# Bismuth and bismuth–antimony sulphosalts from Neogene vein mineralisation, Baia Borşa area, Maramureş, Romania

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## Abstract

Several complex Cu–Pb–Bi, Cu–Pb–Bi–Sb and Ag–Pb–Bi sulphosalt minerals have been identified in samples from hydrothermal vein mineralisation associated with the Toroiaga sub-volcanic body in the Baia Borşa area of Maramureş County, northwest Romania. This is the first chemically-documented report of Bi-sulphosalts in the Neogene metallogenic province around Baia Mare. The investigated samples contain abundant amounts of matildite solid solution within galena, the Cu–Pb/Bi sulphosalts aikinite, friedrichite, krupkaite, hammarite, lindströmite and gladite as well as nuffieldite and berryite. Within the Ag–Pb/Bi group, the majority of analysed grains can be regarded as members of the lillianite homologous series. Three distinct lillianite homologues were identified, which correspond to (i) phases along the lillianite–gustavite solid solution join ($Pb_3Bi_2S_6$–$AgPbBi_3S_6$), (ii) phases within solid solution field of heyrovskyite, and (iii) compositions which best correspond to 'schirmerite', *sensu* Makovicky and Karup-Møller (1977*b*), but may represent disordered gustavite, vikingite or eskimoite. Some of the analysed lillianite homologues contain excess Cu, which may occupy interstitial sites. Furthermore, a large proportion of the lillianite homologues display significant substitution of Sb for Bi within the limits predicted by experimental investigations. Cosalite, also showing a range of compositions including Sb-rich varieties is recognised. Izoklakeite, $Cu_2Pb_{22}(Sb,Bi)_{22}S_{57}$, is an abundant phase throughout the analysed samples, its composition is in good agreement with previously published analyses, except for excess Cu and Fe beyond the limits previously reported. The description of several minerals from this new occurrence and compositional data on them, including the Sb-bearing varieties, provides valuable additional information on compositional limits in natural samples.

KEYWORDS: hydrothermal vein, Bi-sulphosalts, Romania, lillianite homologous series, bismuthinite derivatives, izoklakeite.

## Introduction

THE hydrothermal vein-type deposits of the Neogene metallogenic province in northern Romania are well known for the number, abundance and often spectacular crystal morphology of various Sb-sulphosalts. Indeed, the province represents the type locality for four important minerals of this group (andorite, fizelyite, fülöppite and semseyite; Bologa and Udubaşa, 1995). In contrast, and not surprising given their trace character, there exist few published data about the occurrence of Bi-sulphosalts within these vein systems.

In recent years, a wide, and ever increasing number of Bi-sulphosalt phases have been described from Romanian deposits of various genetic types, although dominantly from skarn occurrences in Banat and elsewhere, for example at Băiţa Bihor. This paper constitutes the first confirmed report of Bi-sulphosalts from a deposit in the Neogene metallogenic province of Maramureş County.

Significantly, some of the mineral phases described here contain both Bi and Sb, the latter substituting for Bi. Although a number of Bi–Sb sulphosalts are known in nature (Mozgova *et al.*, 1990*a*; Moëlo *et al.*, 1995), it is clear from the limited number of references in the literature to minerals in which both Bi and Sb are essential constituents, that these would appear to be an appreciably rarer group than either the Sb- or Bi-sulphosalts. Sulphosalt minerals which contain essential Sb and Bi as well as a group of Bi-

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sulphosalts which may incorporate significant amounts of Sb into their structures, are both previously reported from not more than a dozen or so localities worldwide. The mineral phases described here thus represent an important additional occurrence of sulphosalt phases containing both Bi and Sb. In this paper, a preliminary account of compositional variation is given. Unequivocal confirmation of mineral identities is inhibited by the lack of X-ray diffraction analyses, which are, in turn, denied by the small grain size and their intergrown nature.

## Geological setting

The Neogene Toroiaga-Ţiganul sub-volcanic Massif, situated in the Maramureş Mountains, to the north of Baia Borşa, in northwestern Romania (Fig. 1), is host to a number of important hydrothermal veins which are currently exploited for base and precious metals. The deposits, which belong to the Toroiaga–Birgau–Tibles metallogenic zone, are equivalent to the second and third phases of Neogene metallogenesis in the Baia Mare area. The setting, age relationships and the evolution of the magmatic rocks have been described by Socolescu (1954) and Berza *et al.* (1982) amongst others. Morphology, petrography and genesis of the vein-type deposits, which are several hundred metres long and plunge sharply to SW, has been documented by Szöke and Steclaci (1962), Borcoş (1967), Gridan *et al.* (1979) and Borcoş *et al.* (1982). The polymetallic veins were interpreted by Borcoş (1967) as healing fractures associated with the arrival of the most recent of five injections of magma into the system.

The ore mineralogy of the Toroiaga vein systems has been described in detail by Steclaci in Szöke and Steclaci (1962). Other ore mineralogical contributions have been made by Götz *et al.* (1990), and Damian and Oşan (1993). Borcoş *et al.* (1982) described a vertical zonation within the ores; the chalcopyrite content generally decreasing towards higher levels, while sphalerite, galena, a wide variety of Cu-, Pb- and Ag- sulphosalts as well as gold tend to increase upwards. Borcoş (1967) proposed monoascendence of the fluids and mineralisation at temperatures of 300°C and lower, with the observed zonation suggesting cooler temperatures at upper levels. The main ore minerals are pyrite, pyrrhotite (lower part), chalcopyrite, marcasite, arsenopyrite, sphalerite and galena. The presence of bournonite, semseyite, jamesonite, tetrahedrite, freibergite, boulangerite, geocronite, gratonite, pyrargyrite, matildite and germanite have been optically determined by Szöke and Steclaci (1962) and others. This most probably represents a minimum list of sulphosalts present in the mineralisation, since modern microanalytical determinations of component minerals were lacking until commencement of the present study. Continuing electron probe microanalysis is likely to reveal the presence of others. Gangue minerals are quartz, calcite, dolomite and barite. Socolescu (1954) proposed the presence of porphyry-copper mineralisation beneath the known vein systems. Recent lithogeochemical studies (Chioreanu *et al.*, 1993) tend to support this argument.

A reference suite of samples from the Toroiaga hydrothermal vein system were initially collected by the author in order to compare the compositions of major and minor minerals from the hydrothermal vein ores with those from the Cambrian stratiform metamorphosed massive sulphide deposits of the Baia Borşa area (Cook, 1995; Radu and Cook, 1995; Cook, in prep.). Within this suite of samples, almost randomly chosen from the accessible parts of the Toroiaga deposit, several assemblages of Bi- and Bi–Sb sulphosalts were found. Locality details on the samples containing the minerals in question are given in Table 1; sample locations are shown on the geological sketch map (Fig. 1).

In addition to those from the vein-type mineralisation in which the majority of Bi-sulphosalts were found, four samples of metamorphosed stratiform massive sulphide ores were also found to contain Bi-sulphosalts (Table 1). Observation at the sample location did not reveal the presence of any mineralised microveining in the samples from the Măcârlău, Ivăşcoaia or Catarama deposits. The appearance of Bi-minerals in metamorphosed syngenetic ores, similar to those from epigenetic vein-type ores is somewhat enigmatic and warrants further study. The syngenetic ores at Baia Borşa certainly contain appreciable Bi, at concentrations up to several hundred ppm, although most of this has been shown to be as solid solution within galena (Cook, 1995; Cook, in prep.). Several Bi minerals have long been known to occur within the stratiform deposits of the Baia Borşa orefield, particularly in the Măgura lens, including galenobismutite and bismuthinite (Socolescu *et al.*, 1962). Enrichment in Bi-sulphosalts within the stringer zones of massive pyritic deposits has been documented in both the Kuroko deposits of Japan (Urabe, 1974) and the Iberian pyrite belt (Marcoux and Moëlo, 1993; Marcoux *et al.*, 1996).

The true extent of occurrence of Bi- and Bi–Sb sulphosalts within the Toroiaga vein system is unknown. Their presence in several samples collected by the present author may be coincidental, but more likely suggests that they are relatively widespread throughout the system. The presence of Bi and Bi–Sb sulphosalts within other deposits belonging to the Neogene metallogenic province of

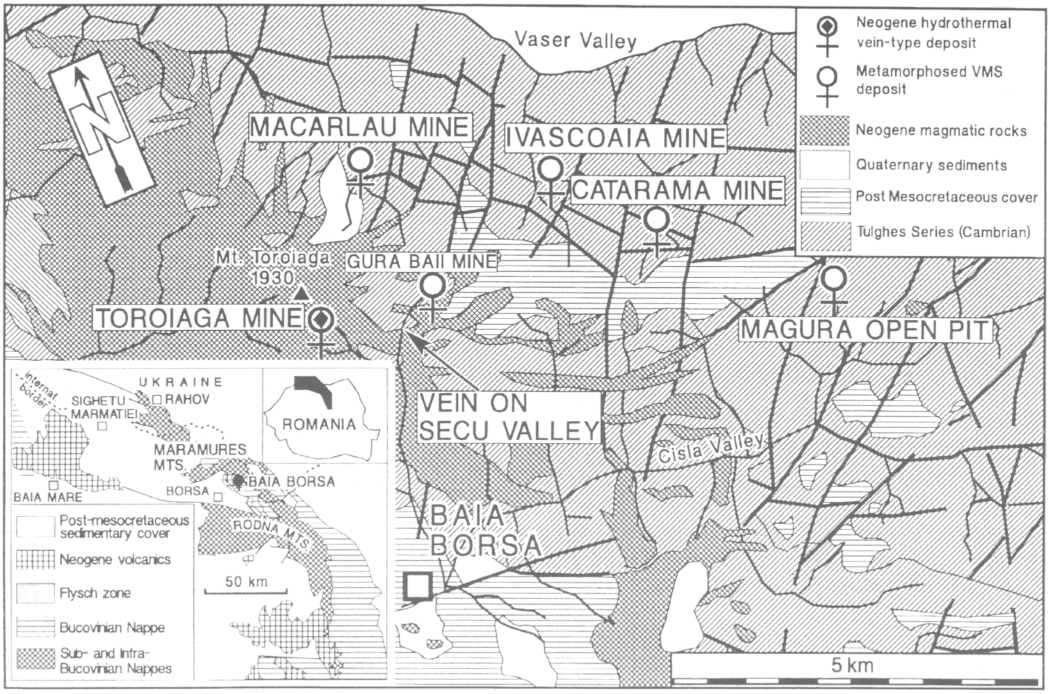
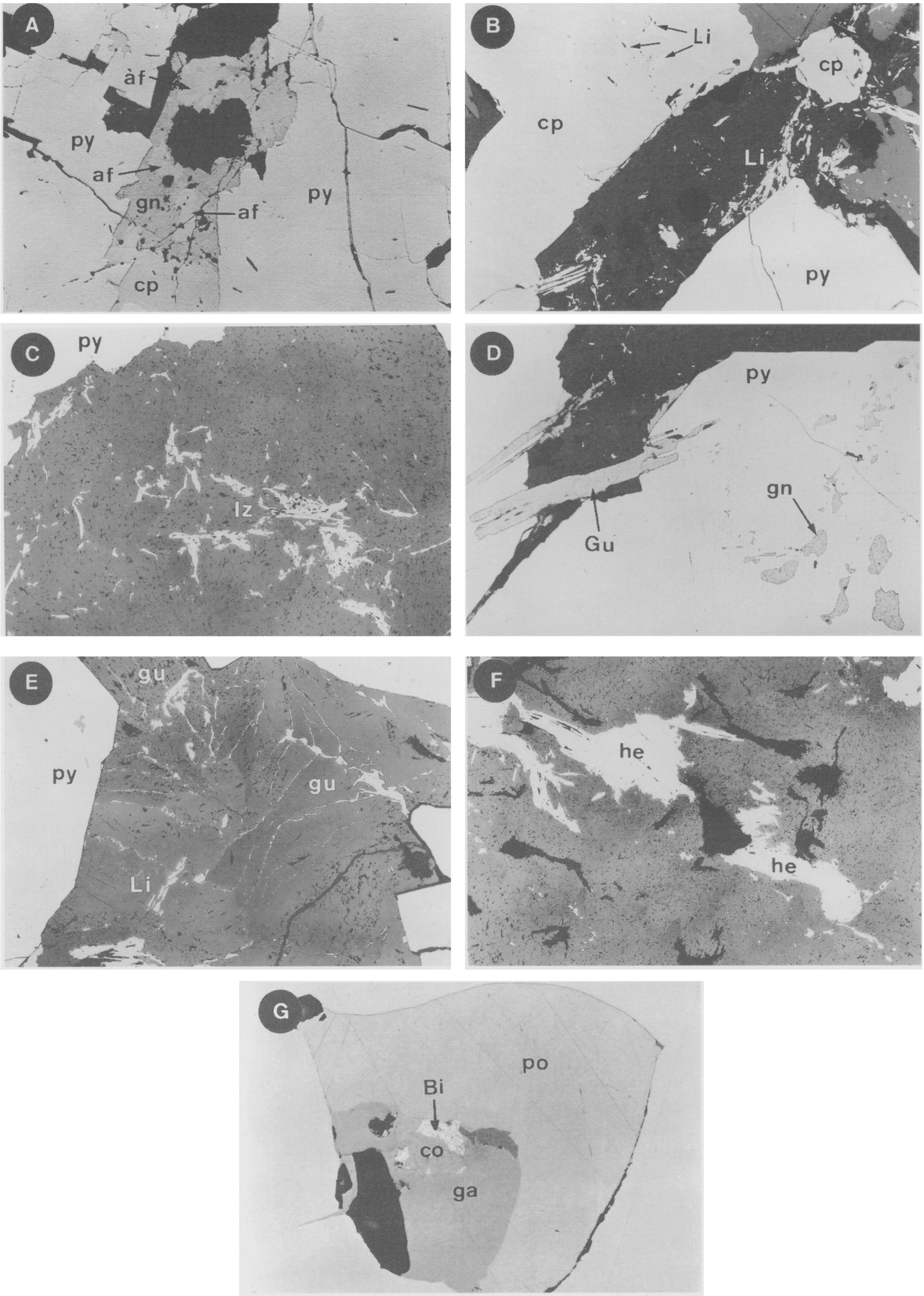


FIG. 1. Geological map of the central part of the Baia Borşa orefield, indicating the location of deposits mentioned in the text and other sample locations.

TABLE 1. Sample localities and Bi-sulphosalt assemblages

| | |
|---|---|
| (i) Underground, Toroiaga Mine (Neogene vein mineralisation): | |
| BB 190 Vein "X" on the +920 level: | Lillianite-gustavite, heyrovskyite, izoklakeite |
| BB 194, 194B, 194C, 194D, 194O Caterina Vein: (level 3) | Lillianite-gustavite, heyrovskyite, 'schirmerite', Izoklakeite. |
| BB 197 Caterina Vein, +1330 Level: | Lillianite-gustavite, 'schirmerite'. |
| (ii) Surface exposures (Neogene vein mineralisation): | |
| BB 334 Mineralised vein, Secu Valley: | Lillianite-gustavite, nuffieldite, cosalite, phase A. |
| BB212, 212A Mineralised fracture, Măgura open pit: (associated with a clearly tectonic breccia) | Bismuthinite derivatives |
| (iii) Other underground samples (metamorphosed VMS deposits): | |
| BB 147 Disseminated ore, Ivăşcoaia Mine: | Bismuthinite derivatives, cosalite |
| BB 158 Massive py-cp ore, Ivăşcoaia Mine: | Bismuthinite derivatives |
| BB 1107 Măcârlău Mine: | Cosalite |
| BB 1759 Catarama Mine: | Bismuthinite derivatives, berryite |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Baia Mare should be investigated. Little data exist to show that they are widespread, although a number of earlier references (e.g. Helke, 1938) mention trace amounts of Bi-sulphosalts in Cavnic and other deposits. Andronescu *et al.* (1962) describe 'schirmerite' from the Ilba deposit. Assemblages including Bi-sulphosalts comparable to those described here are suspected, based on optical determination, to be present in other vein-type ores, particularly at Baiuţ (Damian, pers. comm., 1995).

## Petrographic relationships

All Bi-sulphosalt-bearing samples contain chalcopyrite, with lesser amounts of pyrite, galena, sphalerite and arsenopyrite in a matrix of quartz with minor siderite. Small grains of electrum, enclosed in pyrite, were identified in some samples.

Bi-sulphosalts are recognised in five associations: (i) as oval-shaped inclusions in chalcopyrite or on its grain margins (Figs. 2*a,b*), (ii) as inclusions within and/or on the edge of coarse-grained pyrite (Fig. 2*b,d*), (iii) as elongate idioblastic crystals within the quartz-siderite matrix, commonly fibrous, more rarely massive, which display no specific orientation (Figs. 2*c,e,f*), (iv) as very fine fracture fillings in quartz (Fig. 2*e*), and, (v — rare) as inclusions in pyrite, associated with native Bi (Fig. 2*g*).

Lillianite–gustavite, heyrovskyite and izoklakeite were all observed equally in each association. Aikinite, friedrichite and other bismuthinite derivatives were, however, only observed as inclusions in chalcopyrite. Bismuthinite derivatives, cosalite, nuffieldite and berryite did not, with the exception of one small grain of cosalite, co-exist with lillianite homologues. Bi–(Sb) sulphosalt mineral assemblages observed are listed in Table 1.

In one sample (BB 194), the Bi-sulphosalts comprise as much as 1% of the total volume; several hundred grains of the Bi–Sb phases were observed in the five polished sections cut from this sample. The largest grain measured some 150 × 30 µm, but the majority were considerably less than 50 µm in diameter. In the other samples, the phases were finer grained, generally not exceeding 20 µm in diameter, and were appreciably rarer, being restricted to no more than ten small grains per polished section.

## Electron probe microanalysis

All electron probe microanalyses were carried out on the Cameca SX-50 instrument at the Mineralogical Institute, University of Würzburg, Germany. Standards and radiations used were as follows: pure Bi ($M\alpha$), pure PbS (Pb-$M\alpha$), AsGa (As-$L\alpha$), $FeS_2$ (Fe-$K\alpha$, S-$K\alpha$), pure Cu ($K\alpha$), ZnS (Zn-$K\alpha$), pure Ni ($K\alpha$), pure Co ($L\alpha$), pure Te ($L\alpha$), pure Se ($L\alpha$), pure Ag ($L\alpha$), pure Au ($M\alpha$), HgS (Hg-$M\alpha$), $Sb_2S_3$ (Sb-$L\alpha$), MnTi (Mn-$K\alpha$). No other elements were detected in any of the minerals analysed. A probe current of 15 nA and an accelerating voltage of 15 kV were used. All mineral grains and standards were analysed under the same operating conditions. Minimum detection limits were approx. 0.1 wt.% for all elements.

## Compositional data

*Galena solid solution ($PbS_{ss}$).* Galena is abundant in all samples which contain Bi- and Bi–Sb sulphosalts. All analysed galena grains are characterised compositionally by elevated Ag and Bi contents. Microscopy at high magnifications (>100 ×) and back-scattered electron images revealed no microscopic inclusions of other phases. This, together with the homogeneity of microprobe analyses of individual grains and the excellent correlation of Ag and Bi, suggest that the galenas are members of the galena–matildite solid solution series (Craig, 1967; Foord and Shawe, 1989), hereafter referred to as $PbS_{ss}$. Microprobe analyses indicate the maximum mean values of Ag and Bi in the $PbS_{ss}$ grains are 3.75 and 8.40 wt.% respectively (Table 2). This corresponds to an $AgBiS_2$ substitution of over 17 mol.%. However, such a high degree of substitution was observed in only a single grain; all others were in the 4 to 7 mol.% $AgBiS_2$ range. In all analyses, Bi exceeds Ag by some 10%, suggesting additional Bi solid solution, not coupled with Ag.

FIG. 2. Photomicrographs of Bi-sulphosalt phases in reflected light: (*a*) Bismuthinite derivatives of aikinite-friedrichite composition (af) associated with galena (gn) and chalcopyrite (cp). py: pyrite. Sample BB 212. Field of view: 320 µm. (*b*) Lilianite–gustavite, Li (anal. L5) as small inclusions in chalcopyrite (cp) and within the quartz-siderite matrix (dark) py: pyrite. Sample BB 194D. Field of view: 1100 µm. (*c*) Izoklakeite, Iz, as small grains in siderite (dark). py: pyrite. Sample BB 194C. Field of view: 1440 µm. (*d*) Gustavite, gu, (anal. L13) as needle-shaped laths at the edge of coarse pyrite grains (py), gn: galena Sample BB 194C. Field of view: 510 µm. (*e*) Lillianite, ll, and gustavite, gu (anals. L4 & L12) as fine fracture fillings in quartz (dark) py: pyrite. Sample BB 194D. Field of view: 1200 µm. (*f*) Heyrovskyite, he (anal. H4) within quartz (dark). Sample BB 194C. Field of view: 1500 µm. (*g*) Inclusion of native Bi, with cosalite, co, galena, ga and pyrrhotite, po in pyrite. Sample: BB147. Field of view: 185 µm.

TABLE 2. Microprobe analyses of galena–matildite solid solution ($PbS_{ss}$)

| Sample | BB 194B | BB 194 | BB 19C | BB 192 | BB 212A | BB 212 | BB 334 |
|---|---|---|---|---|---|---|---|
| n | 3 | 17 | 8 | 7 | 2 | 1 | 5 |
| Wt.% (mean of n analyses) | | | | | | | |
| Pb | 75.03 | 81.89 | 83.91 | 82.92 | 80.58 | 83.50 | 83.81 |
| Bi | 8.40 | 3.28 | 2.91 | 2.25 | 2.74 | 2.42 | 1.77 |
| Ag | 3.75 | 1.44 | 1.27 | 1.08 | 1.31 | 1.30 | 0.58 |
| Sb | 0.06 | 0.08 | 0 | 0 | 0 | 0 | 0 |
| S | 14.03 | 13.88 | 13.62 | 13.30 | 12.95 | 13.19 | 13.15 |
| Se | 0.03 | 0.02 | 0 | 0 | 1.20 | 1.11 | 1.13 |
| Te | 0.04 | 0.01 | 0.03 | 0 | 0.85 | 0 | 0.06 |
| Total | 101.35 | 100.61 | 101.74 | 99.55 | 99.63 | 101.52 | 100.50 |
| Atomic proportions: | | | | | | | |
| Pb | 0.827 | 0.929 | 0.940 | 0.950 | 0.926 | 0.944 | 0.968 |
| Bi | 0.091 | 0.039 | 0.032 | 0.026 | 0.031 | 0.028 | 0.020 |
| Ag | 0.080 | 0.032 | 0.028 | 0.024 | 0.029 | 0.028 | 0.013 |
| Sb | 0.001 | 0.002 | 0 | 0 | 0 | 0 | 0 |
| S | 1.000 | 1.019 | 0.986 | 0.985 | 0.962 | 0.963 | 0.980 |
| Se | <0.001 | <0.001 | 0 | 0 | 0.037 | 0.033 | 0.035 |
| Te | <0.001 | <0.001 | <0.001 | 0 | 0.015 | 0 | <0.001 |

The range of $PbS_{ss}$ compositions have been depicted on a $Bi_2S_3$–$AgS_2$–$Pb_2S_2$ ternary diagram, in which each analysis has been plotted (Fig. 3). The $PbS_{ss}$ grains showing the greatest substitution were enclosed in chalcopyrite, in association with lillianite or izoklakeite. An $AgBiS_2$ substitution of 17 mol.% places the analysed compositions among some of the highest yet reported. Kovalenker *et al.* (1993)

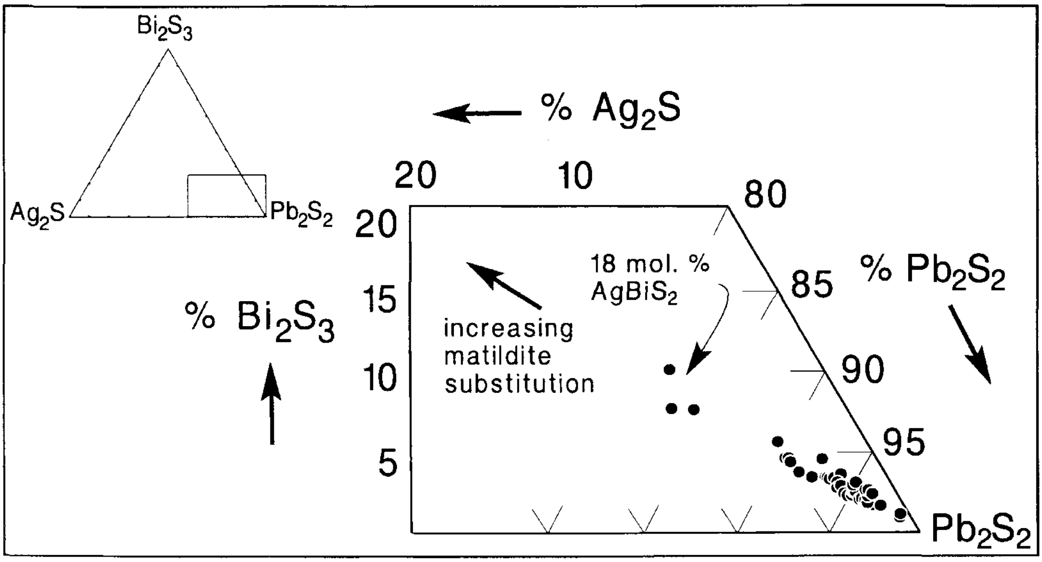

FIG. 3. Chemical compositions of analysed galena-matildite ($PbS_{ss}$) phases, plotted within the PbS–$Bi_2S_3$–$Ag_2S$ ternary system.

described 10 to 20 mol.% $AgBiS_2$ in galena from the Štiavnica-Hodruša orefield, Slovakia and furthermore, gave evidence for no less than six sulphosalt phases with compositions along the galena–matildite join.

*Bi and Bi-Sb sulphosalts.* Electron probe microanalytical data was collected on more than 300 Bi-sulphosalt grains. Several distinct compositional groups were determined, which are here divided into the following: (i) minerals without essential Ag and belonging to the aikinite–bismuthinite series, (ii) minerals containing Ag, in which Cu is minimal or absent, and which may be correlated to phases within the lillianite homologous series, (iii) Cu and Ag-bearing phases with a high Sb/(Sb+Bi) ratio; izoklakeite, (iv) cosalite, (v) nuffieldite and (vi) berryite.

*Aikinite-bismuthinite series ($Cu_xPb_xBi_{12-x}S_{18}$).* Six samples were found to contain minerals of the aikinite–bismuthinite series ($PbCuBiS_3$–$Bi_2S_3$). The majority of the 60 grains analysed have compositions clustered towards the aikinite ($CuPbBiS_3$)–friedrichite ($Cu_5Pb_5Bi_7S_{18}$) end of the series. These are given in wt.% and as formulae calculated on the basis of (Cu+Pb)/2 +Bi = 8 atoms together with $a_n$ values, indicating the position in the aikinite-bismuthinite series, in Table 3. As can be seen from the $Cu_2S$–$PbS$–$Bi_2S_3$ plot (Fig. 4), the spread of compositional data points extends along the region between aikinite and friedrichite, without a discernable gap between them. A small minority of grains displayed compositions richer in Bi, close to those of hammarite ($Cu_2Pb_2Bi_4S_9$), krupkaite ($CuPbBi_3S_6$), lindströmite ($Pb_3Cu_3Bi_7S_{15}$) and gladite ($CuPbBi_5S_9$). Within individual grains, compositional variation was limited, with no evidence of unmixing of different derivatives noted. A single grain with a composition close to bismuthinite (Fig. 4) was observed as an inclusion in Sb-cosalite.

Inspection of the data set (Table 3) reveals amounts of Fe in excess of those normally found within bismuthinite derivatives, ranging up to more than 1 wt.% in some analyses. To test the accuracy of the data, in which Cu:Pb should be 1 in all bismuthinite derivatives, $dn_a$ values were calculated (Makovicky and Makovicky, 1978). This was carried out, (i) excluding Fe (and Ag) from the calculation and (ii) assuming all Fe (and Ag) to be substituting for Cu. In the majority of cases, the error value was less when Fe and Ag were considered, but still gives an apparent excess of (Cu+Fe+Ag) over Pb. It is concluded that some, probably the majority, of Fe does substitute for Cu and is required by stoichiometry. The excess may best be attributed to Fe minerals in the surrounding matrix. The errors are, however, small and generally lie within the accuracy of electron probe microanalysis. Almost all analysed grains of bismuthinite derivatives contained some minor Sb and Se, at concentrations ranging up to 0.54 and 1.80 wt.% respectively.

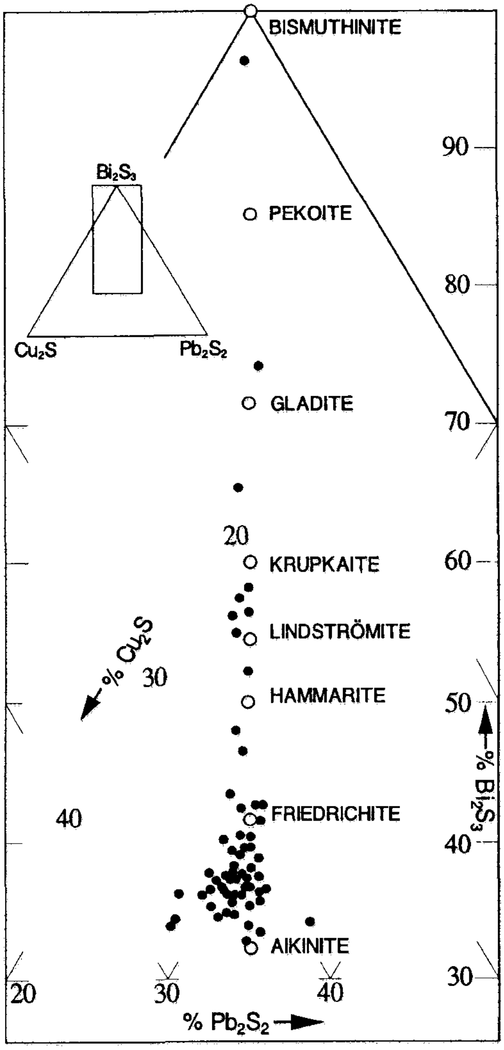

FIG. 4. Chemical compositions of analysed phases within the aikinite-bismuthinite series, plotted on a $PbS$–$Bi_2S_3$–$Cu_2S$ ternary diagram.

The chemistry and structure of minerals within the aikinite-bismuthinite series have been discussed by a number of workers (Harris and Chen, 1976; Mumme and Watts, 1976; Mumme *et al.*, 1976; Makovicky and Makovicky, 1978; Žák, 1980; Pring and Hyde, 1987; Pring, 1989; 1995; Mozgova *et al.*, 1990*b*). Most studies of these minerals in natural samples

TABLE 3. Microprobe analyses of bismuthinite derivatives

| Sample | BB 158 | BB 212 (2) | BB 212a (1) | BB 212a (2) | BB 212a (3) | BB147 2.2 | BB147 2.5 | BB158 9.7 | BB147 3.1 | BB158 9.6 | BB147 3.3 | BB158 9.5 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| n | 19 | 3 | 4 | 6 | 3 | | | | | | | |
| Wt.% (mean of n analyses) | | | | | | | | | | | | |
| Cu | 9.72 | 8.93 | 9.33 | 9.88 | 10.43 | 8.66 | 7.93 | 7.50 | 6.91 | 5.87 | 5.90 | 4.88 |
| Ag | 0.04 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Fe | 0.43 | 0.91 | 0.31 | 0.43 | 0.51 | 0.18 | 0.22 | 0.15 | 0.37 | 0.46 | 0.26 | 0.24 |
| Pb | 32.51 | 30.91 | 31.03 | 32.30 | 22.80 | 29.30 | 24.89 | 24.13 | 23.53 | 19.63 | 19.97 | 15.49 |
| Bi | 39.13 | 41.74 | 42.13 | 40.70 | 38.04 | 43.34 | 47.84 | 50.01 | 51.74 | 55.72 | 55.96 | 61.50 |
| Sb | 0.12 | 0.19 | 0.24 | 0.15 | 0.12 | 0.21 | 0.26 | 0.23 | 0.33 | 0 | 0.54 | 0.10 |
| S | 16.39 | 16.61 | 17.09 | 16.81 | 16.81 | 16.77 | 16.21 | 17.33 | 16.77 | 17.41 | 17.24 | 18.04 |
| Se | 0.81 | 0.54 | 0.52 | 0.57 | 0.48 | 1.56 | 1.80 | 0.67 | 1.23 | 0.25 | 1.42 | 0.31 |
| Te | 0.04 | 0.03 | 0.16 | 0.09 | 0.25 | 0 | 0 | 0 | 0.14 | 0 | 0 | 0 |
| Total | 99.21 | 99.84 | 100.79 | 100.92 | 100.82 | 100.02 | 99.15 | 100.02 | 101.02 | 99.34 | 100.02 | 100.56 |
| Formula to (Cu+Ag+Fe+Pb)/2 + Bi = 8.00 atoms | | | | | | | | | | | | |
| Cu | 3.52 | 3.18 | 3.31 | 3.50 | 3.73 | 3.12 | 2.81 | 2.62 | 2.39 | 2.03 | 2.01 | 1.65 |
| Ag | 0.01 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Fe | 0.18 | 0.31 | 0.12 | 0.17 | 0.20 | 0.07 | 0.09 | 0.06 | 0.15 | 0.18 | 0.10 | 0.09 |
| Pb | 3.62 | 3.38 | 3.38 | 3.51 | 3.75 | 3.24 | 2.70 | 2.59 | 2.49 | 2.08 | 2.09 | 1.60 |
| Bi | 4.31 | 4.51 | 4.55 | 4.38 | 4.14 | 4.75 | 5.15 | 5.32 | 5.43 | 5.86 | 5.80 | 6.31 |
| Sb | 0.02 | 0.04 | 0.04 | 0.03 | 0.02 | 0.04 | 0.05 | 0.04 | 0.06 | 0 | 0.10 | 0.02 |
| (Bi+Sb) | 4.34 | 4.57 | 4.59 | 4.41 | 4.16 | 4.79 | 5.20 | 5.36 | 5.49 | 5.86 | 5.90 | 6.33 |
| S | 11.78 | 11.75 | 12.03 | 11.80 | 11.92 | 11.97 | 11.38 | 12.02 | 11.47 | 11.93 | 11.65 | 12.07 |
| Se | 0.24 | 0.16 | 0.15 | 0.16 | 0.14 | 0.45 | 0.51 | 0.19 | 0.34 | 0.07 | 0.39 | 0.09 |
| Te | 0.01 | 0.01 | 0.03 | 0 | 0.04 | 0 | 0 | 0 | 0.02 | 0 | 0 | 0 |
| (S+Se+Te) | 12.03 | 11.90 | 12.20 | 11.98 | 12.11 | 12.42 | 11.89 | 12.21 | 11.84 | 12.00 | 12.04 | 12.15 |
| $n_a$ (1) | 91.6 ± 3.2 | 86.8 ± 1.9 | 85.4 ± 3.7 | 90.2 ± 5.2 | 96.5 ± 3.2 | 80.4 | 70.0 | 65.9 | 62.8 | 53.6 | 52.5 | 41.8 |
| $n_a$ (2) | 89.2 ± 3.0 | 83.0 ± 1.8 | 83.9 ± 4.2 | 88.0 ± 5.1 | 94.0 ± 2.9 | 79.4 | 68.9 | 65.2 | 60.9 | 51.4 | 51.3 | 40.6 |
| $dn_a$ (1) | −2.4 ± 4.0 | −2.7 ± 3.6 | −1.4 ± 1.4 | −4.0 ± 4.2 | −4.4 ± 2.5 | 1.1 | −4.8 | −2.4 | −1.0 | −3.2 | −0.6 | −3.2 |
| $dn_a$ (2) | 2.3 ± 2.8 | 5.1 ± 3.3 | 1.7 ± 1.1 | 0.3 ± 3.6 | 0.5 ± 3.9 | 2.9 | −2.6 | −0.9 | 2.6 | 1.3 | 1.9 | −1.1 |

(1) with Fe & Ag included with Cu
(2) without Fe & Ag included with Cu

have indicated a nearly continuous compositional range between individual members of the series (e.g. high-Bi and low-Bi varieties). Although each member of the series, with the exceptions of bismuthinite, krupkaite and aikinite, represents an ordered superstructure (in the case of friedrichite, for example, intergrowth of 4 aikinite and 2 krupkaite ribbons), the spread of intermediate compositions can be related to disordering of ribbons. Pring (1989) showed disordering accounts for observed compositional variation right across the aikinite-krupkaite compositional range. Disordered intergrowths of aikinite and krupkaite ribbons, as well as disordered intergrowths of the superstructures were identified. Solid solution does not play a significant role. However, in most experimental studies, the development of well-ordered superstructures could be prevented by rapid quenching, leading to disordering on the unit cell level. This may explain the difficulties experienced in preparation of synthetic superstructure phases within this series.

*Lillianite homologous series.* Several distinct groups of compositions have been determined in the analysed suite which correspond to phases within the lillianite homologous series (Makovicky and Karup-Møller, 1977*a,b*). These can be divided into: (i) those with a composition along or close to the lillianite – gustavite join, which are here subdivided into those without detectable copper and those with minor Cu contents, (ii) compositions corresponding to the heyrovskyite solid solution series, and (iii) a number of phases which are best described as 'schirmerite', *sensu* Makovicky and Karup-Møller (1977*b*); i.e. not only the mineral schirmerite itself, with defined compositional limits, but also vikingite, ourayite and possibly additional lillianite homologues, which are disordered and do not display ideal stoichiometry.

Lillianite–gustavite and 'schirmerite' compositions predominate in the analysed suite; heyrovskyite solid solution compositions were only determined in five grain aggregates. Compositional variation among all the lillianite homologues is expressed in $Bi_2S_3$ – PbS – $Ag_2S$ space in Fig. 5. Each analysis is plotted individually in this figure. For the purposes of the tabular listings, however, the data have been grouped together; each group representing multiple analyses on a single grain or a cluster of grains with similar compositions. The mean analyses of each group are given in Tables 4–7. Each group of analyses is numbered (L1 to L17, H1 to H4, S1 to S8); the numbers appearing both in the tables, and also on Fig. 5.

*(i) Lillianite-gustavite solid solution series ($Pb_3Bi_2S_6$-$AgPbBi_3S_6$).* A range of compositions (Tables 4 and 5, Fig. 5) are attributed to members of the lillianite–gustavite solid solution series. These range from compositions close to end member lillianite to compositions closer to gustavite, and extend across the region of the miscibility gap which has been proposed to exist between $Gu_{55}$ and $Gu_{85}$ (Makovicky and Karup-Møller, 1977*b*). Nearly all analysed grains contained significant amounts of Sb, with the mol. Sb/(Sb+Bi) ratio varying from 2 to as much as 34%. There would appear to be a weak positive correlation between Sb content and extent of gustavite substitution.

*Cu-free varieties.* Cu is normally absent or very minor in all lillianite homologues. No Cu was detected in about half the lillianite–gustavite grains analysed (Table 4). N values after Makovicky and Karup-Møller (1977*a*), using the atomic ratios of Ag, Pb and Bi, were calculated. N is ideally 4 for phases along the lillianite–gustavite join and show a narrow range from 3.96 to 4.15, with an average of approximately 4.05. Makovicky and Karup-Møller (1977*b*) have indicated that variation from ideal N values may arise through disorder phenomena brought about by rapid crystallisation. Most members of the lillianite–gustavite series in the literature show some deviation from the ideal N value of 4 (e.g. Czamanske and Hall, 1975; Makovicky and Karup-Møller, 1977*b*; Ontoev *et al.*, 1980).

*Cu-bearing varieties.* Lillianite with contents of Cu ranging from 0.2 to as much as 1.5 wt.% were analysed (Table 5). In no single analysis does the Cu/(Cu+Ag) ratio exceed 0.2. This suite, like the above Cu-free varieties also shows excellent correspondence of N values to 4 (ranging from 3.75 to 4.14; mean, 4.01). The compositional range along the lillianite–gustavite join is actually wider than in the Cu-free varieties. Sb/(Sb+Bi) ratios vary between 6 and 33 mol.%. It is assumed that the Cu is substituting for Ag. Formula calculation suggests, however, that although much of the Cu can be accommodated in terms of the $(Ag+Cu)+Pb \rightleftharpoons 2Bi$ substitution, some of the Cu is excess and cannot reliably be assigned to any given site. There is no apparent correlation between Cu content and any other variable. Any possibility that the Cu derives from the surrounding chalcopyrite is ruled out; as many Cu-bearing lillianites were found enclosed in gangue as in chalcopyrite.

*(ii) Heyrovskyite solid solution.* Four compositions were detected which correspond to members of the heyrovskyite solid solution series ($hey_{ss}$); Table 6, Fig. 5. Although end-member heyrovskyite, with the formula $AgPb_{10}Bi_5S_{18}$, according to Clark (1993), is almost free of (Ag,Cu), most natural members of the series contain, often significant, amounts of both elements (e.g. Klomínský *et al.*, 1971; Czamanske and Hall, 1975; Karup-Møller and Makovicky, 1981; Moëlo *et al.*, 1987; Vinigradova *et al.*, 1992). Chang *et al.* (1988) suggested an extensive solid solution in

the $Ag_2S$–$Cu_2S$–PbS–$Bi_2S_3$ system at 500°C, ranging from the Cu–Ag-free end-member to $Ag_{0.76}Cu_{1.31}Pb_{3.18}Bi_{3.18}S_9$. This latter composition does not, however, plot on the n = 7 join of Makovicky and Karup-Møller (1977*a,b*) and may not correspond to heyrovskyite.

Heyrovskyite from Baia Borşa has compositions falling along the central part of this solid solution join (Fig. 5), with N values close to 7 (6.74 to 7.16). All were Sb-bearing; the Sb-richest variety corresponding to the Ag-Cu poorest variety. Chang *et al.* (1980) showed up to 33% substitution of Sb for Bi in $hey_{ss}$ at 500°C. Ertl *et al.* (1994) recently reported Sb-bearing heyrovskyite with 1.31 to 10.22 wt.% Sb, corresponding to Sb/(Sb+Bi) ratios averaging 28.7, but ranging as high as 45.3 mol.%.

*(iii) Other lillianite homologues.* A large number of grains analysed in the present study lie in, or close to, the compositional field of 'schirmerite' (Table 7, Fig. 5), ranging from compositions just below the N = 4 join to close to the N = 7 join. Makovicky and Karup-Møller (1977*b*) redefined schirmerite as a disordered monoclinic phase with a compositional range for schirmerite extending from that of gustavite to a point on the N = 7 join with the composition $Pb_3Ag_{1.5}Bi_{3.5}S_9$. This compositional range overlaps

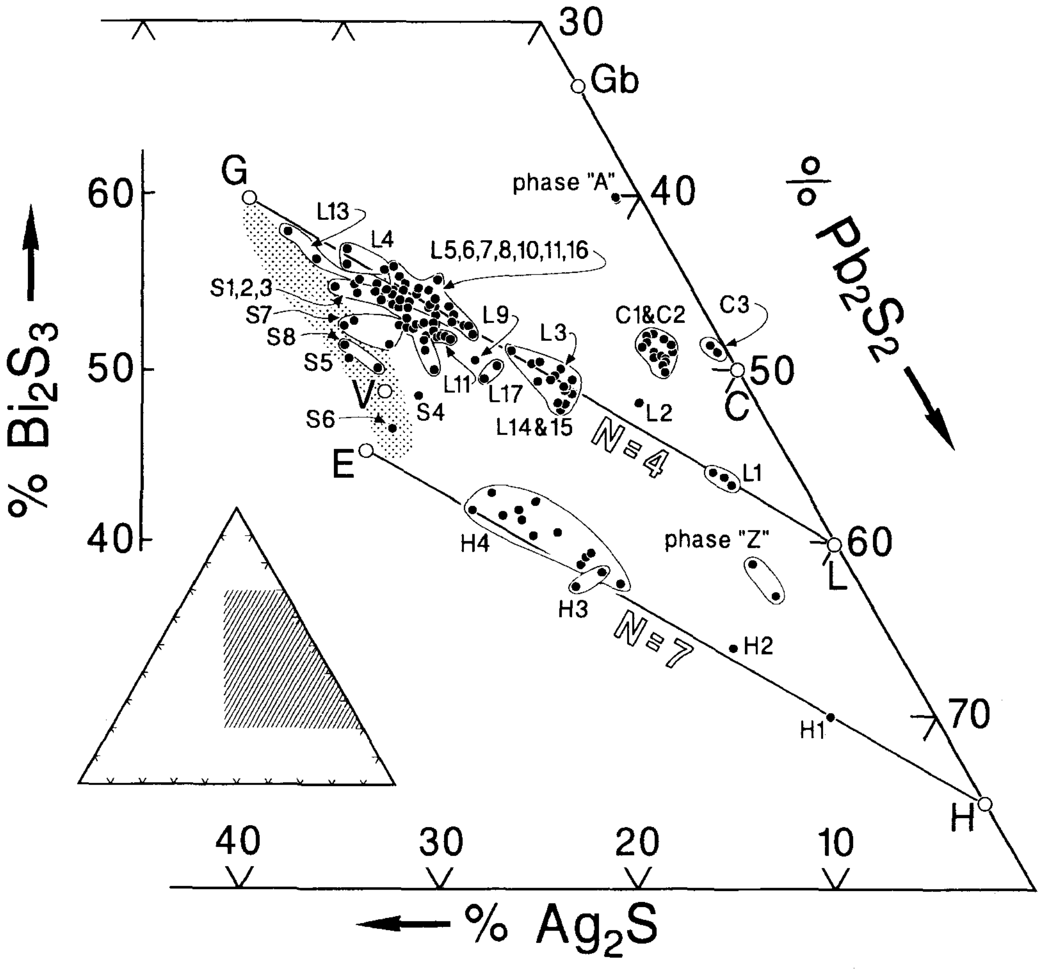

FIG. 5. Chemical compositions of analysed phases identified as members of the lillianite homologous series, plotted on a PbS–$Bi_2S_3$–$Ag_2S$ ternary diagram. Numbers refer to analyses tabulated and discussed in the text. H: heyrovskyite, L: Lillianite, G: gustavite, V: Vikingite, E: Eskimoite, C: Cosalite, Gb: Galenobismutite. Shaded area: Schirmerite (after Makovicky and Karup-Møller, 1977*a,b*). In the interests of clarity, cosalite analyses C4 have not been plotted.

TABLE 4. Microprobe analyses of lillianite–gustavite (without Cu)

| Sample | BB 190 (2) | BB 1940 (B) | BB 194 (R) | BB 194C (2) | BB 194C (Q) |
|---|---|---|---|---|---|
| n | 7 | 3 | 12 | 3 | 7 |
| | (L13) | (L14) | (L15) | (L16) | (L17) |
| Wt.% (mean of n analyses) | | | | | |
| Cu | 0 | 0 | 0 | 0 | 0 |
| Ag | 8.07 | 4.37 | 4.62 | 7.04 | 6.53 |
| Fe | 0.13 | 0.16 | 0.21 | 0.44 | 0.58 |
| Pb | 25.72 | 35.42 | 35.38 | 28.73 | 31.10 |
| Bi | 43.85 | 42.94 | 42.25 | 43.48 | 44.28 |
| Sb | 4.68 | 0.67 | 0.65 | 4.38 | 1.29 |
| S | 17.17 | 15.90 | 16.44 | 16.92 | 16.69 |
| Se | 0.28 | 0.15 | 0.13 | 0.24 | 0.18 |
| Te | 0.35 | 0.09 | 0.16 | 0 | 0.14 |
| Total | 100.24 | 99.70 | 99.84 | 101.24 | 100.78 |
| Formula to 5 (Ag+Fe+Pb+Sb+Bi) | | | | | |
| Cu | 0 | 0 | 0 | 0 | 0 |
| Ag | 0.83 | 0.48 | 0.50 | 0.72 | 0.68 |
| Fe | 0.03 | 0.03 | 0.04 | 0.09 | 0.12 |
| Pb | 1.38 | 2.01 | 2.01 | 1.52 | 1.69 |
| Bi | 2.33 | 2.42 | 2.38 | 2.28 | 2.39 |
| Sb | 0.43 | 0.06 | 0.06 | 0.40 | 0.12 |
| (Bi+Sb) | 2.76 | 2.48 | 2.44 | 2.68 | 2.51 |
| S | 5.96 | 5.83 | 6.04 | 5.79 | 5.87 |
| Se | 0.04 | 0.02 | 0.02 | 0.03 | 0.03 |
| Te | 0.03 | 0.01 | 0.01 | 0 | 0.01 |
| (S+Se+Te) | 6.03 | 5.86 | 6.07 | 5.83 | 5.91 |
| Sb/(Sb+Bi) % | 15.4 ± 1.9 | 2.6 ± 0.5 | 2.6 ± 0.6 | 14.7 ± 1.4 | 4.7 ± 0.9 |
| N | 4.16 ± 0.04 | 3.96 ± 0.04 | 4.12 ± 0.18 | 4.01 ± 0.06 | 4.35 ± 0.15 |

that of, not only gustavite, but also that of the ordered structures, vikingite (N = 5.5) and eskimoite (N = 7). Makovicky and Karup-Møller (1977*b*) suggested the name schirmerite should be used for those phases within this compositional field displaying structural disorder and compositional variations. It is, therefore, possible that the compositions described in this paper represent not only true schirmerite, but very possibly also other homologues, including gustavite, vikingite and eskimoite. In many occurrences of members of the lillianite homologous series (e.g. Moëlo *et al.*, 1987; Breskovska *et al.*, 1988), these minerals occur together. Compositional data or optical properties (Karup-Møller, 1977) alone are insufficient to designate the analysed minerals as schirmerite, other known lillianite homologues or even as new homologues (e.g. with N = 5).

Consideration of the data points on Fig. 5 shows a clustering of schirmerite-like compositions, within and to the right of the schirmerite field. Calculated N values range from 4.30 to 6.37. Breskovska *et al.* (1988) described a comparable range of compositions to those described here, and similarly noted several compositions which fell outside the schirmerite field. These authors argued that these data might represent previously unreported lillianite homologues, a view which can also be considered for some of the data reported here. All analysed grains show Sb substitution within the ranges seen in lillianite–gustavite; up to 15 % Sb/(Sb+Bi). All contain minor amounts of Cu.

Two further compositions, Phase 'Z' in Table 7, plot away from the others and cannot be considered as schirmerite. They are characterised by an appreciably lower Ag and Bi content and no detectable Cu. N values are close to 5. An unequivocal identity for this phase cannot be established. They may possibly, however, represent an additional, previously unreported, N = 5 homologue.

Table 5. Microprobe analyses of lillianite - gustavite (with Cu)

| Sample | BB 194D(3) | BB 334(G) | BB 194D(2) | BB 194O(CE) | BB 194D(1) | BB 19O(J1) | BB 194D(1) | BB 19O(2A1) | BB 1940-A | BB 194B 1/2 | BB 197 | BB 194(Ca) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | 9 | 3 | 4 | 5 | 3 |  | 3 |  |  |  | 5 | 4 |
|  | (L5) | (L1) | (L4) | (L6) | (L7) | (L3) | (L8) | (L2) | (L9) | (L10) | (L11) | (L12) |
| Wt.% (mean of n samples) |  |  |  |  |  |  |  |  |  |  |  |  |
| Cu | 0.52 | 0.24 | 0.23 | 0.54 | 0.21 | 0.23 | 0.21 | 0.87 | 0.58 | 0.20 | 0.76 | 1.53 |
| Ag | 6.51 | 1.75 | 7.77 | 7.36 | 6.71 | 4.16 | 6.71 | 2.82 | 5.92 | 6.53 | 6.77 | 6.67 |
| Fe | 0.35 | 0.82 | 0.39 | 0.25 | 0.28 | 0.42 | 0.28 | 0.39 | 0.31 | 0.19 | 0.43 | 0.67 |
| Pb | 29.38 | 44.70 | 25.89 | 27.54 | 30.33 | 35.61 | 30.33 | 40.79 | 31.57 | 9.34 | 30.87 | 28.75 |
| Bi | 45.65 | 35.85 | 46.41 | 44.04 | 42.13 | 43.40 | 42.13 | 28.74 | 43.70 | 43.76 | 40.54 | 46.17 |
| Sb | 2.51 | 1.18 | 3.99 | 4.27 | 4.09 | 0.51 | 4.09 | 8.50 | 2.07 | 2.68 | 4.53 | 1.19 |
| S | 16.77 | 15.25 | 17.09 | 16.87 | 16.92 | 16.24 | 16.92 | 17.01 | 16.46 | 16.55 | 16.78 | 16.84 |
| Se | 0.14 | 2.12 | 0.17 | 0.16 | 0.25 | 0.29 | 0.25 | 0.25 | 0.16 | 0.22 | 0.23 | 0.17 |
| Te | 0.02 | 0 | 0.04 | 0.09 | 0.04 | 0.23 | 0.04 | 0.51 | 0.18 | 0 | 0.13 | 0.12 |
| Total | 101.85 | 101.90 | 101.97 | 101.12 | 100.95 | 101.09 | 100.95 | 99.88 | 100.95 | 99.47 | 101.05 | 102.09 |
| Formula to 5 (Cu+Ag+Fe+Pb+Sb+Bi) |  |  |  |  |  |  |  |  |  |  |  |  |
| Cu | 0.09 | 0.04 | 0.04 | 0.09 | 0.04 | 0.04 | 0.04 | 0.15 | 0.10 | 0.04 | 0.13 | 0.26 |
| Ag | 0.66 | 0.19 | 0.74 | 0.74 | 0.69 | 0.45 | 0.69 | 0.29 | 0.61 | 0.69 | 0.68 | 0.66 |
| Fe | 0.06 | 0.17 | 0.08 | 0.05 | 0.05 | 0.09 | 0.05 | 0.08 | 0.06 | 0.04 | 0.08 | 0.13 |
| Pb | 1.56 | 2.50 | 2.40 | 1.44 | 1.62 | 1.98 | 1.62 | 2.18 | 1.70 | 1.61 | 1.61 | 1.49 |
| Bi | 2.40 | 1.99 | 0.36 | 2.29 | 2.23 | 2.40 | 2.23 | 1.53 | 2.33 | 2.38 | 2.10 | 2.36 |
| Sb | 0.23 | 0.11 | 0.36 | 0.38 | 0.37 | 0.05 | 0.37 | 0.77 | 0.19 | 0.25 | 0.40 | 0.10 |
| (Bi+Sb) | 2.62 | 2.10 | 2.76 | 2.67 | 2.60 | 2.44 | 2.60 | 2.30 | 2.52 | 2.63 | 2.50 | 2.47 |
| S | 5.74 | 5.51 | 5.76 | 5.72 | 5.84 | 5.84 | 5.84 | 5.88 | 5.73 | 5.87 | 5.66 | 5.62 |
| Se | 0.02 | 0.31 | 0.02 | 0.02 | 0.04 | 0.04 | 0.04 | 0.04 | 0.02 | 0.03 | 0.03 | 0.02 |
| Te | 0.00 | 0 | 0.00 | 0.01 | 0.01 | 0.02 | 0.01 | 0.04 | 0.02 | 0 | 0.01 | 0.01 |
| (S+Se+Te) | 5.77 | 5.82 | 5.79 | 5.75 | 5.88 | 5.91 | 5.88 | 5.96 | 5.77 | 5.90 | 5.70 | 5.66 |
| Sb/(Sb+Bi) | 8.5 ± 5.7 | 5.4 ± 0.6 | 12.9 ± 0.9 | 14.3 ± 5.6 | 14.1 ± 4.7 | 2.0 | 14.1 ± 4.7 | 33.7 | 7.5 | 9.5 | 16.1 ± 2.6 | 4.2 ± 0.1 |
| N | 3.94 ± 0.06 | 4.01 ± 0.02 | 3.94 ± 0.11 | 4.04 ± 0.28 | 4.14 ± 0.19 | 3.87 | 4.14 ± 0.19 | 3.75 | 4.06 | 4.07 | 4.14 ± 0.19 | 4.11 ± 0.17 |

TABLE 6. Microprobe analyses of heyrovskyite

| Sample | BB 194C (3) | BB 194 (4) | BB 190 (20) | BB 194D (3.1) |
|---|---|---|---|---|
| n | 12 | 2 | | |
| | (H4) | (H3) | (N2) | (H1) |
| Wt.% (mean of n analyses) | | | | |
| Cu | 0 | 0.35 | 0.10 | 0.64 |
| Ag | 7.08 | 6.53 | 3.88 | 2.51 |
| Fe | 0 | 0.17 | 0.69 | 0.49 |
| Pb | 41.31 | 43.43 | 51.39 | 58.82 |
| Bi | 35.13 | 32.23 | 29.75 | 19.79 |
| Sb | 1.57 | 1.74 | 0.35 | 4.36 |
| S | 15.79 | 15.86 | 15.31 | 15.29 |
| Se | 0.15 | 0.10 | 0.16 | 0.20 |
| Te | 0.08 | 0.18 | 0.14 | 0.00 |
| Total | 101.11 | 100.58 | 101.77 | 102.10 |
| Formula to 8 (Cu+Ag+Fe+Pb+Sb+Bi) | | | | |
| Cu | 0 | 0.10 | 0.03 | 0.18 |
| Ag | 1.18 | 1.08 | 0.65 | 0.41 |
| Fe | 0 | 0.06 | 0.22 | 0.15 |
| Pb | 3.58 | 3.75 | 4.48 | 4.98 |
| Bi | 3.01 | 2.76 | 2.57 | 1.66 |
| Sb | 0.23 | 0.26 | 0.05 | 0.63 |
| (Bi+Sb) | 3.25 | 3.02 | 2.62 | 2.29 |
| S | 8.83 | 8.85 | 8.62 | 8.36 |
| Se | 0.03 | 0.02 | 0.03 | 0.04 |
| Te | 0.01 | 0.03 | 0.02 | 0 |
| (S+Se+Te) | 8.88 | 8.90 | 8.68 | 8.40 |
| Sb/(Sb+Bi)% | 7.1 ± 1.7 | 8.5 ± 4.5 | 2.0 | 27.4 |
| N | 6.74 ± 0.31 | 7.16 ± 0.90 | 6.86 | 7.16 |

*Izoklakeite.* Izoklakeite is a relatively rare Bi–Sb sulphosalt containing both essential Cu and Ag. Since the original descriptions of izoklakeite in the Izok Lake and Vena deposits (Harris *et al.*, 1986; Makovicky and Mumme, 1986; Zakrzewski and Makovicky, 1986), the mineral has been identified in a number of other deposits. In addition, earlier descriptions of a mineral having a comparable composition are now regarded as izoklakeite (Moëlo *et al.*, 1995). Microprobe analyses of izoklakeite are given in Table 8. Analyses have been calculated to a total of 46 (Ag+Pb+Sb+Bi) and agree well with the simplified formula $Cu_2Ag_2Pb_{22}(Bi,Sb)_{22}S_{57}$. They fall within the compositional ranges shown by the izoklakeite–giessenite series from the ten known occurences (Moëlo *et al.*, 1995).

In contrast to previously published analyses, however, the Baia Borşa minerals frequently contain some Cu (together with Fe) beyond the limit of 2 atoms per formula unit, attaining a maximum of 3.08 in some analysed grains. This relative Cu enrichment cannot, unlike the varieties reported by Moëlo *et al.* (1995) from Les Chalanches, be met by a deficiency of Ag, for which 2 atoms p.f.u. is also exceeded (typically 2.1 to 2.4) in most analyses. Similarly, the other exchange mechanisms discussed by Moëlo *et al.* (1995), such as $Cu^+ + (Sb,Bi)^{3+} \rightleftharpoons Pb^{2+} + Fe^{2+}$ cannot be invoked to account for the observed compositions, since (Sb,Bi) is very close to 22 atoms p.f.u.. An explanation may be sought in the relatively low Pb contents in the Baia Borşa samples, which are typically only 21.0 to 21.6 atoms p.f.u.. It is suggested that this may be evidence for the exchange $Cu^+ + Fe^{3+} \rightleftharpoons Pb^{2+}$, although this cannot explain all the excess (Cu+Ag+Fe). Moëlo *et al.* (1995) suggested the following generalised structural formula for the izoklakeite–giessenite series:

TABLE 7. Microprobe analyses of schirmerite and lillianite homologues with N = 5

| Sample | BB 194 (C) | BB 194 (G) | BB 194 (Da) | BB 194 (G2) | BB 194B 2.4 | BB 194B 2.5 | BB 197 (1) | BB 197 (7) | BB 194C (10) |
|---|---|---|---|---|---|---|---|---|---|
| n | 6 | 7 | 3 | | | | 4 | 2 | 2 |
| | (S1) | (S2) | (S3) | (S4) | (S5) | (S6) | (S7) | (S8) | (phase 'Z') |
| Wt.% (mean of n analyses) | | | | | | | | | |
| Cu | 0.30 | 0.28 | 0.13 | 0.16 | 0.93 | 0.87 | 1.14 | 0.44 | 0 |
| Ag | 7.04 | 7.54 | 7.99 | 8.33 | 9.59 | 9.51 | 8.81 | 9.35 | 2.25 |
| Fe | 0.33 | 0.47 | 0.61 | 0.26 | 0.36 | 0.47 | 0.66 | 0.47 | 0 |
| Pb | 29.76 | 28.20 | 27.46 | 31.64 | 27.49 | 31.64 | 29.12 | 28.52 | 51.26 |
| Bi | 44.89 | 42.71 | 43.17 | 38.65 | 45.95 | 42.55 | 29.85 | 41.90 | 25.27 |
| Sb | 1.52 | 3.98 | 3.63 | 4.04 | 1.12 | 0.87 | 13.19 | 3.86 | 5.15 |
| S | 16.80 | 17.02 | 17.05 | 17.06 | 16.27 | 16.34 | 18.01 | 16.77 | 16.22 |
| Se | 0.11 | 0.20 | 0.24 | 0.16 | 0.10 | 0.12 | 0.24 | 0.24 | 0.06 |
| Te | 0.12 | 0.12 | 0.10 | 0 | 0.20 | 0.15 | 0.06 | 0.17 | 0.09 |
| Total | 100.86 | 100.51 | 100.38 | 100.30 | 102.01 | 102.27 | 101.06 | 101.70 | 100.27 |
| Formula to 5 (Cu+Ag+Fe+Pb+Sb+Bi) | | | | | | | | | |
| Cu | 0.05 | 0.05 | 0.02 | 0.03 | 0.16 | 0.14 | 0.18 | 0.07 | 0 |
| Ag | 0.73 | 0.77 | 0.81 | 0.85 | 0.94 | 0.93 | 0.81 | 0.94 | 0.24 |
| Fe | 0.07 | 0.09 | 0.12 | 0.05 | 0.07 | 0.09 | 0.12 | 0.09 | 0 |
| Pb | 1.61 | 1.49 | 1.45 | 1.68 | 1.41 | 1.61 | 1.40 | 1.46 | 2.87 |
| Bi | 2.40 | 2.24 | 2.27 | 2.03 | 2.33 | 2.15 | 1.42 | 2.13 | 1.40 |
| Sb | 0.14 | 0.36 | 0.33 | 0.36 | 0.10 | 0.08 | 1.08 | 0.34 | 0.49 |
| (Bi+Sb) | 2.54 | 2.60 | 2.59 | 2.40 | 2.43 | 2.22 | 2.50 | 2.46 | 1.89 |
| S | 5.87 | 5.82 | 5.83 | 5.85 | 5.38 | 5.38 | 5.58 | 5.54 | 5.87 |
| Se | 0.02 | 0.03 | 0.03 | 0.02 | 0.01 | 0.02 | 0.03 | 0.03 | 0.01 |
| Te | 0.01 | 0.01 | 0.03 | 0 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 |
| (S+Se+Te) | 5.89 | 5.86 | 5.87 | 5.87 | 5.41 | 5.41 | 5.62 | 5.59 | 5.88 |
| Sb/(Sb+Bi)% | 5.5 ± 1.5 | 13.8 | 12.5 ± 4.2 | 15.2 | 4.0 | 3.4 | 43.1 ± 8.9 | 13.7 ± 0.5 | 25.9 ± 0.1 |
| N | 4.39 ± 0.21 | 4.30 ± 0.09 | 4.47 ± 0.30 | 5.36 | 5.43 | 6.37 | 4.60 ± 0.31 | 5.27 ± 0.05 | 5.06 ± 0.22 |

TABLE 8. Microprobe analyses of izoklakeite–giessenite

| Sample<br>n | BB 190 (2)<br>10 | BB 190 (3)<br>6 | BB 190 (7)<br>4 | BB 194D (1)<br>5 | BB 194C (4)<br>8 | BB 194D (2)<br>4 | BB 194 (30A)<br>4 | BB 194D (3)<br>8 | BB 194D (10) | BB 194C 3.10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Wt.% (mean ± standard deviations) | | | | | | | | | | |
| Cu | 0.98 ± 0.06 | 0.97 ± 0.08 | 1.30 ± 0.18 | 1.12 ± 0.13 | 1.14 ± 0.08 | 1.18 ± 0.06 | 1.22 ± 0.07 | 1.18 ± 0.06 | 1.12 | 1.04 |
| Ag | 2.62 ± 0.24 | 2.75 ± 0.33 | 2.72 ± 0.22 | 2.34 ± 0.12 | 2.21 ± 0.24 | 2.20 ± 0.29 | 2.37 ± 0.12 | 2.32 ± 0.30 | 2.57 | 2.48 |
| Fe | 0.26 ± 0.24 | 0.32 ± 0.13 | 0.56 ± 0.12 | 0.44 ± 0.36 | 0.65 ± 0.31 | 0.87 ± 0.28 | 0.19 ± 0.07 | 0.49 ± 0.15 | 0.45 | 0.20 |
| Pb | 43.83 ± 1.18 | 42.38 ± 1.27 | 43.34 ± 0.51 | 42.84 ± 0.69 | 42.98 ± 1.15 | 44.58 ± 2.13 | 43.23 ± 1.15 | 42.67 ± 1.36 | 41.64 | 41.04 |
| Bi | 22.30 ± 1.55 | 22.83 ± 2.77 | 21.15 ± 1.80 | 27.82 ± 3.57 | 26.23 ± 2.13 | 20.36 ± 2.90 | 23.62 ± 2.95 | 27.17 ± 2.29 | 31.68 | 30.48 |
| Sb | 12.82 ± 1.29 | 12.53 ± 1.64 | 14.57 ± 1.03 | 9.78 ± 2.36 | 10.72 ± 1.41 | 14.25 ± 2.90 | 11.88 ± 2.12 | 9.86 ± 1.65 | 7.28 | 8.03 |
| S | 17.44 ± 0.16 | 17.47 ± 0.09 | 17.87 ± 0.15 | 17.25 ± 0.30 | 17.15 ± 0.25 | 17.56 ± 0.18 | 17.56 ± 0.31 | 17.11 ± 0.22 | 16.81 | 16.91 |
| Se | 0.13 ± 0.04 | 0.14 ± 0.04 | 0.06 ± 0.04 | 0.11 ± 0.07 | 0.08 ± 0.07 | 0.07 ± 0.08 | 0.08 ± 0.05 | 0 | 0 | 0.17 |
| Te | 0.34 ± 0.08 | 0.27 ± 0.09 | 0.27 ± 0.11 | 0.00 | 0.03 ± 0.05 | 0.03 ± 0.06 | 0.05 ± 0.06 | 0.03 ± 0.06 | 0 | 0.17 |
| Total | 100.74 | 100.65 | 101.82 | 101.72 | 101.19 | 101.09 | 100.18 | 100.83 | 101.55 | 100.52 |
| Formula to 46 (Ag+Pb+Sb+Bi) | | | | | | | | | | |
| Cu | 1.59 ± 0.10 | 1.56 ± 0.14 | 2.07 ± 0.29 | 1.84 ± 0.21 | 1.88 ± 0.14 | 1.90 ± 0.13 | 2.00 ± 0.09 | 1.95 ± 0.09 | 1.86 | 1.74 |
| Ag | 2.50 ± 0.21 | 2.62 ± 0.33 | 2.54 ± 0.19 | 2.26 ± 0.10 | 2.14 ± 0.24 | 2.08 ± 0.26 | 2.29 ± 0.14 | 2.26 ± 0.32 | 2.51 | 2.44 |
| Fe | 0.47 ± 0.16 | 0.59 ± 0.25 | 1.00 ± 0.22 | 0.82 ± 0.68 | 1.20 ± 0.57 | 1.22 ± 0.11 | 0.35 ± 0.14 | 0.91 ± 0.28 | 0.85 | 0.38 |
| Pb | 21.73 ± 0.67 | 21.05 ± 0.52 | 21.14 ± 0.15 | 21.52 ± 0.17 | 21.61 ± 0.40 | 21.99 ± 1.34 | 21.75 ± 0.29 | 21.60 ± 0.45 | 21.19 | 21.05 |
| Bi | 10.96 ± 0.81 | 11.74 ± 1.44 | 10.23 ± 0.85 | 13.86 ± 1.89 | 13.08 ± 1.19 | 9.96 ± 1.37 | 11.81 ± 1.69 | 13.66 ± 1.30 | 15.99 | 15.50 |
| Sb | 10.82 ± 1.02 | 10.59 ± 1.31 | 12.09 ± 0.87 | 8.36 ± 1.91 | 9.17 ± 1.12 | 11.96 ± 0.82 | 10.16 ± 1.67 | 8.48 ± 1.28 | 6.31 | 7.01 |
| (Bi+Sb) | 21.78 ± 0.61 | 22.33 ± 0.25 | 22.32 ± 0.05 | 22.22 ± 0.18 | 22.25 ± 0.24 | 21.92 ± 1.10 | 21.96 ± 0.17 | 22.14 ± 0.32 | 22.29 | 22.51 |
| S | 55.88 ± 0.54 | 56.09 ± 0.35 | 56.32 ± 0.84 | 56.02 ± 0.56 | 55.73 ± 0.45 | 55.98 ± 1.17 | 57.10 ± 0.34 | 56.01 ± 0.42 | 55.30 | 56.05 |
| Se | 0.16 ± 0.06 | 0.18 ± 0.05 | 0.07 ± 0.05 | 0.15 ± 0.09 | 0.11 ± 0.09 | 0.09 ± 0.11 | 0.10 ± 0.07 | 0 | 0 | 0.23 |
| Te | 0.28 ± 0.06 | 0.21 ± 0.08 | 0.22 ± 0.09 | 0 | 0.02 ± 0.02 | 0.02 ± 0.05 | 0.04 ± 0.05 | 0.03 ± 0.05 | 0 | 0.14 |
| (S+Se+Te) | 56.32 ± 0.57 | 56.49 ± 0.39 | 56.60 ± 0.91 | 56.17 ± 0.49 | 55.86 ± 0.41 | 56.10 ± 1.22 | 57.24 ± 0.32 | 56.03 ± 0.43 | 55.30 | 56.42 |
| Sb/(Sb+Bi)% | 49.6 ± 4.0 | 47.4 ± 6.2 | 54.2 ± 3.9 | 37.6 ± 8.6 | 41.2 ± 4.9 | 54.6 ± 4.6 | 47.3 ± 7.6 | 38.3 ± 5.8 | 28.3 | 31.1 |
| x | 0.47 | 0.59 | 1.00 | 0.82 | 1.20 | 1.22 | 0.35 | 0.91 | 0.85 | 0.38 |
| y | 0.50 | 0.53 | 0.46 | 0.62 | 0.59 | 0.45 | 0.53 | 0.62 | 0.72 | 0.69 |
| z ((Cu+Ag+Fe)−2) | 2.56 | 2.77 | 3.61 | 2.92 | 3.22 | 3.20 | 2.64 | 3.12 | 3.22 | 2.56 |
| z (Pb = 26−2z+x) | 1.90 | 2.18 | 1.93 | 1.83 | 1.60 | 1.40 | 1.95 | 1.75 | 1.98 | 2.29 |

TABLE 9. Microprobe analyses of cosalite

| Sample | BB 334 (C) | BB 334 (2) | BB 1107 | BB 147 (2) |
|---|---|---|---|---|
| n | 14 | 41 | 3 | 2 |
| | (C1) | (C4) | (C2) | (C3) |
| Wt.% (mean of n analyses) | | | | |
| Cu | 0.56 | 0.53 | 1.32 | 0.20 |
| Ag | 1.68 | 1.67 | 1.24 | 0.31 |
| Fe | 0.11 | 0.30 | 0.10 | 0.59 |
| Pb | 38.92 | 38.86 | 37.64 | 40.49 |
| Bi | 37.75 | 37.49 | 40.98 | 36.28 |
| Sb | 3.79 | 3.50 | 1.16 | 4.33 |
| S | 16.16 | 15.48 | 15.57 | 16.58 |
| Se | 1.54 | 1.77 | 1.96 | 0.46 |
| Te | 0 | 0 | 0 | 0 |
| Total | 100.48 | 99.60 | 100.03 | 99.22 |
| Formula to (Cu+Ag+Fe+Pb+Sb+Bi) = 4 | | | | |
| Cu | 0.08 | 0.08 | 0.21 | 0.03 |
| Ag | 0.15 | 0.15 | 0.11 | 0.03 |
| Fe | 0.02 | 0.05 | 0.02 | 0.10 |
| Pb | 1.76 | 1.77 | 1.72 | 1.86 |
| Bi | 1.70 | 1.69 | 1.86 | 1.65 |
| Sb | 0.29 | 0.27 | 0.09 | 0.34 |
| (Sb+Bi) | 1.99 | 1.96 | 1.95 | 1.99 |
| S | 4.74 | 4.55 | 4.60 | 4.91 |
| Se | 0.18 | 0.21 | 0.23 | 0.06 |
| Te | 0 | 0 | 0 | 0 |
| (S+Se+Te) | 4.92 | 4.76 | 4.83 | 4.97 |
| Sb/(Sb+Bi) | 14.7 ± 0.6 | 13.4 ± 1.4 | 4.6 ± 0.3 | 17.0 ± 1.4 |

$(Cu_{2-x}Fe_x)_2(Pb_{26-2z+x}(Ag,Cu)_z(Sb_{1-y}Bi_y)_{20+z-x})_{46}\ S_{57}$, in which $0 \leqslant x \leqslant 1$, $0.44 \leqslant y \leqslant 0.85$ and $0 \leqslant z \leqslant 2.2$. Comparison of $z$ values calculated on the basis of both (Cu+Ag+Fe)−2 and Pb = $26-2z+x$ (Table 8) illustrates this discrepancy, with as much as 1.6 atom excess (Cu+Ag+Fe). As with other Bi-sulphosalts analysed in this study, Cu+Fe from neighbouring sulphides is considered unlikely to be the cause of the excess. Mol.% Sb/(Sb+Bi) ranges between 28.4 to 54.6, with individual analyses as high as 58.8%. They thus lie within the same range as those previously described and extend into the field of giessenite. Compositions close to the Sb rich end of the spectrum, i.e. izoklakeite, predominate.

*Cosalite*. A number of grains have compositions (Table 9) corresponding closely to cosalite (ideally, $Pb_2Bi_2S_5$). Small amounts of Cu and Ag are commonly present in cosalite, substituting for Pb (e.g. Karup-Møller, 1973, 1977), although the compositional limits are poorly constrained. Among the analysed suite, compositions range from $(Cu,Ag,Fe)_{0.16}Pb_{1.86}(Bi,Sb)_{1.99}(S,Se)_{4.97}$ to $(Cu,Ag,Fe)_{0.34}Pb_{1.72}(Bi,Sb)_{1.95}(S,Se)_{4.83}$, in accordance with (Cu,Ag) $\rightleftharpoons$ Pb substitution. Analysed cosalites contain significant Sb, the Sb/(Sb+Bi) ratio ranging from 4.6 to 17.0%. Similar extents of replacement of Bi by Sb have been reported from numerous russian localities (Mozgova and Bortnikov, 1980). Lee *et al.* (1993) reported an average of 23% replacement of Bi by Sb in cosalite from South Korea. Experimental studies (Chang *et al.*, 1980) support substantial Sb substitution into the cosalite structure.

*Phase A*. Two grains (Table 10) have a composition close to, but distinct from, cosalite with which they are intergrown. They are characterized compositionally by Bi enrichment and fall between cosalite and galenobismuthite in $PbS-Bi_2S_3-Ag_2S$ space (Fig. 5). Parallels may be drawn with the mineral eclarite, $(Cu,Fe)Pb_9Bi_{12}S_{28}$ (Paar *et al.*, 1983; Kupčik, 1983). Eclarite is known only from the type locality (Bärenbad, Hollerbachstal, Austria),

TABLE 10. Microprobe analyses of nuffieldite, berryite and phase A

| Sample | Nuffieldite<br>BB 334 | Berryite(?)<br>BB 1759 (8) | Phase A<br>BB 334 (E) |
|---|---|---|---|
| n | 6 | 3 | 2 |
| Wt.% (mean of n analyses) | | | |
| Cu | 5.35 ± 0.47 | 5.32 ± 0.26 | 1.47 ± 0.01 |
| Ag | 0.09 ± 0.09 | 9.25 ± 0.40 | 0.59 ± 0.01 |
| Fe | 0.55 ± 0.27 | 0.27 ± 0.07 | 0.66 ± 0.10 |
| Pb | 32.36 ± 0.42 | 20.11 ± 0.14 | 32.09 ± 0.15 |
| Bi | 40.26 ± 0.56 | 45.59 ± 0.40 | 47.03 ± 0.42 |
| Sb | 4.52 ± 0.25 | 0.25 ± 0.07 | 1.90 ± 0.04 |
| S | 16.66 ± 0.28 | 15.43 ± 0.26 | 17.17 ± 0.18 |
| Se | 1.42 ± 0.16 | 1.44 ± 0.17 | 0.54 ± 0.04 |
| Te | 0.02 ± 0.05 | 0 | 0 |
| Total | 101.23 | 97.66 | 101.43 |
| | Formula (Pb+Sb+Bi) = 5 | Formula S = 11 | Formula (Cu+Ag+Fe+Pb+Sb+Bi) = 22 |
| Cu | 1.09 ± 0.09 | 1.87 ± 0.07 | 1.17 ± 0.02 |
| Ag | 0.01 ± 0.01 | 1.89 ± 0.10 | 0.27 ± 0.00 |
| Fe | 0.13 ± 0.06 | 0.11 ± 0.03 | 0.59 ± 0.10 |
| Pb | 2.02 ± 0.02 | 2.14 ± 0.01 | 7.82 ± 0.23 |
| B | 2.50 ± 0.04 | 4.80 ± 0.02 | 11.36 ± 0.23 |
| Sb | 0.48 ± 0.03 | 0.04 ± 0.02 | 0.79 ± 0.02 |
| (Sb+Bi) | 2.98 ± 0.02 | 4.85 ± 0.00 | 12.15 ± 0.25 |
| S | 6.73 ± 0.11 | 10.60 ± 0.05 | 27.02 ± 0.02 |
| Se | 0.23 ± 0.03 | 0.40 ± 0.05 | 0.32 ± 0.01 |
| Te | 0 | 0 | 0 |
| (S+Se+Te) | 6.97 ± 0.11 | 11.00 | 27.34 ± 0.02 |
| Sb/(Sb+Bi) | 16.2 ± 0.9 | 0.5 ± 0.2 | 6.5 ± 0.1 |

and therefore compositional limits are unknown. Calculated in terms of 22 metal atoms, Phase A has the composition $(Cu_{1.17}Ag_{0.27}Fe_{0.59})_{2.03}Pb_{7.82}(Bi_{11.36}Sb_{0.79})_{12.15}S_{27.34}$, which compares reasonably closely with the formulae $(Cu_{0.73}Ag_{0.21}Fe_{0.67})_{1.61}Pb_{8.56}(Bi_{11.19}Sb_{0.62})_{11.81}S_{27.99}$ and $(Cu_{0.72}Ag_{0.04}Fe_{0.56})_{1.32}Pb_{8.43}(Bi_{11.57}Sb_{0.67})_{12.24}S_{27.71}$ given by Paar *et al.* for two eclarite grains from Bärenbad. Enrichment in (Cu,Ag,Fe) and deficiency in Pb are readily explained by a degree of substitution. A strong resemblance in petrographic appearance and location within a pyritic gold-bearing sulphide vein together with cosalite is noted between eclarite as described by Paar *et al.* (1983) and Phase 'A' from Baia Borşa.

Phase A also plots within the compositional field of cannizzarite. Cannizzarite, for which the structural formula was defined as $Pb_{46}Bi_{54}S_{127}$ (Matzat, 1979) displays a much wider range of compositions in natural samples (Mozgova *et al.*, 1985). If the minor Cu, Ag and Fe analysed in the Baia Borşa samples are allocated to the Pb position, the analysed grains also fit remarkably well to the structural formula for cannizzarite. In the absence of structural data, however, a certain identity cannot be established for the grains in question.

*Nuffieldite.* Six grains of a sulphosalt with a characteristic high Cu/Ag ratio, differing from other Bi-sulphosalts described in this paper, were noted. All were observed in a single sample and are intergrown with cosalite. Their composition is, however, comparable to nuffieldite, a rare sulphosalt, with the formula $(Cu_{1-x}Pb_2(Pb_yBi_{1-y-z}Sb_z)Bi_2S_{7-y})$, where $x$ and $y$ have similar values and $y$ ranges between 0.2 and 0.55. Moëlo (1989), Maurel and Moëlo (1990) and Moëlo *et al.* (1995) have shown that Sb would appear to be an essential component of nuffieldite, essential for its stabilisation. This explained why the phase has not been synthesised in the $Cu_2S$–PbS–$Bi_2S_3$ system. The compositions from Baia Borşa (Table 10) and calculated formula, on the basis of (Pb+Bi+Sb) = 5 after Moëlo *et al.* (1995); $Cu_{1.05}Ag_{0.02}Fe_{0.18}Pb_{2.02}(Bi_{0.50}Sb_{0.49})_{0.99}Bi_2(S,Se)_{7.11}$ agree reasonably well with published compositions, reviewed by Mozgova *et al.* (1994), with the exception of the relatively high Fe and Se contents. The Sb contents lie towards the upper limits previously reported.

*Berryite (?).* A phase with the composition $Ag_{1.89}Cu_{1.87}Fe_{0.11}Pb_{2.14}(Bi_{4.80}Sb_{0.04})_{4.85}S_{11}$, calculated to 11 S atoms, was observed as small (5–15 μm) inclusions in chalcopyrite, together with friedrichite. Such a composition (Table 10) does not match with any known lillianite homologues. The phase was initially ascribed to the benjaminite solid solution series, which was shown by Chang *et al.* (1988) to have a broad compositional range, with the formula defined as $Ag_{3.43-(x+y)}Cu_{y+(n+1)z}Pb_{2x}Bi_{6.85-(x+z)}S_{12}$, with $0 < x < 1.53$, $0 < y < 0.55$, $0 < z < 1.41$ and $n = 2$. Calculation of $x$, $y$, $z$ and n, however, indicated that the mineral does not belong to the benjaminite solid solution series, since, although $x$, $y$ and $z$ lie within prescribed limits (1.166, 0.204 and 0.4, respectively), the n value is calculated to be 3.8. Likewise, the mineral composition does not accord with formulae for either the pavonite or $Cu_3Bi_5S_9$ solid solution series (Chang *et al.*, 1988). The composition is closest to the formula for berryite, a diagnosis supported by the high Σ Metal/S and Cu/Ag ratios and low degree (< 1%) of Sb substitution for Bi. However, excess (Cu,Ag) is present, when compared with some berryite compositions in the literature (Karup-Møller, 1966; Nuffield and Harris, 1966), who gave the formula $(Cu,Ag)_3Pb_2Bi_5S_{11}$. Lowry *et al.* (1994) also ascribed to berryite a Ag–Cu–Pb–Bi sulphosalt with a composition directly comparable to that under discussion here, with similar enrichment in (Cu+Ag) and Pb and poor in Bi. The natural compositional limits for berryite are poorly constrained. Bortnikov *et al.* (1985) gave the formula for berryite as $(Cu,Ag)_5Pb_2Bi_7S_{16}$ and showed natural berryite from the Kanimansur deposit to have a limited compositional range with minor exchange of (Cu+Pb) for Bi and Cu:Ag ratios varying from 1.31 to 1.64.

### Reflectance data

Reflectance spectra of gustavite, heyrovskyite and izoklakeite were measured in air and immersion oil (Fig. 6). These were made on the three grains large enough (>100 μm) to be suitable for such measurements and correspond to analyses L16 (Fig. 2*d*), H4 (Fig. 2*f*) and sample BB194C (4) respectively. Measurements were carried out at the Ruhr-Universität Bochum using instrumentation similar to that described by Bernhardt (1987). A Leitz Orthoplan microscope and Hamamatsu R1477 photomultiplier system were used. A Zeiss WTiC standard was employed in air and immersion oil (DIN 58.884). In both media, the effective numeric apertures were 0.20. An excellent correspondence with published reflectance spectra is seen in all three cases, supporting their identities interpreted on the basis of compositional data.

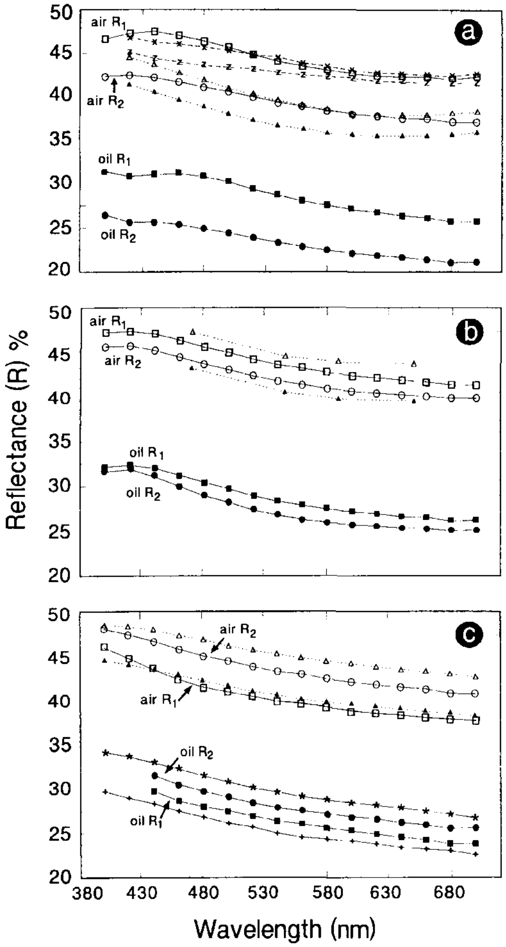

FIG. 6. Reflectance spectra in air and immersion oil: (*a*) gustavite, analysis L16 (open circles and squares; filled circles and squares). Literature data for gustavite from Finashin *et al.* (1981), open and filled triangles — $R_1$ and $R_2$; Sb-gustavite from Mozgova *et al.* (1987), $R_1$ and $R_2$ — x and z symbols; (*b*) heyrovskyite, analysis H4 (open circles and squares; filled circles and squares). Literature data for heyrovskyite from Klomínský *et al.* (1971); open and filled triangles, $R_1$ and $R_2$; (*c*) izoklakeite, sample BB194C (4) (open circles and squares, filled circles and squares). Literature data for izoklakeite from Harris *et al.* (1986): $R_1$ and $R_2$ (oil) — crosses and stars; $R_1$ and $R_2$ (air) — open and filled triangles.

## Discussion

This study has documented the occurrence of several unusual Sb-bearing Bi-sulphosalts and has provided compositional and reflectance data. In the absence of X-ray diffraction data or single crystal studies, conclusive identification of specific minerals cannot be given. The small size of the grains and their commonly intergrown character largely prohibits carrying out these structural investigations, although efforts are continuing to provide this data.

*Comparison with other similar occurrences.* Sb-rich lillianite homologues are exceedingly rare in nature and their occurrence in the Toroiaga deposit is noteworthy. Although many descriptions of lillianite homologues have indicated the presence of minor amounts of Sb (e.g. Syritso and Senderova, 1964; Karup-Møller, 1972; Harris and Chen, 1975), these seldom exceed 8 mol.% Sb/(Sb+Bi). To the author's knowledge, this find represents the fourth reported occurrence of members of the lillianite–gustavite solid solution series containing appreciable Sb contents. The earlier reports were from the Darwin vein deposits, S. California (Czamanske and Hall, 1975), the Sn–W deposit at Alyaskitovoe, Yakutia, Russia (Mozgova *et al.*, 1987) and from Rotgülden, Salzburg/Carinthia, Austria (Paar *et al.*, 1993). In the Darwin deposit, the degree of Sb substitution is lower, typically in the 12 to 16 mol.% range. Mozgova *et al.* (1987) described Sb-gustavite co-existing with Bi-andorite and suggested at least partial solid solition between gustavite and andorite. Extensive gustavite–andorite solid solution was similarly proposed by Paar *et al.* (1993); Paar (pers. comm., 1996) for Sb-gustavite with up to 10.4 wt.% Sb in association with Sb-minerals in the Rötgulden mine. Sb-rich lillianite was described from the Darasun and Ustarasay localities in Eastern Trans-baikal (Sakharova and Krivitskaya, 1970; Mozgova and Bortnikov, 1980), in which Sb substitutions of 46.4, 41.3 and 46.7 mol.% were reported. These minerals were, however, reinterpreted by Zakrewski and Makovicky (1986) not as lillianite, but as possible kobellite homologues. Moëlo *et al.* (1995) demonstrated the minerals from Darasun and Ustarasay to be izoklakeite.

The present paper has also described the second occurrence of Sb-rich heyrovskyite after that reported by Ertl *et al.* (1994), in which up to half the Bi atoms are replaced by Sb.

Sulphosalt minerals containing Bi *and* Sb are both small in number and are extremely scarce in nature, at least in comparison with those sulphosalt phases containing Sb or Bi alone. Moëlo *et al.* (1995) have compiled data on some known Bi–Sb sulphosalts and have attempted to show compositional ranges of recognised phases and solid solution series. The following mineral phases are known: (i) the kobellite homologous series (kobellite, tintinaite, giessenite, izoklakeite; Zakrzewski and Makovicky, 1986; Makovicky and Mumme, 1986), (ii) jaskólskiite and bismuthian meneghinite (Balitskaya *et al.*, 1987; Wagner and Cook, 1996), both of which belong to the meneghinite homologous series (Zakrzewski, 1984; Makovicky and Nørrestam, 1985), (iii) the occurrence of Bi-rich varieties of bournonite, boulangerite, owyheeite, zinckenite, jamesonite, chalcostibite, robinsonite and other Pb–Sb sulphosalts (Jambor and Lachance, 1968; Borodaev and Mozgova, 1975; Bortnikov and Tsepin, 1987; Balitskaya *et al.*, 1987; Mozgova *et al.*, 1990*a*; Wagner and Cook, 1996, and others). To these should be added Sb-rich varieties of various members of the lillianite homologous series (Mozgova and Bortnikov, 1980; Ertl *et al.*, 1994 and this study) which were not covered by Moëlo *et al.* (1995), as well as other Sb-bearing Bi-sulphosalts such as cosalite (Sakharova and Krivitskaya, 1970; Mozgova *et al.*, 1990*a*; Lee *et al.*, 1993).

Although no other Sb–Bi minerals are known in nature, the potential existence of further phases in the $PbS$–$Cu_2S$–$Ag_2S$–$Bi_2S_3$–$Sb_2S_3$ system has, however, been predicted on the basis of crystal structural considerations, notably within the kobellite homologous series (Zakrzewski and Makovicky, 1986).

Although parts of the $PbS$–$Cu_2S$–$Ag_2S$–$Bi_2S_3$–$Sb_2S_3$ system have been studied experimentally (e.g. Chen and Chang, 1974; Goodell, 1975; Hoda and Chang, 1975; Chang and Hoda, 1977; Chang *et al.*, 1980, 1988), crucial data on phases in the complete system containing both $Bi_2S_3$ and $Sb_2S_3$ are to date lacking. Various binary and ternary sub-systems within the $Ag_2S$–$Cu_2S$–$Bi_2S_3$–$Sb_2S_3$–$PbS$ system have been investigated. However, experimental work is often only preliminary and much remains yet to be done, particularly within the quarternary and quinternary sub-systems. Considerable difficulties in defining the compositional limits for naturally occurring phases and reproducing these phases by experiment have been experienced. Variation in naturally occurring phases are often wider than that shown experimentally. Furthermore, the effects of other components (e.g. Fe) on natural compositions are largely unstudied. The description, therefore, of naturally occurring minerals within the $Ag_2S$–$Cu_2S$–$Bi_2S_3$–$Sb_2S_3$–$PbS$ system is essential to their understanding. In the case presented here, the data showing Sb substitution in minerals of the lillianite homologous series corroborates well with experimental data presented by Chang *et al.*, (1980), which clearly showed that up to about 45% of Bi within lillianite may be replaced by Sb.

*Temperatures of formation.* Given the scarcity of Bi–Sb sulphosalts of the type described here in natural occurrences, only indirect estimates of formation temperature may be given. Consideration of the available experimental data, geothermometry applied to the Toroiaga veins, and comparison with other occurrences of lillianite minerals all point to temperatures in excess of 350°C.

The experimental study of Chang *et al.* (1980) showed levels of Sb substitution in lillianite at the extents described here only in the runs carried out at 500°C and that the extent of solid solution between lillianite and its Sb-analogue shrinks rapidly as temperatures drop towards 400°C. Furthermore, Hoda and Chang (1975) showed nearly complete solid solition between lillianite and gustavite only at temperatures above 400°C.

Earlier estimates of mineralisation temperatures for the Toroiaga vein system were given by Borcoş (1967) based on fluid-inclusion methods. Recently, Cook (in press) has proposed that these estimates (<300°C) are too low and probably reflect cooling temperatures. Cook cited new geothermometric data from the S-isotopic composition of coexisting sulphide pairs to suggest temperatures between 300 and 450°C. Since the spread in the estimates derived from the S-isotope data is rather wide, and the data may also be interpreted in terms of disequilibrium between co-existing mineral pairs, they do not represent unequivocal evidence for higher temperatures. Temperatures in excess of 350°C are, nevertheless, in agreement with the geological situation and the opinion of many geologists working in the area.

Further indirect evidence for temperatures of at least 350°C derive from the occurrences of similar minerals in other localities. Moëlo *et al.* (1987) have suggested formation of various lillianite homologues at temperatures of 350–400°C and have shown them to be unstable at lower temperatures. Czamanske and Hall (1975) suggest temperatures of above 350°C for deposition of sulphosalts at the Darwin deposit. On the other hand, Karup-Møller (1977) quotes fluid-inclusion derived temperatures <300°C for the gustavite–cosalite–galena paragenesis at Ivigtut and Paar (pers. comm., 1996) favours temperatures of <200°C for the Sb-gustavite at Rotgülden.

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