{chim} = 6.06$, composition semblable à celle de la vikingite) sont aussi présents. Une eskimoïte(?) ou heyrovskyite argentifère ayant $N_{chim} = 8.19$ est présente dans le minerai à teneur élevée en argent de la mine Jackass. L'échantillon provenant de Leadville contient des quantités importantes de galène et de matildite, ainsi que hessite, "canfieldite tellureuse" $Ag_8SnS_4Te_2$, et de rares indices d'aikinite et deux sulfosels de Cu–Pb–Bi–Ag non-identifiés, dont un pourrait être de la galène enrichie en Cu + Bi. Un sulfosel de Pb–Pb–Ag contenant de l'antimoine, très probablement de l'ourayite (Our$_{73}$), a été découvert dans la mine Wombat, district de Montezuma, au Colorado. À quatre des cinq endroits étudiés, il est clair que des stades multiples de minéralisation, qui pourraient même impliquer des événements de réchauffement, sont à l'origine de la multiplicité de solutions solides PbS_{ss} et des assemblages complexes de sulfosels de Pb–Bi–Ag–Cu.

(Traduit par la Rédaction)

Mots-clés: galène, PbS_{ss}, sulfosels de Pb–Bi–Ag–Cu, Californie, Colorado, Pennsylvanie.

INTRODUCTION

Where galena and complex sulfosalts are associated in base- and precious-metal deposits, both show complex variations in composition and physical properties (e.g., Karup-Møller 1973, Czamanske & Hall 1975, Pattrick 1984, Foord et al. 1985, 1988, Jeppsson 1987, Gaspar et al. 1987, Moëlo et al. 1987). A rigorous structural and chemical classification of these minerals thus is difficult (e.g., Nowacki 1969, Makovicky & Karup-Møller 1977a,b, Makovicky 1977, 1981, Kostov & Minčeva-Stefanova 1982). Moreover, because of past difficulties in defining the mineralogical character of the galena–sulfosalt assemblage in different mineral deposits, it has been difficult to relate mineralogy to geological environment. Godovikov (1965, 1972) reviewed the then current knowledge of Bi-sulfosalts and other Bi–Pb–Ag–Cu–Sb sulfides and sulfosalts, and compiled available compositions for these minerals. However, much of Godovikov's work is now superseded. This report reviews some of the historical studies of galena, sulfosalts and their associations; it briefly describes the geological settings of five localities from which galena or sulfosalts (or both), and associated sulfides were collected: mines in the Ouray, Leadville and Montezuma districts, Colorado; the Darwin district, California, and Pequea, Pennsylvania.

We attempt to clarify some of the complex interrelations of the minerals; we suggest that much of the complexity of the galena–sulfosalt associations is the result of multiple episodes of mineralization. Additional detailed studies will be needed to correlate specific mineralizing events and mineral compositions.

REVIEW AND BACKGROUND

Trace and minor elements in galena

Numerous papers have been published on the occurrence of minor and trace elements in galena (e.g., Wasserstein 1951, Fleischer 1955, Marshall & Joensuu 1961, Godovikov 1966, Samsoni 1966, Hall & Heyl 1968, Badalov & Povarennykh 1969, Graeser 1969, 1971, Blackburn & Schwendeman 1977). Trace to major amounts of combined silver and bismuth have long been noted in some occurrences (e.g., Nissen & Hoyt 1915, Chapman & Stevens 1933, Oftedal 1942, Khetchikov 1958, Ontoyev et al. 1960, Paronikyan 1967). Malakhov (1968) examined the contents of Bi and Sb in more than 200 different samples from a variety of host rocks and depths. It was not certain in many cases whether or not other metals detected in analyses of galena were present in solid solution, as inclusions of other minerals, or both. Thus, in addressing the problem of the chemical composition of galena, Nesterova (1958) concluded,

on the basis of analyses of 40 samples of Soviet galena that the presence of other metals in galena is due to inclusions of other minerals. A similar conclusion was reached by Khetchikov (1958), who examined the Bi-content of galena from a polymetallic skarn-type deposit and concluded that most of the Bi was contained in microscopic inclusions of galenobismutite. Edwards (1954) also considered galena showing more than about 0.1% Ag to invariably contain included or exsolved Ag-bearing minerals. Galena and other minerals visually indistinguishable from galena were ideally suited for analysis by electron microprobe when it became commonly available as an analytical tool in the late 1960s. Many samples of visually homogeneous "galena" were found upon examination to be composed of galena mixed with other minerals. Thus, for example, a Se-bearing "galena" (sample H-2) examined by Coleman (1959) from Darwin, California was later found by Czamanske & Hall (1975) to consist of galena and an exsolved sulfosalt ("schirmerite"). Careful attention is necessary in connection with examinations of "galena" and Bi–Pb–Ag(Cu) sulfosalts containing elevated amounts of elements such as Sb, Se, Te, Bi, Hg and Ag, particularly samples from geochemically complex areas, or erroneous or incomplete identification of minerals actually present may result. Electron-microprobe studies combined with X-ray studies generally are required, and in some cases, single-crystal X-ray studies are necessary to provide unambiguous identification of mineral species (e.g., Karup-Møller 1977). Specialized etching and staining techniques may in many cases also reveal additional information that is not evident under normal conditions of microprobe operation (e.g., Harris & Chen 1975, Scott 1976). High-magnification back-scattered electron images, taken with a scanning electron microscope or electron microprobe with an SEM attachment, also are very useful for distinguishing between phases with very similar mean atomic numbers.

In some cases, primary galena from hydrothermal deposits has been shown to contain anomalous and significant levels of Bi, Ag, Te, Se, Sb, Cu, Tl and Zn. However, Bi, Ag and Sb are most abundant (Fleischer 1955), and only Sb, Bi, Ag, Te, Se, Cu and As have been reported in amounts greater than 1 wt.%. A Bi–Hg-substituted galena was reported by Foord et al. (1988). The substitution of Bi into galena, and the consequent decrease in cell edge, were demonstrated by Wasserstein (1951), who realized the potential of using X-ray diffraction and chemical analysis of galena as an indicator in problems of correlation in the Witwatersrand 'reef'.

Examination by optical and microprobe methods of various occurrences from New Brunswick (Boorman 1968) showed that silver was contained principally within various associated and included sul-

fosalts, and only minor amounts (less than about 0.1%) occur in solid solution. Each deposit has a distinctive galena–sulfosalt assemblage; for example, the Mount Pleasant deposit has Bi-sulfosalts and no Sb-sulfosalts, whereas for all of the other deposits examined, the opposite is true.

Experimental studies, such as those of Van Hook (1960), show that galena may contain Ag only in slight excess over Bi even at high temperatures, whereas it may contain considerably more Bi than Ag (e.g., Karup-Møller 1977). Bi-free galena contains only small amounts of Ag (0.4 wt.% or less) whereas Ag-free galena may contain more than 10 wt.% Bi (Karup-Møller 1977). According to Makovicky (1977), Bi-bearing galena contains random vacancies and possesses a defect-type structure. However, a rigorous structure-refinement or TEM study of a Bi-rich and Ag-poor galena is necessary to resolve this question. Karup-Møller (1977) suggested that the Bi excess in such cases may be due to the existence of domain-type structures similar to those of the lillianite homologues.

Octahedral cleavage or parting in galena has long been noted and attributed to the content of Bi (e.g., Wahlstrom 1937, Oftedal 1942, Chukhrov 1944, Karup-Møller 1971). Wahlstrom (1937) considered the octahedral parting to be controlled by closely spaced layers of tetradymite that parallel the octahedral planes of the galena. The parting was believed to be due to mechanical stresses during or after ore formation. Heating in a closed tube resulted in a loss of the octahedral parting and development of cubic cleavage. Oftedal (1942) refined the observations of Wahlstrom (1937) and noted that various specimens of Norwegian Bi-bearing (1–2%) galena may or may not be characterized by octahedral parting, but if Ag also is present and is about one-half the weight fraction of Bi, the galena does not exhibit octahedral parting. He attributed this to the substitutional scheme 2Pb for (Ag + Bi). Where Bi is present in excess of the amount of Ag required to balance it, or if Bi alone is present, then octahedral parting is developed. Bi-bearing galena from Gladhammar, Sweden, containing aikinite exsolved along {111} cleavage, was described by Karup-Møller (1971). The host galena contains 0.5–1.0 wt.% Bi but no Ag or Cu, substantiating the observations of Oftedal (1942). This correlation is also supported by observations of the galena from the Pequea silver mine, Lancaster County, Pennsylvania, where galena containing as much as 2 wt.% Ag and 7 wt.% Bi (A. V. Heyl, pers. comm., 1982) may show octahedral cleavage. Galena from Pequea examined in this study, however, contains equal amounts (atomic) of Ag and Bi, and shows only cubic cleavage. Paar & Meixner (1977) reported that some samples of Bi-bearing galena contain inclusions of native Bi and bismuthinite along the {111} cleavage planes, sub-

stantiating the earlier results of Chukhrov (1944).

Khetchikov (1958) found that galena containing 2 wt.% Bi shows dominant octahedral faces and a tabular form, whereas galena with only a few tenths of a percent Bi shows well-developed cubic faces. The high-Bi galena was found to contain exsolved galenobismutite. Marshall & Joensuu (1961) found no progressive change in either Ag or Bi content with crystal habit in galena from Mississippi-Valley-type deposits. Other factors, particularly temperature, were considered more important in determining habit.

Secondary or supergene galena, though rare (Taylor 1958, Clark & Sillitoe 1971, Frenzel et al. 1973), commonly contains substantial amounts of copper in solid solution, although experimental data (Craig & Kullerud 1968) indicate that only extremely limited solid-solution of copper in galena is possible below 200°C. Supergene galena, comprising as much as 5% of the ore, has formed at Broken Hill, New South Wales, Australia, in the transition zone between the sulfide and oxidized ore. Within this zone, it forms a thin rim on relict masses of sphalerite, and farther into the sulfide core it penetrates the sphalerite along cracks and cleavages. Clark & Sillitoe (1971) reported as much as 13 wt.% Cu in galena associated with djurleite at the Arco de Oro mine, Zapallar district, Atacama, Chile. A second case of Cu-bearing galena, also secondary and associated with Pb-bearing covellite, was reported by Frenzel et al. (1973). Those authors proposed that cuprian galena is a metastable solid-solution that has been preserved because of special environmental factors.

A cuprian galena with as much as 2.05 wt.% Cu and no other elements in significant concentrations was reported from the Långban deposit (Burke 1980). A higher-temperature exsolution-type origin was inferred because of its mode of occurrence as droplets and rounded veinlets in enclosing sulfides and sulfosalts.

An antimonian galena with 4.5 to 5.4% Sb, in the form of stringers associated with Sb-oxides that developed from twinnite, Pb(Sb,As)$_2$S$_4$, was reported by Mozgova et al. (1979). Moëlo (1983) described anisotropic Sb- and As-bearing galena, the formation of which was related to a high rate of crystallization at low temperature by the substitution of Sb in three-fold coordination for Pb.

Thus, it appears that both cuprian and antimonian galenas may exist in nature, but these varieties commonly are secondary and formed at very low temperatures. Both types likely are metastable, but more work must be done to verify this speculation.

The existence of a complete solid-solution series between galena and clausthalite was shown to exist by Heier (1953) and again by Coleman (1959). Necheliustov et al. (1962) examined the isomorphous substitution at low levels (less than 0.1% of each)
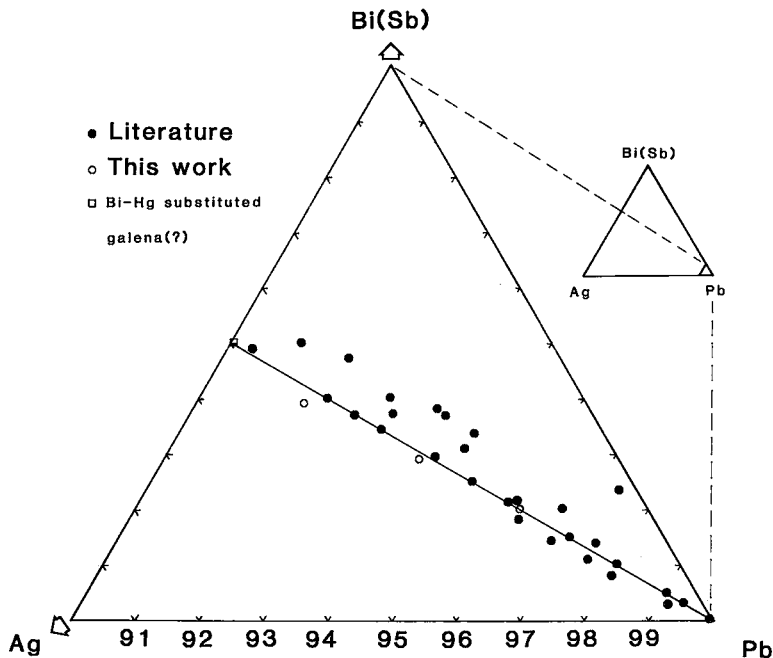
FIG. 1a. Triangular plot (atomic) showing a portion of the system Pb–Bi(Sb)–Ag and compositions of galena and PbSss analyzed in this study, as well as selected data from the literature. Data points (solid circles) from the literature include: Nesterova (1958): 1 sample, Ontoyev *et al.* (1960): 4 samples, Karup-Møller (1973): average of 10 grains, Czamanske & Hall (1975): 7 samples, Karup-Møller (1977): 9 samples, Paar *et al.* (1980): average of 7 samples, Makovicky & Karup-Møller (1984): 1 sample, Boldyreva (1985): 1 sample, and Gaspar *et al.* (1987): 3 samples. Open square is Bi–Hg-substituted galena(?) from the Outlaw mine (Foord *et al.* 1988). Open circles are two galena samples from the Dandy vein and one from the Pequea mine. See Karup-Møller & Pauly (1979) for additional compositions of galena from the cryolite deposit at Ivigtut, Greenland.

of Se and Te for S in galena and found these elements also to correlate with Bi and Ag (or Sb and Tl) contents. A galena with inclusions of tetradymite examined by Stupkina (1966) shows solid-solution substitution of both Te and Se for S as well as Bi and Ag for Pb. The cell edge of 5.945 Å indicates expansion due to substitution of the Se and Te for S, and the approximate 13 mol.% of $AgBiS_2$ is probably present as matildite.

Galena solid-solution (Pbss)

A silver- and bismuth-bearing (6.04% Ag, 12.15% Bi and 0.24% Sb) galena was reported from the Greenback orebody in the Leadville district, Colorado, by Chapman & Stevens (1933). The composition of this galena, corrected for minor amounts of admixed pyrite, chalcopyrite and sphalerite, is plotted as a point on Figure 1b. Debye–Scherrer X-ray films of the material (Chapman & Stevens 1933) show a pattern very similar to normal galena.

However, it is likely that some exsolved matildite or other sulfosalts are present, based on results obtained from etching with nitric acid. We have arbitrarily considered any galena with a structural content of more than 0.5 wt.% combined metals, other than Pb, to be galena solid-solution (PbSss).

Some of the first detailed studies of natural PbSss were made by Ontoyev *et al.* (1960). Studies after 1970 using the electron-microprobe approach, such as those by Karup-Møller (1973), Czamanske & Hall (1975), Nash (1975), Karup-Møller (1977), Karup-Møller & Pauly (1979), Karup-Møller & Makovicky (1981), Makovicky & Karup-Møller (1984), Boldyreva (1985), Gaspar *et al.* (1987) and Moëlo *et al.* (1987), have confirmed and refined the earlier proposals of the existence of such natural PbSss (Figs. 1a, b).

Jeppsson (1987) has examined the relationship between cell parameters and substitution of $AgBiS_2$ and $AgSbS_2$ in synthetic and natural galena. The synthetic α-$AgBiS_2$ – 2PbS solid-solution series
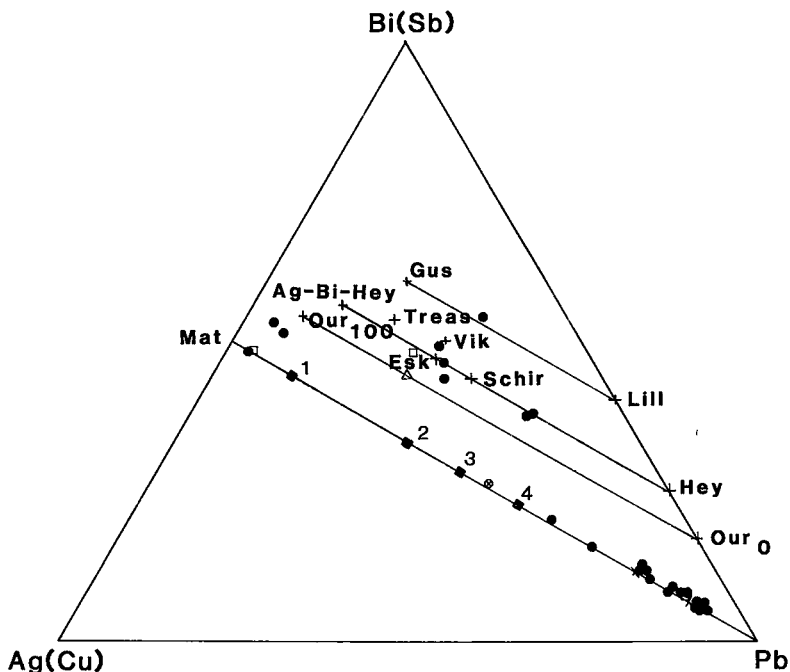
FIG. 1b. Triangular plot (atomic) showing compositions of minerals analyzed in this study in terms of the system Pb–Bi(Sb)–Ag(Cu). Symbols: open circle: "galena" from Leadville, Colorado (Chapman & Stevens 1933), solid circles: samples from the Dandy vein system and from the literature: Ontoyev et al. (1960): 2 samples, Czamanske & Hall (1975): 7 samples, Karup-Møller (1977): 4 samples, Karup-Møller & Mackovicky (1981): 7 samples, Gaspar et al. (1987): 2 samples, Foord et al. (1988): 2 samples, open triangle: ourayite from the Wombat mine; crosses: range of galena–matildite intergrowths and Cu-Bi-substituted galena(?) from Leadville, open squares: samples from the Jackass mine. Nos. 1 – 4: compositions from Bortnikov et al. (1987), viz. $Ag_4PbBi_4S_9$, $AgPbBiS_3$, $Ag_2Pb_3Bi_2S_7$ and $Ag_3Pb_7Bi_3S_{13}$.

show a closer approach to ideality than α-$AgSbS_2$ – 2PbS, at least for PbS-rich compositions.

As much as 7 mol.% of $AgBiS_2$ has been found in galena from Ivigtut, Greenland (Karup-Møller 1977) and from France (Moëlo et al. 1987). A comparable amount, averaging 7.6 mol.%, was found in galena coexisting with Ag- and Bi-rich heyrovskyite, exsolved lamellae of lillianite homologues and other minerals from Castlegar, British Columbia (Karup-Møller & Makovicky 1981). A galena with 25 mol.% $AgBiS_2$ in solid solution, enclosed in pyrite, and coexisting with a galena with 11.7 mol.% $AgBiS_2$ and a Pb–Bi–Ag sulfosalt, subsequently identified as probable ourayite, from the Fairview mine, Round Mountain, Nevada, was described by Foord et al. (1985, 1988). Recent studies, such as those of Czamanske & Hall (1975), Karup-Møller (1977), Parr et al. (1980), Makovicky & Karup-Møller (1984) and Pattrick (1984), have shown that the galena component of matildite-galena inter-

growths plot on or very close to the galena–matildite join, whereas galena directly associated with Pb–Bi–Ag sulfosalts is enriched in Bi relative to Ag and plots to the right of the galena–matildite join (Figs. 1a, b).

Four Pb–Bi–Ag sulfosalts intermediate in composition between galena and matildite were reported from the Kanimansur area, Karamazar, U.S.S.R. (Bortnikov et al. 1987): viz. $Ag_3Pb_7Bi_3S_{13}$, $Ag_2Pb_3Bi_2S_7$, $AgPbBiS_3$ and $Ag_4PbBi_4S_9$ (see Fig. 1b). These compounds, all less than about 20 micrometers in maximum dimension, were identified only on the basis of electron-microprobe data and are reported to have the optical properties of matildite.

If Ag and Bi both are available to substitute for Pb, substitution can readily occur, particularly in systems low in Cu, Sb and Zn. On the other hand, if Ag and Sb are available at the time of crystallization and Bi is rare or absent, as for example at the

Wood River lead–silver deposit, Blaine County, Idaho (Hall & Czamanske 1972), then minor solid-solution involving Ag and Sb may occur, provided the temperature is high enough (350–400°C). If Cu, Zn and other metals also are present at the time of crystallization, then the Sb and Ag will be incorporated into minerals such as tetrahedrite–tennantite, and only a few wt.% at most of Ag and Sb will substitute into galena (Åmcoff 1976). The ionic radius of Bi^{3+} (0.96 Å) is closer to the radius of Pb^{2+} (1.20 Å) than Sb^{3+} (0.76 Å). Jeppsson (1987) also found that silver in Sb-rich deposits was incorporated into a variety of Ag–Sb sulfosalts, especially tetrahedrite. In the presence of Bi, large amounts of silver can be accommodated in the structure. At the Tsumeb mine, the Ag content of the ore is directly proportional to the Cu content, there is no correlation between Ag and Pb, and As is much more plentiful than Sb. Thus, Ag is not enriched in galena where Sb (and Bi) are absent. Also, at the Darwin Pb–Ag–Zn mine, high silver values in galena can be correlated with Bi concentrations. Sb contents in galena are very low, and much Sb is present as minute inclusions of tetrahedrite. Sb is known to be extremely scarce in the entire district. Galena with high silver values contains varied Sb values (Hall 1971). The most plausible way of explaining the affinity between Ag and PbS is in the coupled substitution $Ag^+ + Sb^{3+}(Bi^{3+}) \rightleftharpoons 2Pb^{2+}$ (Nash 1975, Hoda & Chang 1975, Åmcoff 1976, Karup-Møller 1977, Karup-Møller & Pauly 1979, Jeppsson 1987, Gaspar et al. 1987).

Examination of Ag–Bi–Sb contents in galena from the Real de Angeles Ag–Pb–Zn deposit, Zacatecas, Mexico, shows significant but relatively low levels of all three elements (all less than 1 wt.% each) (Pearson et al. 1984, M. F. Pearson, pers. comm., 1985). Galena provides the main economic source of Ag in the deposit (M. F. Pearson, pers. comm., 1985). Variable but relatively low levels of Ag ($\sim$ 0.5%), Bi ($\sim$ 0.3%) and Sb ($\sim$ 0.5%) were found in individual crystals of galena, as well as evidence of spatial zonation in the deposit. The silver-bearing minerals in addition to galena are: freibergite, stephanite and argentite. Because Bi is extremely low in the deposit, no substantial amounts of discrete matildite or Pb–Bi–Ag sulfosalts were formed. Galena from the Wood River deposits (Hall & Czamanske 1972) contain Ag and Sb in a 1:1 atomic ratio (200–2400 ppm each), with additional Ag and Sb present in microscopic inclusions of Ag–Sb sulfosalts. Much of the Ag and Sb in laboratory-purified galena is present predominantly in inclusions of diaphorite. Some of the galena from the Lead–Silver King prospect, Nye County, Nevada, also shows an approximate 1:1 atomic ratio of Sb and Ag (Foord et al. 1988). Galena from the Caribou mine, Boulder County, Colorado, also contains very low levels of Ag and Bi (H. W. Miller, pers. comm., 1983) because Bi is essentially absent in the system, thus preventing the $2Pb \rightleftharpoons Bi + Ag$ substitution. Primary silver-bearing minerals include pyrargyrite, polybasite, jalpaite and stromeyerite (H. W. Miller, pers. comm., 1983; Francis 1987).

An example of another deposit where Bi is absent or very low, but Ag is present in moderate quantities in the ore, is that of the St. Cloud Zn–Cu–Ag–Pb mine, Chloride mining district, Sierra County, New Mexico. In order of decreasing abundance, the ore minerals are sphalerite, bornite, betekhtinite $Cu_{13}(Pb,Fe,Ag)_2S_9$ (Hlava & Irving 1985), galena, chalcocite and stromeyerite. Chalcopyrite and pyrite also are present. Emission spectrographic analyses (N. M. Conklin, analyst, U.S. Geological Survey) of two samples of bornite (possibly containing minor amounts of betekhtinite) show 1500 ppm Ag in each. Neither Bi nor Sb was detected. The coexisting galena contains 70 ppm Ag, 150 ppm Sb and 10 ppm Bi. In thus another example, the available Ag is present chiefly in minerals other than galena.

It is well known that one or more distinct generations of galena are distinguished in various base- and precious-metal deposits. Such generations are commonly recognized and distinguished both visually and by chemical properties. Examples have been described by Khetchikov (1958), Radtke et al. (1969), Czamanske & Hall (1975) and Karup-Møller & Pauly (1979). In many instances, earlier generations of galena have a large grain-size and are relatively 'clean', whereas later generations are finer grained and contain significant amounts of other elements, such as those mentioned above. However, as at the Kti–Tberda deposit (Ontoyev et al. 1982), where separate mineralizing events have occurred widely separated in time, a second generation of galena may be nearly pure.

Multiple episodes of mineralization, with physically and chemically different generations of galena and other sulfosalts, have been indicated in the Round Mountain – Manhattan area, Nevada (Shawe 1985, Shawe et al. 1986, Foord et al. 1988), the Darwin district, California (Czamanske & Hall 1975) and the Red Mountain – Idarado district, Colorado (Mayor & Fisher 1972, Lipman et al. 1976). Several stages of mineralization were recognized in the Leadville district, Colorado (Chapman & Stevens 1933, Chapman 1941) and likewise for the Montezuma district (Lovering 1935, Botinelly 1979). The mineralogical work done in this study may provide data useful in the interpretation of the mineralization histories in the respective districts.

Matildite

Harris & Thorpe (1967) determined the full cell, and confirmed the hexagonal symmetry of natural

β-AgBiS$_2$ (matildite). The mineral is found most often as either oriented or random myrmekitic intergrowths in galena (*e.g.*, Boldyreva 1970, Petruk *et al*. 1971, Harris & Owens 1973, Karup-Møller & Pauly 1979, Makovicky & Karup-Møller 1984, Boldyreva 1985). It may occur in a texturally pseudocubic lattice along {111} and {100}, as well as other planes in galena. Matildite has been interpreted to form penecontemporaneously with galena or to form as a decomposition product of a high-temperature PbS–AgBiS$_2$ solid-solution series (Karup-Møller & Pauly 1979). The high-temperature form of AgBiS$_2$, α-AgBiS$_2$, was redefined as schapbachite (Hey 1982), and is not known to occur in nature.

Some matildite occurs in the absence of galena, *e.g.*, intergrowths with aikinite, wittichenite and emplectite (Sakharova 1969). Its formation was attributed to geochemical factors involving breakdown of chalcopyrite, with the addition of Bi and some Pb and Ag, at temperatures less than 220°C (below the 215°C crest of the PbS–AgBiS$_2$ solvus).

The presence of matildite, β-AgBiS$_2$, in solid solution in galena has been well characterized (Wernick 1960, Van Hook 1960, Craig 1967, Nenasheva 1972); the common association of matildite and galena is believed to represent exsolution at a solvus with a crest at 215 ± 15°C, as determined on natural PbS–AgBiS$_2$ intergrowths (Craig 1967). Nenasheva (1972) determined a solvus crest of about 210°C for compositions with greater than 40 mol.% PbS, in agreement with the data of Craig (1967). However, an ordered compound having the composition Ag$_4$PbBi$_4$S$_9$ and appearing at 220°C, was reportedly found at 20 mol.% PbS (Nenasheva 1972, 1975). This synthetic compound was equated with schirmerite, but subsequent studies of natural schirmerite have shown it to have a substantially different composition (Makovicky & Karup-Møller 1977b). Recently, Bortnikov *et al*. (1987) have reported a natural compound with the composition Ag$_4$PbBi$_4$S$_9$. Above 220°C, there is a complete solid-solution series between AgBiS$_2$ and PbS (Craig 1967, Nenasheva 1972, 1975, Hoda & Chang 1975). The degree of solid solution of AgBiS$_2$ in PbS has been an important question for many years. The high Bi and Ag contents of some samples of galena are due to the existence of a high-temperature pseudocubic (disordered) form of AgBiS$_2$ that is isostructural with PbS and forms a complete solid-solution with PbS (Craig 1967). Numerous workers favor stoichiometric substitution involving 2Pb $\leftrightarrows$ Bi(Sb) + Ag(Cu) (*e.g.*, Necheliustov *et al*. 1962, Nash 1975, Åmcoff 1976, Blackburn & Schwendeman 1977, Karup-Møller 1977, Karup-Møller & Pauly 1979), and this mechanism is supported by structural crystallographic data (Makovicky 1981, Kostov & Minčeva-Stefanova 1982). This type of substitution is extensive both for the lillianite-

gustavite (Pb$_3$Bi$_2$S$_6$ – PbAgBi$_{13}$S$_6$) and the heyrovskyite solid-solution series (Pb$_{12}$Bi$_4$S$_{18}$ – Pb$_2$Ag$_5$Bi$_9$S$_{18}$) (Makovicky & Karup-Møller 1977b, Czamanske & Hall 1975, Karup-Møller & Makovicky 1981, Chang *et al*. 1988). The phase relations in the low temperature ($\leq$ 500°C) system AgSbS$_2$ – PbS and the solubility of AgSbS$_2$ in PbS have been examined by Nenasheva (1971), Hoda & Chang (1975) and Åmcoff (1976) and found to be very low (less than 4 mol.% at 300°C and less than 2 mol.% at 200°C). The extremely low (less than 1 mol.%) solubility of Cu into the structure of primary hydrothermal galena, incorporated as CuSbS$_2$ $\leftrightarrows$ PbS, analogous to that of AgBiS$_2$ $\leftrightarrows$ PbS, was determined experimentally by Craig & Kullerud (1968) and later restated by Karup-Møller (1971).

Some lead occurs in solid solution in matildite, as do silver and bismuth in galena. Matildite samples with 4.7 and 5.75 wt.% Pb, respectively, were reported by Boldyreva (1985) and Gaspar *et al*. (1987). The matildite exsolved from the Jackass mine galena contains about 4 wt.% Pb (Table 1, Fig. 1b). Matildite from Darwin containing 3.5 wt.% Pb was reported by Czamanske & Hall (1975). The lead contents may be microprobe artifacts or due to repeated "fractal" exsolution lamellae of galena.

If the four Pb–Bi–Ag sulfosalts reported by Bortnikov *et al*. (1987) are discrete minerals, then phase relationships in the low-temperature region of the system PbS – AgBiS$_2$ are more complex than would be expected solely from experimental studies (*e.g.*, Nenasheva 1972, 1975, Craig 1967, Hoda & Chang 1975). Bortnikov *et al*. (1987) have proposed that admixed elements would stabilize minerals that are metastable or that remain at temperatures below the experimental temperatures. Sluggish kinetics are favored by those authors. The nature of galena-matildite intergrowths was examined by Boldyreva (1985), who concluded that the experimentally synthesized compound Ag$_4$PbBi$_4$S$_9$ may not exist in nature.

TABLE 1. COMPOSITION* OF SEVEN SULFOSALTS EXSOLVED OR INCLUDED IN Ag- AND Bi-BEARING GALENA FROM THE DANDY VEIN SYSTEM, IDARADO MINE, OURAY, COLORADO

Sample nos.	8C	8C,8G		6D	8C	6E,6G,6H,8B,8C	80	8Q
mineral	esk(?) or hey	heyrovskyite		Cu-esk or hey	Gus65 Lil35	aikinite-friedrichite	Fried	N-6 phase (treasureite or eskimoite?)
no. of points	(2)	(5) (1)	(4)	(5)	(2)	(10)	(2)	(2)
Element								
Cu	0.8	0.4	0.3	3.8	0.5	9.4	8.7	0.2
S	16.9	16.3	15.2	16.2	16.7	17.3	17.1	16.2
Pb	31.7	43.2	44.5	31.4	29.6	32.6	31.8	27.8
Bi	41.3	33.3	34.5	44.9	47.5	40.7	42.9	45.9
Ag	9.6	5.8	5.7	4.5	5.9	0.0	0.0	9.7
Te	---	---	0.1	0.1	0.1	---	0.0	0.1
Total	100.3	99.0	100.3	100.9	100.3	100.0	100.5	99.9

* as determined by electron microprobe. Sb, Zn, As and Fe sought but not detected. —- Not determined.

X-ray-diffraction studies

One of the first precise measurements of the accepted cell-edge of pure galena (5.936 Å) was that of Wasserstein (1951). He also showed that annealing of galena at 300-400°C for a few minutes resulted in greatly sharpened lines in the back-reflection region of the diffractogram. Broadening of the lines was shown to be caused by distortion (curved lattice planes) induced by grinding of the sample for X-ray analysis. This problem was largely avoided in the present study as well as in that of Foord *et al.* (1988) by the use of a Gandolfi camera and fragments of material gently broken off. All of the lines in the back-reflection region are sharp and show excellent resolution of the $K\alpha_1$ and $K\alpha_2$ lines. Cell edges were determined from measurement of the highest five 2θ reflections. An essentially pure sample of galena (several broken fragments) from the Tri-state district was examined both before and after heating (500°C in air for 3 minutes) by X-ray diffraction; the lines in the back-reflection region were further sharpened by the heat treatment, for the purpose of cell-edge determination.

Determination of *a* for galena samples containing Ag and Bi (Boldyreva & Chernysheva 1965, Karup-Møller 1973, Karup-Møller & Makovicky 1981, Foord *et al.* 1985, 1988) has shown the effect of the substitution $2Pb \rightleftharpoons Bi^{3+} + Ag^+$: *a* decreases by about 0.003 Å for each wt.% of Ag + Bi ± Sb.

Electron-microprobe analyses were done on an ARL-EMX-SEMQ instrument at operating voltages of 15 or 20 kV, 10 nanoamperes sample current (on brass), 20 to 40 second count-times on peaks and 2 to 4 second count-times on background positions. Standards used included PbS, FeS_2, $FeAsS$, $PbTe$, $HgTe$, ZnS, $PbSe$ and several synthetic Pb-Bi-Cu-Ag sulfosalts. $L\alpha$ and $M\alpha$ lines were used except for Bi, for which the $M\beta$ line was used. Data were reduced using a modified version of MAGIC IV (Colby 1968).

Emission spectrographic analyses were done on a Jarrell-Ash 3.1 meter direct-reading spectrograph, using the method described by Myers *et al.* (1961).

DESCRIPTION OF LOCALITIES STUDIED

Dandy vein system, Idarado mine, Ouray County, Colorado

The Dandy vein system is part of a richly productive group of ore deposits whose northwest-trending and circumferential structures formed at about 27.5 Ma on the northwest side of the Silverton caldera, in the western San Juan Mountains (Lipman *et al.* 1976). Sphalerite, galena, chalcopyrite and pyrite occur with lesser amounts of sulfosalt minerals in replacement ores in the Eocene Telluride conglomer-

ate, and in northwest-trending and ring-fracture veins that cut the conglomerate ores (Mayor & Fisher 1972). Major gangue minerals in the conglomerate ores are quartz, epidote, chlorite, rhodonite, pyroxmangite, thulite and carbonates; lesser amounts of sericite and clay minerals are present. Gangue minerals in the veins are similar but also include fluorite. The ores were deposited much later than the formation of the structures in which they occur. According to Lipman *et al.* (1976), replacement ore in the Idarado mine was deposited about 17.0 ± 0.6 Ma (K-Ar age on K-feldspar), whereas sericite from the same material gave an age (K-Ar) of 13.1 ± 0.4 Ma. Late-stage gold-quartz ore in the nearby Camp Bird – Pandora vein system and associated replacement ore were dated as about 10 Ma (10.5 ± 0.5 Ma, K-Ar age on adularia and 10.2 ± 0.3 Ma, K-Ar age on fine-grained K-feldspar, respectively) (Lipman *et al.* 1976). A dike emplaced after the main ore-stage in the Idarado mine gave an age of 11.0 ± 1.2 Ma (fission-track age on zircon) (Lipman *et al.* 1976).

In the Idarado mine, three N65°W-trending and steeply southwest-dipping quartz-sulfide-sulfosalt-oxide veins ranging from 0.3 to 1 m thick, referred to as the Dandy Nos. 1, 2 and 3 veins, respectively, intersect as *en échelon* offshoots the Basin vein, one of the nearly east-west-trending base-metal veins. The Dandy No. 1 and No. 2 veins are about 20 m apart, and the No.2 and No. 3 veins are about 30 m apart along the Basin vein drift. The Basin vein, averaging about 1 m wide, and the Dandy No. 1 and No. 2 veins locally contain specular hematite and Pb-Bi-Ag-(Cu) sulfosalts, as well as the simple sulfides; sulfides and sulfosalts are scattered throughout the veins. The sulfosalts are more common near or in association with galena. The Dandy No. 2 vein seems to contain less galena and more Pb-Bi-Ag-Cu sulfosalts than the Dandy No. 1 vein. No samples were collected from the Dandy No. 3 vein. All samples were collected along the Basin 2900 East Drift of the Idarado mine by F. S. Fisher (U.S. Geological Survey) in 1972.

Darwin District, Inyo County, California

At Darwin, a sequence of upper Paleozoic limestones, shales and siltstones was intruded by a biotite-hornblende quartz monzonite stock of Jurassic(?) age. The Paleozoic rocks within about 1000 m of the stock generally are altered to calc-hornfels and to tactite consisting of calc-silicate minerals. 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. Most of the ore is massive and occurs in veins, bedded deposits and steep irregular replacement-type bodies. The ore consists of galena, sphalerite, pyrite, and lesser amounts of chalcopyrite, pyrrhotite, magne-

tite, arsenopyrite, scheelite, tetrahedrite and Pb–Bi–Ag sulfosalts, some of which contain Se and Te. Gangue minerals are calcite, fluorite, host-rock calc-silicate minerals and a little jasperoid. Significantly, Czamanske & Hall (1975) recognized four different assemblages of sulfide minerals. The most common is a pyrite + sphalerite + galena ± chalcopyrite and scheelite assemblage that includes all the replacement ore in calc-silicate rock near the Darwin stock. The second association is a pyrite + pyrrhotite + magnetite + sphalerite + galena assemblage that occurs on the footwall of the Davis thrust fault and furthest from the Darwin stock. The third is fine-grained heavy galena ore containing abundant Ag, Bi and Se and minor associated pyrite. This type is represented by the high-grade ore exposed in the Jackass mine. A fourth type, which is minor, is a late Ag + Bi + Se + Te sulfosalt assemblage observed only on the 400 level in the Independence workings of the Darwin mine (Czamanske & Hall 1975). The geology of the Darwin district was summarized by Hall & MacKevett (1958, 1962). Detailed mineralog-ical studies were reported by Czamanske & Hall (1975).

Pequea mine, Lancaster County, Pennsylvania

Ag- and Bi-bearing galena from the old (pre-Revolutionary War) Pequea silver mine, Conestoga Township, Lancaster County, Pennsylvania, also were examined. Material collected in 1963 was provided by A. V. Heyl (U.S. Geological Survey). Tiny veinlets, and veins of quartz as much as 2 m thick, contain isolated crystals and lenses of galena up to several cm wide and thick. The Vin-tage Dolomite of Cambrian age is the host rock for the deposit. Minor amounts of pyrite, chalcopyrite and sphalerite are associated with argentiferous galena, along with various secondary minerals (Freedman 1972). A complete summary of the infor-mation concerning the Pequea mine area is given by Smith (1977).

The Leadville district, Colorado

The Leadville district is located on the west flank of the Mosquito Range in central Colorado. The ore deposits, which produced mostly silver, zinc, lead and gold, are principally blanket or manto replacement-type deposits, but in the eastern part of the district, many veins occur as well (Tweto 1968). The age of the primary mineralization is about 34 Ma (T. B. Thompson, written comm., 1987), and extensive oxidation took place in Miocene time. High-bismuth silver–gold ore (but not bismuth ore *per se*) was described by Chapman (1941), who iden-tified in it galenobismutite, aikinite and alaskaite (a mixture), as well as Bi- and Ag-bearing galena [prob-

ably containing some exsolved matildite] (Chapman & Stevens 1933). These Bi-bearing minerals are associated with tellurides (*e.g.*, altaite and hessite) and native gold, as well as native bismuth and tellu-rium. Chapman (1941) assigned all of these minerals to a paragenetically late "bismuth stage", which fol-lowed stages of galena, sphalerite and pyrite depo-sition. Evidence for a distinctly late stage of bismuth mineralization is best shown in the Greenback mine, along the Tucson–Maid fault (Chapman 1941).

The Wombat mine, Montezuma district, Colorado

The Montezuma district of central Colorado, located on the Continental Divide, south of Loveland Pass, is a small base-metal and silver mining district containing vein deposits associated with a Tertiary quartz monzonite porphyry stock transecting Precambrian gneisses (Lovering 1935, Botinelly 1979). Ore minerals of the Montezuma district are dominantly galena, sphalerite, pyrite and tetrahedrite–tennantite, but a large variety of unusual sulfides and Pb–Bi–Ag–Cu sulfosalts occurs in the area (Botinelly 1979). On the basis of X-ray powder data only, Botinelly identified aikinite, matildite, ber-ryite, galenobismutite, pavonite, hammarite, lillianite and schirmerite from the district. A variety of antimony- and arsenic-bearing sulfosalts also were identified in the district. Minerals identified from X-ray powder-diffraction data from the Wombat mine (T. Botinelly, pers. comm., 1983) include: pyrite, chalcopyrite, sphalerite, galena, bismuthinite, matil-dite, pyrargyrite, arsenpolybasite, 'schirmerite' and galenobismutite. In this study, vein material consist-ing of 1- to 3-mm veinlets of a grey sulfosalt coated by black sooty acanthite in quartz, collected by R. R. Cobban (Denver Museum of Natural History) from the Wombat mine dump on the south side of Lenawee Mountain, near Soda Spring, was deter-mined to be an Sb-bearing member of the lillianite homologues.

MINERALOGICAL RESULTS OF PRESENT STUDIES

Results of our studies are organized in the follow-ing pages on the basis of geographic areas. Composi-tional data for mineral species and groups are presented for each area. Galena, PbS_{ss} and associated sulfosalts in the Dandy vein system, Idarado mine, Colorado, the Jackass mine, Darwin district, California, and the Pequea mine, Pennsyl-vania are described, followed by data for galena and associated sulfosalts from one locality at Lead-ville and for one Bi–Pb–Ag-sulfosalt from the Montezuma district, Colorado.

A good correlation exists between *a* and the sum of Ag, Bi and Sb contents in galena samples for which this information is available (Karup-Møller

& Makovicky 1981, Foord *et al.* 1988). In the majority of cases, the ratio Bi/Ag is about 2:1 (wt.%), or 1:1 (atomic %), reflecting the coupled substitution $2Pb \rightleftharpoons Bi^{3+} + Ag^{+}$. However, in other cases, the ratio (wt.%) is close to either 0 or 1. For those samples, the total content of Bi + Ag + Sb is less than 0.5 wt.%. Where substantial substitution of Ag + Bi ± Sb is involved, the ratio is very nearly 2 and reflects the coupled substitution. Figures 1a and 1b show the compositions that we determined by electron microprobe as well as determinations from the literature, plotted along the galena–matildite join. It can be seen that some of the points show a slight excess in Bi. If this excess is real, it may be due to (a) vacancies, (b) exsolution of Bi-rich phases along {111}, or (c) unit-cell twinning on (131) applied sparsely and randomly (Karup-Møller 1977, Makovicky 1977). As already stated, this phenomenon suggested to Karup-Møller (1977) that the Bi-excess in galena may be due to domain-

Fig. 2. Back-scattered electron photographs of galena (medium grey), aikinite (dark grey), and Pb–Bi–Ag sulfosalt (light grey) from the Dandy vein, Idarado mine, Ouray, Colorado. Sample 80. 2a. Symplectitc intergrowth of Ag–Bi-bearing galena and aikinite, and lath of Ag–Bi–Pb sulfosalt. Bar scale: 10 μm. 2b. Closer view of part of the area shown in 2a.

type structures similar to those of the lillianite homologues.

Dandy vein system, Idarado mine, Ouray, Colorado

A suite of 12 polished sections from vein ore samples from two *en échelon* offshoots (known as the Dandy No. 1 and Dandy No. 2 veins) of the Basin vein in the Idarado mine was studied by Mosburg (1972). Minerals recognized by Mosburg are: quartz, chalcopyrite, pyrite, sphalerite, magnetite, hematite, silver and bismuth-bearing galena and three unidentified Pb-Bi-Ag-Cu sulfosalts. These same polished sections were provided to us by Frederick S. Fisher of the U.S. Geological Survey for additional mineralogical study. The unidentified sulfosalts occur only as inclusions and intergrowths in the galena, where they may also be in contact with other common sulfides. We also have documented the presence of matildite exsolved from high-temperature galena. Besides matildite, we have determined the presence of seven Pb-Bi-Ag-Cu sulfosalts (see Table 1).

Electron-microprobe analyses indicate that the most common previously unidentified sulfosalt is a member of the aikinite-bismuthinite series and is either aikinite or friedrichite. Two samples yield compositions indicating friedrichite and three others yield compositions intermediate between aikinite and friedrichite. X-ray powder-diffraction studies of this mineral by Mosburg (1972) gave a pattern resembling that of pure aikinite but with the lines slightly shifted to lower *d*-values. Her compositional data also indicate compositions between aikinite and friedrichite; friedrichite was not described until 1978, by Chen *et al.* (1978). Single-crystal X-ray studies will be necessary to determine whether the mineral is a nonstoichiometric aikinite or a nonstoichiometric friedrichite. Pring (1989) has shown that variation from ideal compositions in the aikinite-bismuthinite series is due to disordered intergrowth of krupkaite and aikinite units rather than from solid solution. Figures 2a and 2b show a symplectitic intergrowth of aikinite and Ag- and Bi-bearing galena, with one lath of an unidentified Pb-Bi-Ag sulfosalt hosted by the galena. Electron-microprobe data for seven sulfosalts are given in Table 1. These data sets, along with others, are plotted in terms of atomic percent on Figures 1a, b and 3.

Mosburg was unable to identify her second sulfosalt, a silver-rich variety and her third sulfosalt of intermediate Cu–Ag content, because of the then imperfect knowledge about the the gustavite–lillianite homologous series, and because of lack of sufficiently precise X-ray data.

In this study, only aikinite-friedrichite has been positively identified among Mosburg's three unidentified Pb-Bi-Ag-Cu sulfosalts from the Dandy vein system. Other sulfosalts (characterized by electron-
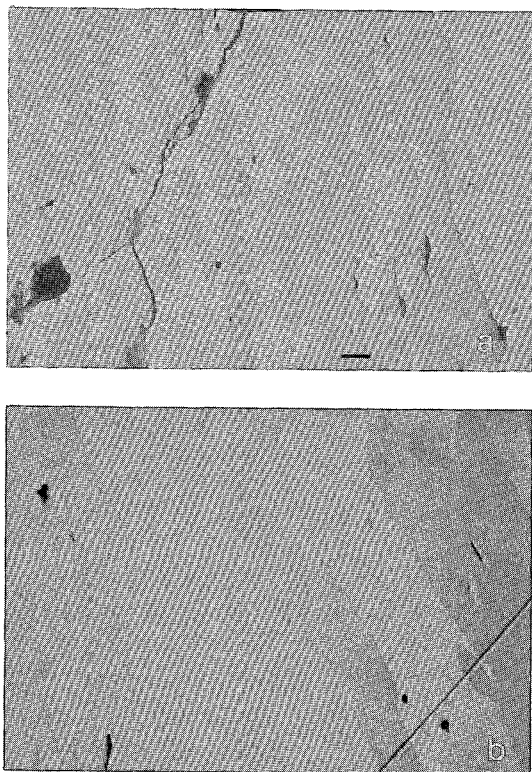
microprobe analyses) are present as grains too small for X-ray-diffraction studies. However, based on our current expanded knowledge (Craig 1967, Salanci & Moh 1969, Goodell 1975, Bente 1980, Mariolacos 1979, 1980) of the phase equilibria in the system Pb–Bi–Ag–Cu–S, and on our expanded mineralogical knowledge (Makovicky & Karup-Møller 1977a,b, Makovicky 1981, Karup-Møller & Makovicky 1981, Žák & Prachař 1981), identification of these other six sulfosalts may with some limits be based upon the microprobe compositional data and X-ray powder-diffraction data only.

One of the seven sulfosalts, found only in one (8C) of the ten sections examined, is a member of the lillianite–gustavite series, with the composition $Gus_{65}Lill_{35}$ (Table 1, Fig. 1b). The mineral occurs as laths and subhedral grains in galena and aikinite–friedrichite. No exsolution is evident, and it is homogeneous in composition. The compositions of this and the other sulfosalts and galena from the Dandy vein system are shown in Figures 1b and 3. Similar material was found in one assemblage from Nye County, Nevada examined by Foord *et al.* (1988).

Another sulfosalt, found in the same section (8C), may be eskimoite(?) or heyrovskyite$_{ss}$ (however, N_{chem} = 8.4, but this may be due to the influence of the host). The mineral occurs as sparse euhedral laths in aikinite and galena. The laths are 3 – 4 μm long and 1 μm wide. An average composition for the mineral is given in Table 1 and is shown on Figure 1b.

The composition of a possible copper analogue of eskimoite(?) or heyrovskyite$_{ss}$(?) is given in Table 1, and plots along the N = 7 line (Fig. 1b), very nearly on the position of eskimoite (Karup-Møller 1977; calculated N_{chem} = 7.25). The mineral was found in one polished section (6D). Silver- and bismuth-substituted heyrovskyite from Castlegar, B.C. (Karup-Møller & Makovicky 1981) has essentially the same composition as eskimoite from Ivigtut, Greenland (Makovicky & Karup-Møller 1977a,b) and may be considered dimorphous with eskimoite. Some of the Se-rich heyrovskyite from Darwin, California (Czamanske & Hall 1975, Makovicky & Karup-Møller 1984) also has a composition very similar to that of eskimoite and schirmerite. If this phase is structurally an eskimoite, then it is the Cu-dominant equivalent species, analogous to pavonite and cupropavonite.

A mineral with the composition of heyrovskyite$_{ss}$ also plots along the N = 7 line between eskimoite and Ag-free heyrovskyite (Table 1, Fig. 1). The mineral was found in two sections (8C, 8G). Calculated N_{chem} values are 7.62 and 7.12, respectively. X-ray-diffraction studies of material from 8G show a mixture of a mineral with lines matching those of heyrovskyite and minor galena.

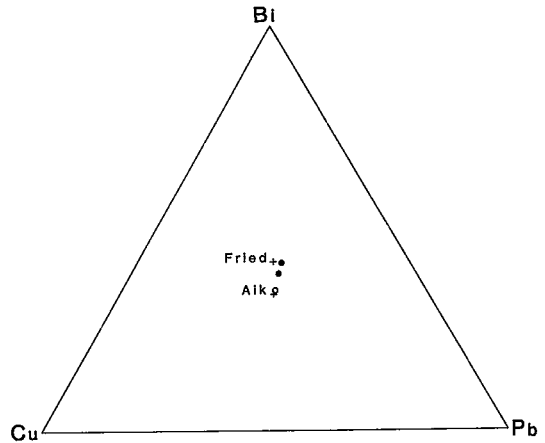One polished section (8Q) contains laths hosted

FIG. 3. Triangular plot (atomic) showing compositions of sulfosalt minerals examined in this study in terms of the system Pb–Bi–Cu. Symbols: solid circles: samples from Dandy vein system; open circle: aikinite from Leadville, Colorado; plus signs: end-member aikinite and friedrichite.

TABLE 2. COMPOSITION* OF GALENA AND GALENA-MATILDITE INTERGROWTHS FROM THE DANDY VEIN SYSTEM, IDARADO MINE, OURAY, COLORADO

Sample nos.	6A	6B	6D	6D	6E	6G	6H	8B	8C	8O	8Q
mineral	G	G	G+M	G	G	G	G	G	G	G	G
no. of points	(4)	(2)	(2)	(4)	(2)	(2)	(2)	(3)	(2)	(2)	(4)
Element											
Cu	0.1	0.1	0.1	0.0	0.1	0.2	0.0	0.0	0.1	0.0	0.0
Sb	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0
S	13.6	13.7	14.5	14.2	14.0	14.0	14.0	13.6	14.0	13.9	13.8
Pb	79.6	78.6	63.7	76.9	78.4	80.1	75.9	77.4	81.1	77.0	77.8
Bi	4.4	4.7	14.6	5.6	4.6	3.4	5.9	5.7	2.5	5.4	5.1
Ag	2.4	2.5	7.7	3.0	2.7	2.0	3.1	3.2	1.4	2.9	2.8
Total	100.1	99.6	100.6	99.7	99.8	99.7	98.9	100.0	99.2	99.2	99.5

* as determined by electron microprobe. Zn, As and Fe sought but not detected.

by Ag- and Bi-bearing galena, which may be either vikingite (N = 5.5) or another member of the lillianite–gustavite homologous series with N = 6, *e.g.*, treasureite series (calculated N_{chem} = 6.06). The laths measure approximately 2 x 10 μm and show no evidence of exsolution. The Dandy vein sulfosalts, owing to their extremely small grain-size, could not be studied by X-ray powder diffraction or single-crystal methods to firmly establish their identities.

The Ag- and Bi-bearing galena (PbS_{ss}) from the Dandy vein system also was examined with the electron microprobe; average compositions for ten samples are given in Table 2 and Figure 1. It can be seen that all samples lie along the PbS–AgBiS$_2$ join. One "galena" from sample 6D has the composition $Gal_{68}Mat_{32}$; under high magnification, it is found to be an intergrowth of Ag- and Bi-bearing galena and matildite.
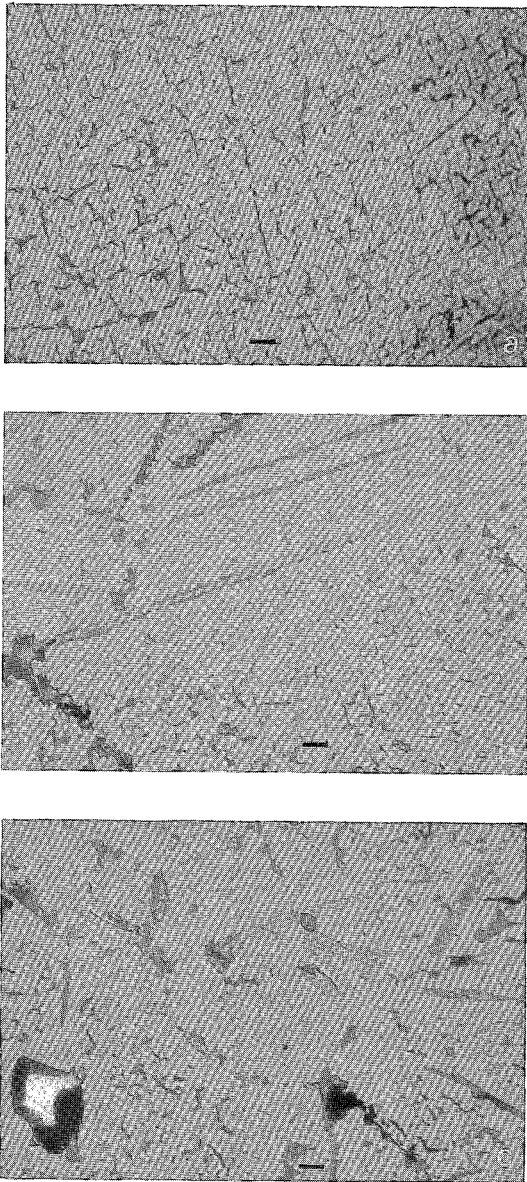
FIG. 4. Back-scattered electron photographs of galena containing intergrowths and exsolved grains of matildite, and eskimoite(?) from the 150 level, Jackass mine, Darwin district, California. 4a. Exsolution of matildite in galena; grey: galena, black: matildite. 4b. Exsolution of matildite and eskimoite(?) in galena; white: galena, grey: eskimoite(?), black: matildite. Note absence of exsolution adjacent to matildite and eskimoite(?). 4c. Intergrowth and exsolution of eskimoite(?) and matildite in galena; white: galena, grey: eskimoite(?), black: matildite. Note the distinct absence of exsolution bodies near larger grains of eskimoite(?) and matildite. Some apparent replacement of eskimoite(?) by matildite is shown in the upper center. Bar scale: 10 μm.

Jackass mine, Darwin district, Inyo County, California

Samples of high-grade (11.5% Ag) Pb–Ag ore were collected by J. A. McGlasson (Western Nuclear Corp.) from a 10-cm-wide sulfide–sulfosalt vein exposed on the 150 level, 15 m north of the main shaft, and on an east-striking structure that cuts siliceous limestone altered to calc-silicate hornfels. The vein is considered to belong to the third stage of Czamanske & Hall (1975). Mineralized material consists of acanthite, Ag- and Bi-bearing galena, sphalerite, chalcopyrite, malachite, limonite, anglesite, cerussite and scheelite in an iron and carbonate gangue with minor quartz (J.A. McGlasson, pers. comm., 1985). A 15-cm-wide channel sample that included some wallrock assayed: 32% Pb, 0.052% Zn, 0.12% Cu, 11.5% Ag and 8 ppm Au. An emission spectrographic analysis (N. M. Conklin, analyst, U.S. Geological Survey) of the "galena" from the sample gave: Fe 0.07%, Mg < 0.001%, Ca 0.2%, Mn 15 ppm, Ag > 2%, Au 20 ppm, Ba 5 ppm, Bi > 10%, Cu 1500 ppm, Pb > 10%, Sn 50 ppm, Sr 15 ppm, Te 1.5% and Si 0.3%. All other elements were not detected at their respective limits of determination.

Electron-microprobe and SEM examination of the material showed that galena comprises the majority of a mixture of galena, matildite and Ag-bearing ^{7}L, following the nomenclature of Makovicky & Karup-Møller (1977a), which may be either eskimoite(?) or Ag-bearing heyrovskyite(?). However, the value for N_{chem} is equal to 8.1. The sections are visibly homogeneous even at high power (400 times), but BSE imaging techniques clearly showed three main sulfide–sulfosalt minerals to be present. X-ray-diffraction studies, using a 114.6-mm Gandolfi camera, confirmed the presence of these three minerals. Crystals were not large enough for single-crystal camera studies. Silver and bismuth contents in the galena host are highest in places farthest from exsolved intergrowths of matildite and Ag-bearing ^{7}L. Exsolution of the matildite and Ag-bearing ^{7}L formed laths and linear bodies parallel to crystallographic directions, as well as irregularly shaped masses within the host galena. Some matildite can be seen to be clearly later than the Ag-bearing ^{7}L because it veins this mineral and forms the cement in locally developed sulfide–sulfosalt microbreccia. Figure 4a shows an area of what appears in normal light to be optically homogeneous galena but, as seen in a BSE image, is in fact galena that encloses fine-scale exsolution lamellae and irregular and pinch-and-swell bodies of matildite. Figures 4b and 4c show galena enclosing Ag-bearing ^{7}L and lesser amounts of matildite chiefly in the form of oriented exsolution-intergrowths. Figure 4b also shows barbs of matil-

dite on long laths of Ag-bearing ^7L within a matrix of galena that is clean and free of any obvious exsolution products near the matildite and Ag-bearing ^7L. In all cases, galena adjacent to Ag-bearing ^7L is homogeneous in appearance; Ag and Bi contents are lowest near the Ag-bearing ^7L and increase with distance from this mineral. This halo effect and depletion in Ag and Bi also were noted around grains of a similar mineral from the Dandy vein system (Mosburg 1972). Results of electron-microprobe analyses for the Jackass mine Ag-bearing ^7L, galena and matildite are given in Table 3 and plotted on Figures 1b and 3.

Pequea mine, Lancaster County, Pennsylvania

Two samples of Ag- and Bi-bearing galena, collected by A. V. Heyl (U.S. Geological Survey) were analyzed by semiquantitative and quantitative emission spectroscopy (Table 4). Single-crystal precession-camera studies of the Pequea mine galena (AVH-3-8) did not show the presence of any intergrown minerals. Electron-microprobe analyses (average of 13 points) of sample no. AVH-63-Z yielded the following composition (weight %): S 13.6, Pb 84.2, Bi 1.35, Ag 0.75, total 99.90. Other elements were looked for and not detected: Sb, Fe, Te, Zn and Cu. This composition is shown on Figure 1a. The results for Ag and Bi agree well with those (see Table 4) determined by quantitative emission spectrography on a second portion of the sample (AVH-3-8). The second galena is uniform in composition; no other intergrown minerals were seen by BSE-imaging techniques. A structural formula, based on 1 sulfur atom, is: $(Pb_{0.96}Ag_{0.02}Bi_{0.02})S$.

Leadville district, Colorado

A sample of sulfide and sulfosalt ore labeled "kobellite" from an unspecified mine in the Leadville district, Colorado, and collected prior to about 1930, from the Lazard Cahn collection, was provided by Dr. W. W. Pinch (Pinch Mineralogical Museum, Rochester, N.Y.) for study. Based on the known distribution of Bi and Te in the district, and on comparison to Bi-rich ores described by Chapman (1941), the material likely came from one of three areas: Tucson mine, Iron Hill, or the Greenback mine (ore body), which was the source of the 'galena' analyzed by Chapman & Stevens (1933). No kobellite was found. Major minerals present are pyrite, chalcopyrite and Ag- and Bi-bearing galena. Matildite is exsolved from the galena and forms a reticulate network of submicrometer-sized elongate bodies along the octahedral cleavage. Some veinlets of matildite also are present (Fig. 5a). The galena adjacent to the veinlets is "cleaned up", like the material from the Jackass mine. Additional matildite occurs

TABLE 3. COMPOSITION† OF GALENA AND ASSOCIATED SULFOSALTS FROM THE 150 LEVEL, JACKASS MINE, DARWIN DISTRICT, INYO COUNTY, CALIFORNIA

Mineral	galena	matildite	eskimoite(?) or Ag-bearing heyrovskyite(?)
Element			
Sb	0.2	0.1	0.3
Te	0.0	1.2	0.2
Cu	0.0	0.0	0.1
S	13.6	15.4	15.3
Pb	76.0	3.7*	25.6
Bi	6.2	52.4	45.6
Ag	3.1	26.8	12.3
Total	99.3	99.6	99.4

† as determined by electron microprobe. As, Fe and Zn sought but not detected. * Some or all of the Pb may be due to a combination of edge effects from the host galena and repeated "fractal" exsolution lamellae of galena.

TABLE 4. COMPOSITION† OF PbS_{ss} FROM THE PEQUEA SILVER MINE, LANCASTER COUNTY, PENNSYLVANIA

Sample	AVH-3-8	AVH-63-Z
Element		
Si	700	10
Fe	70	N10
Mg	<10	<10
Ca	30	N10
Ag	7600+	>2%
As	<20*	4*
Au	<0.8*	<0.2*
Bi	16000+(>0.2*)	>2% (>0.2*)
Cd	100(20*)	150(100*)
Cu	15	2
Hg	H	H
Mo	7	N5
P	28*	7*
Pb	major	major
Sb	N100(<4*)	N100(100*)
Se	280*	700*
Sn	7	7
Te	120*	200*
Tl	400*	100*
Zn	40*	1*

† as determined by emission spectrographic analysis. Values are quoted in parts per million, except for those indicated in weight %. H: interference. * Values from special determination of chalcophile elements by quantitative emission spectrography (C. Heropoulos, U.S. Geological Survey, analyst). + Values from quantitative six-step emission spectrography (N.M. Conklin, U.S. Geological Survey, analyst). All other elements not detected at respective limits of determination.

as rounded inclusions within the galena. Small amounts of hessite, Ag_2Te, and a mineral with the composition $Ag_8SnTe_2S_4$ are present in clot-like myrmekitic aggregates intergrown with galena and exsolved matildite (Fig. 5b). Individual clots attain several hundred micrometers across, but individual grains of hessite and the $Ag_8SnTe_2S_4$ are ≤ 50 micrometers across. This mineral is what has been called "tellurian canfieldite." Optical properties are close to those reported for this mineral (Soeda *et al.* 1984). In polished section, the "tellurian canfieldite" looks like tetrahedrite–tennantite: a smooth grey, isotropic mineral lacking crystal form, twinning or cleavage. In air, some grains show weak reflection pleochroism from grey to yellowish grey. Anisotropy is weak without tint, and the mineral displays weak orange internal reflection. Mean reflectances at the four standard wavelengths are: 29.6% (470 nm), 28.6% (546 nm), 27.8% (589 nm), and 26.9% (650
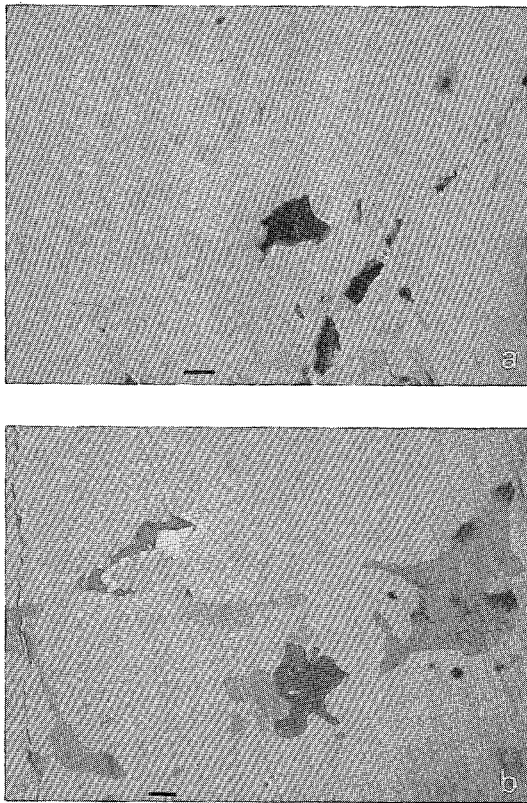
FIG. 5. Back-scattered electron photographs of galena, matildite, hessite, tellurian canfieldite(?), and two unidentified sulfosalts in a sample of high-grade silver ore from the Leadville district, Colorado. 5a. Tellurian canfieldite(?) (medium grey) included within galena–matildite intergrowth (light grey). Some larger bodies of matildite are darker than galena but lighter than the tellurian canfieldite(?) Veinlet contains inclusions of two unidentified sulfosalts. Bar scale: 10 μm. 5b. Galena–matildite host (light grey) with inclusions of tellurian canfieldite(?) (dark grey) and hessite (medium grey). Bar scale: 5 μm.

TABLE 5. COMPOSITION[†] OF GALENA–MALTILDITE INTERGROWTHS, HESSITE, "TELLURIAN CANFIELDITE(?)", AIKINITE AND TWO UNIDENTIFIED SULFOSALTS FROM A SAMPLE OF HIGH-GRADE SILVER ORE FROM THE LEADVILLE DISTRICT, LAKE COUNTY, COLORADO

Mineral	G+M*	Hessite*	"Te-canfieldite"**	Unk 1*	Unk 2*	Aikinite*
no of. points	(11)	(2)	(5)	(6)	(2)	(4)
Element	Range					
Cu	0.0-0.2	0.0	0.0	16.0	7.7	10.6
Sb	0.0-0.1	0.0	0.0	0.0	0.0	0.0
Te	0.0-0.2	36.4	19.3	0.0	0.0	0.0
S	13.8-14.0	0.0	9.7	17.8	16.2	16.7
Pb	69.6-77.0	0.0	0.0	20.1	50.0	35.5
Bi	10.8-5.5	0.0	0.0	39.8	27.5	37.5
Ag	5.6-3.1	64.3	62.8	6.5	0.5	0.2
Sn	---	---	8.6	---	---	---
Total	99.8-100.1	100.7	100.4	100.2	101.9	100.5

[†] as determined by electron microprobe. * Fe and Zn sought but not detected. ** Fe, Zn, As, Ge, Se, Hg, Cl and F sought but not detected. --- Not determined.

nm). Because of the paucity and small grain-size, X-ray-diffraction studies were not possible. "Tellurian canfieldite" is an uncommon mineral reported from only about seven localities world-wide (Karup-Møller & Pauly 1979, Soeda et al. 1984, Wimmers 1985). It has also been found from the A.Y. and Minnie mine in the Leadville district, Colorado, with a mineral assemblage similar to that of the material described here (G.K. Czamanske, pers. comm., 1988). Both canfieldite and "tellurian canfieldite" have been found at Panasqueira, Portugal (Wimmers 1985). Extremely sparse amounts of aikinite and two unidentified Cu–Pb–Bi–Ag sulfosalts are present in late-stage cross-cutting veinlets (Fig. 5a). One of the unidentified sulfosalts may be interpreted in terms of its chemistry to be Cu–Bi substituted galena. A structural formula, calculated on the basis of 1 S atom, is then: $(Pb_{0.48}Bi^{3+}_{0.26}Cu^{1+}_{0.24}Ag^{1+}_{0.01})_{\Sigma0.99}S$. Only two grains, each < 5 μm across, were found. Results of electron-microprobe analyses of the hessite, "tellurian canfieldite," galena–matildite intergrowths, aikinite and two unidentified sulfosalts are given in Table 5. Compositions of the aikinite, the galena–matildite intergrowths and the two unidentified sulfosalts are plotted in Figures 1b and 3.

A structural formula, based on 4 S atoms, for the "tellurian canfieldite" is: $Ag_{7.69}Sn_{0.96}Te_{2.00}S_{4.00}$. Virtually all other reported examples of "tellurian canfieldite" are deficient in Ag (i.e., < 8.00), as is the Leadville material. Further studies are in progress to determine if canfieldite and "tellurian canfieldite" are two distinct mineral species.

Wombat mine, Montezuma district, Colorado

Two polished sections prepared of vein quartz containing a lead-grey sulfosalt, collected by R.R. Cobban (Denver Museum of Natural History) from the dump of the Wombat mine on Lenawee Mountain, contain what appears to be a single-phase, homogeneous mineral whose composition plots on the ourayite series (N = 11) line. The mineral occurs as elongate and flattened prisms up to 0.5 mm in width and 2 mm in length or as intergrown clumps of crystals up to 3 mm across made up of interlocking sheaves of individual crystals. The exterior portion of all crystals is coated with aggregates of sooty black acanthite containing minor pyrite and chlorargyrite. The acanthite coating is up to 30–40 μm in thickness. The acanthite also veins the ourayite(?) crystals. The composition, in weight percent, of the mineral (average of 10 points) is: Sb 1.8(1), Te 0.1(1), S 16.3(3), Pb 31.5(5), Bi 39.2(6), Ag 11.4(5), total 100.3. A notable feature of this probable ourayite is its content of nearly 2 wt.% Sb. A structural formula calculated on the basis of 104 S atoms is: $Ag_{21.6}(Bi_{38.4}Sb_{3.0})_{41.4}Pb_{31.1}S_{104}$. The composition of the ourayite (Our_{73}) is shown in Figure 1b. X-ray

powder-diffraction data for this mineral are close to those given for ourayite. Additional studies are under way to fully characterize this mineral.

In polished section and in air, the mineral is white and shows no reflection pleochroism. Bireflectance is about 3%. Reflectance values for the four standard wavelengths are: R_1 43.5% R_2 46.1% (470 nm), R_1 43.0% R_2 46.0% (546 nm), R_1 42.5% R_2 45.3% (589 nm), R_1 42.5% R_2 45.0% (650 nm). Anisotropy is strong, from blue grey to cream-yellow. Under crossed polars, what appear to be macroscopic single crystals are seen to be a composite of intergrown crystals.

DISCUSSION AND CONCLUSIONS

Trace and minor elements in galena may be involved in an isomorphous substitution for Pb or S (or both), or may be present as inclusions of other minerals. Elements known to substitute for Pb are Bi, Ag, Sb, Hg and Cu. All of these elements have been found in amounts greater than 1 wt.%. Galena solid-solution (PbS_{ss}) along the galena–matildite join involves coupled substitution of Ag^+ and Bi^{3+}, but other combinations also are possible: Ag^+ and Sb^{3+}, Hg^+ and Bi^{3+}, and possibly Cu^+ and Bi^{3+}. Galena from areas containing Ag and Bi should be examined with particular care to determine if PbS_{ss} exists or other minerals are present. Multiple generations of galena serve as an aid in deciphering different stages of mineralization. The occurrences of multiple-generation galena are restricted to base- and precious-metal deposits where sufficient amounts of Ag and Bi are both present in lead-rich environments. In these environments, galena is thought to originate by either incomplete exsolution resulting from rapid cooling, or by multiple heating events in varied geochemical (including hydrothermal) environments.

Abundant data, such as those from phase equilibria (e.g., Craig 1967), fluid inclusions (e.g., Nedachi et al. 1973), and stable isotopes, indicate that most of the mineral assemblages belonging to the system Ag–(Cu)–Pb–Bi–S have crystallized at temperatures between 200 and 400°C. Galena + Pb-Bi-Ag(Cu) sulfosalt assemblages at Ivigtut, Greenland are interpreted to have crystallized at 300 to 550°C (Karup-Møller 1973, 1977, Karup-Møller & Pauly 1979). Galena and associated sulfosalts in the Darwin district, California, were interpreted to have crystallized at a temperature greater than 350°C (Czamanske & Hall 1975).

Bi and Sb contents in 204 samples of galena from 84 deposits representing a depth range of 300 to 5000 m were examined by Malakhov (1968). Malakhov concluded that the ratio Sb:Bi principally reflects the temperature of crystallization of the galena. Very low Sb:Bi values, of less than 0.06, are characteristic of high-temperature galena; higher Sb:Bi values, in the range 6.0 to 13, are typical of low-temperature galena.

The galena samples studied here are mostly from districts for which geological and laboratory (fluid-inclusion and stable isotope) evidence indicates multiple episodes of mineralization at temperatures of about 300–500°C and at more than 1 km depth (e.g., Darwin: Czamanske & Hall 1975; and Red Mountain – Idarado: Mayor & Fisher 1972; Pequea had only one stage). The Sb:Bi value in these samples of galena is low, which suggests formation at a relatively high temperature and considerable depth. Galena from the Jackass mine (Darwin) has a value of <0.07, that from the Dandy vein system (Red Mountain – Idarado) a value of <0.03, and that from the Pequea silver mine, a value of <0.00X. Galena from the Leadville district has an Sb:Bi ratio of about 0.01. The Jackass, Dandy and Pequea samples are from vein-type deposits hosted in sedimentary rocks, although in both the Darwin and Red Mountain – Idarado districts, galena is found also in replacement deposits. The Leadville sample represents the "bismuth stage" of vein mineralization, but galena at Leadville occurs also in replacement deposits in limestone (Tweto 1968). Additional studies of galena that occurs in replacement deposits formed during other stages of mineralization in these districts are needed to test whether or not Sb:Bi values would provide more definitive evidence of separate stages.

Values of the ratio Sb:Bi for galena from the Round Mountain – Manhattan area range from <0.0001 to 25 (Foord et al. 1988). The values show a wide variation and, moreover, two populations, one with values >2 and the other with values <1. For example, samples of galena from one locality (Lead–Silver King prospect) have two distinct chemical compositions, based on major-, minor- and trace-element contents (Foord et al. 1988). Two samples (DRS–79–18, DRS–74–142b) have low Ag and Bi contents and elevated Sb contents (suggestive of relatively low T and shallow depth) compared to that of a third sample (DRS–74–142a), which has high Ag and Bi and low Sb (suggestive of relatively high T and greater depth). Thus, two generations of galena appear to be present, one a low-temperature form and one a high-temperature form.

Ketchikov (1958) found two generations of galena in a polymetallic skarn deposit in the Soviet Far East: 1) high Bi, early, and 2) no Bi, late. However, within the first generation of galena, great heterogeneity (as much as 2 wt.% Bi difference) was found from closely spaced samples and from the same type of ore. This heterogeneity was attributed to inclusions of galenobismutite. The two generations of galena from the Kti-Tberda deposit (Ontoyev et al. 1982) deposited in Paleozoic and Mesozoic times, respectively, are another example of two distinctly separate episodes of mineralization.

Major questions that still remain to be answered are why and how high-temperature ($>215°C$) galena solid-solutions of different Ag and Bi contents exsolve or become intergrown with the wide variety of observed Bi–Pb–Ag(Cu) sulfosalts. Intergrowths of galena and β-matildite alone are moderately common and represent exsolution from an originally homogeneous higher-temperature PbS_{ss}. If an excess of Bi is present, any number of the Pb–Bi–Ag sulfosalts may crystallize with the PbS_{ss} or exsolve from it as intergrowths. Should Cu also be present, a still greater number of possible sulfosalts may coexist with the PbS_{ss}. Thus at the Jackass mine, Darwin district, an excess of Bi at the time of PbS_{ss} crystallization resulted in coprecipitation or exsolution of eskimoite(?). Exsolution of matildite, β-$AgBiS_2$, from the PbS_{ss} occurred below about $215°C$.

In summary, available chemical data for galena coupled with information on the geological environments of its formation indicate that galena with or without associated Pb–Bi–Ag(Cu) sulfosalt assemblages may be used as an 'indicator'' of multiple and chemically complex stages of mineralization, and as a possible geothermometer. Complete mineralogical study must be made of Bi–Pb–Ag(Cu) sulfosalts to ensure correct identifications and conclusions. In addition to optical studies and microprobe analyses, high-magnification SEM studies and single-crystal X-ray-diffraction studies also are necessary to correctly characterize the sulfosalts in question.

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