

**BISMUTH SULFPHOSALTS FROM HYDROTHERMAL VEIN DEPOSITS
OF NEOGENE AGE, N.W. ROMANIA**

by

Nigel J. Cook

Mineralogisches Institut der Universität Würzburg
Am Hubland, D-97074 Würzburg

Lecture to the Austrian Mineralogical Society
23rd June 1997 in Salzburg

Abstract

Cu-Pb-Bi and Ag-Pb-Bi sulphosalts and related Ag- and Bi- minerals are recognised as important accessory phases within polymetallic vein mineralisation of Neogene age, N.W. Romania. Paragenetic and mineral compositional data are given for assemblages from the Băiut-Văratec deposit, from which they have not previously been reported. In this new occurrence, bismuthinite derivatives, lillianite-gustavite, „schirmerite“, heyrovskýite, matildite, berryite and wittichenite are the most abundant Bi-sulphosalts. These mineral assemblages are comparable with those recently described from the Toroioaga vein systems, Baia Borşa district (COOK, 1997).

Both occurrences are restricted to a distinct ore type consisting of pyrite + chalcopyrite ± galena. These ores can be regarded as the products of a distinct „higher sulphidation“ mineralising event. They are temporally and, to some extent, also spatially distinct from sphalerite-galena-chalcopyrite-Pb-Sb sulphosalt ores. Bi-sulphosalts are important companions of Au mineralisation and are possibly also indicators of higher temperature fluids and/or proximity to porphyry copper systems. Their apparently widespread distribution in vein ores of the Neogene metallogenic province, N.W. Romania is therefore not only of topographic interest but also of direct relevance to regional metallogenic studies and prospecting efforts in the area.

Introduction

Hydrothermal vein-type deposits of the Neogene metallogenic province of northwest Romania are well-known for their abundance and variety of various Pb-Sb and Ag-Pb-Sb sulphosalt minerals. The presence of Cu-Pb-Bi and Ag-Pb-Bi sulphosalts had, until recently, not previously been confirmed from these deposits.

COOK (1997) described an occurrence of a complex suite of Bi- and Bi-Sb sulphosalts within polymetallic sulphide veins associated with the Toroioaga Massif, within the Baia Borşa Ore-field (Fig. 1), some 70 km east of Baia Mare. A summary of these results are given in this paper. In addition, comparable Bi-sulphosalt bearing mineral assemblages and their chemical compositions are also described from hydrothermal veins of the Băiuţ (Văratec) deposit. These data represent the first confirmation that Bi-sulphosalts are also accessory phases within several hydrothermal vein deposits in the Baia Mare area. The confirmed presence of Bi-sulphosalts has implications for the genetic evolution of both deposits.

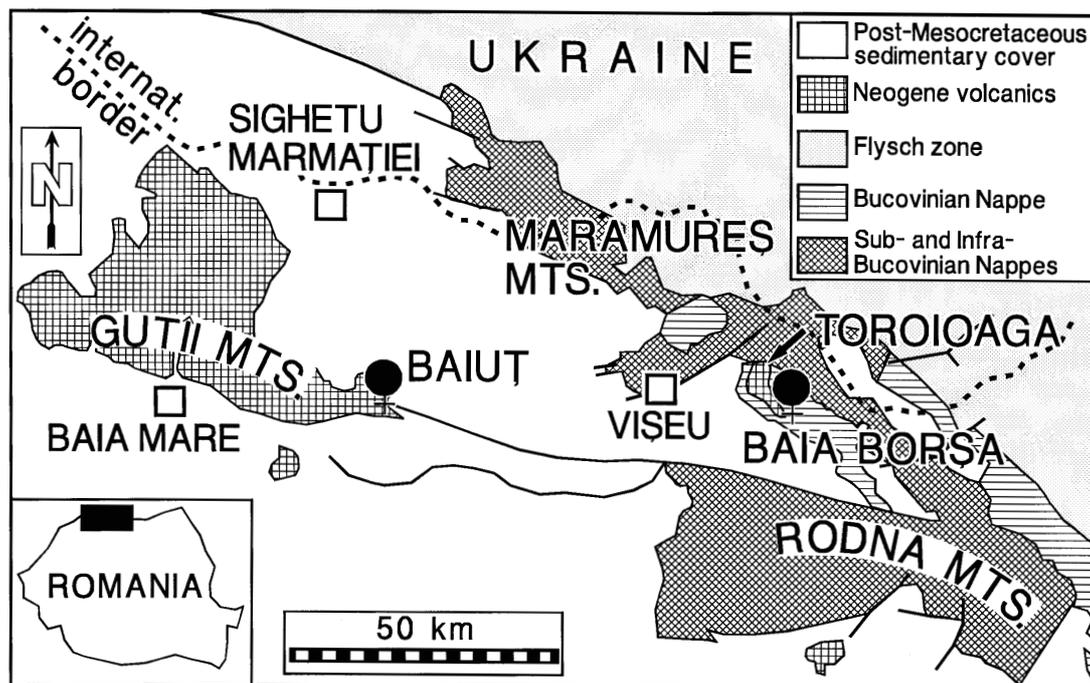


Fig. 1
Geological sketch map showing the location of ore deposits referred to in the text.

THE TOROIOAGA OCCURRENCE

The polymetallic veins, which are exploited in the Toroioaga Mine for base and precious metals, are several hundred metres in length, plunge sharply to SW and occur within sub-volcanic Pontian andesites and along faulted contacts between igneous rocks and adjacent lithologies (SOCOLESCU, 1952; SZÖKE & STECLACI, 1962; BORCOŞ, 1967; BERZA et al., 1982; BORCOŞ et al., 1982). Minor mineralised fractures relating to the Neogene magmatic event occur throughout the orefield and are locally superimposed upon metamorphosed volcanogenic massive sulphide deposits of Cambrian age.

The lower limits of the Toroioaga mineralisation are not currently known. Recently, an analysis of geochemical distributions in the Toroioaga deposit (CHIOREANU et al., 1993; CHIOREANU, 1996), has given tantalising evidence for porphyry-type Cu ± Au mineralisation at deeper levels.

This interpretation also considers a low-sulphidation Pb-Zn rich mineralisation adjacent to the porphyry body and in western parts of the deposit, which is overprinted by a later high-sulphidation mineralisation.

The Bi-sulphosalt bearing assemblage is interpreted as belonging to this later mineralisation event, which is concentrated at higher levels and prevails in the central and eastern parts of the vein system. CHIOREANU (1996) has argued that the Torioaga system can be considered analagous to complex epithermal systems elsewhere, e.g. Northern Luzon, Phillipines (ARRIBAS et al., 1995). Although the Cu-(Bi)-(Au)-rich type of mineralisation cannot be termed high sulphidation type in the defined sense (ARRIBAS, 1995), because of the absence of certain key minerals such as enargite, luzonite, bornite, this style of mineralisation clearly differs markedly from the Pb-Zn-(Sb) rich mineralisation which prevails elsewhere in the Torioaga veins. The term „higher sulphidation“ is accordingly preferred, supported by the absence of pyrrhotite in such assemblages.

Bismuth sulphosalts

Based on microscopic and microanalytical analysis of 17 polished sections, COOK (1997) identified a suite of Bi-sulphosalts within several major veins, including the principal „Caterina“ vein and also from smaller mineralised fractures in the crystalline rocks hosting the igneous complex. Their relative abundance in samples from different parts of the deposit indicates Bi-sulphosalts to be widely distributed throughout significant parts of the Torioaga vein system. The compositions of the 744 Bi-sulphosalt grains observed have, in each case, been verified by electron probe microanalysis. Investigation of supplementary sample material from the „Caterina“ vein collected during September 1996 has echoed the earlier findings, with a similar range of bismuthinite derivatives and lillianite homologues also identified in these new samples.

Bismuth sulphosalts occur almost exclusively in pyrite-chalcopyrite-rich samples, in which the matrix consists of both quartz and siderite. Also present are minor amounts of sphalerite and galena, the latter containing up to as much as 17 mol. % matildite (AgBi_2) in solid solution. Bi-sulphosalts may account for as much as 1 vol. % of the sample and are recognised in four mineral associations: (i) as inclusions in chalcopyrite or on grain margins of chalcopyrite, (ii) as inclusions in coarse-grained pyrite, (iii) as aggregates of elongate needles within the quartz-siderite matrix, and (iv) as fine fracture fillings in quartz. Grain size is generally less than 20 μm , although grains of both lillianite and heyrovskyite up to 150 μm are present (Figs. 2a and b).

The following Bi-sulphosalt assemblages are observed: Lillianite-gustavite \pm heyrovskýite \pm „schirmerite“ \pm izoklakeite; bismuthinite derivatives \pm berryite; cosalite \pm native Bi; cosalite \pm nuffieldite \pm phase „A“. Lillianite-gustavite, heyrovskýite, „schirmerite“ and izoklakeite occur in all four textural associations and commonly coexist with one another. Intergrowths of two or more lillianite homologues and of gustavite with izoklakeite are widespread. In the Torioaga sample suite, lillianite homologues are not observed in the same samples as bismuthinite derivatives and were never seen coexisting with cosalite, nuffieldite or berryite. Bismuthinite derivatives and berryite are only observed as inclusions in chalcopyrite.

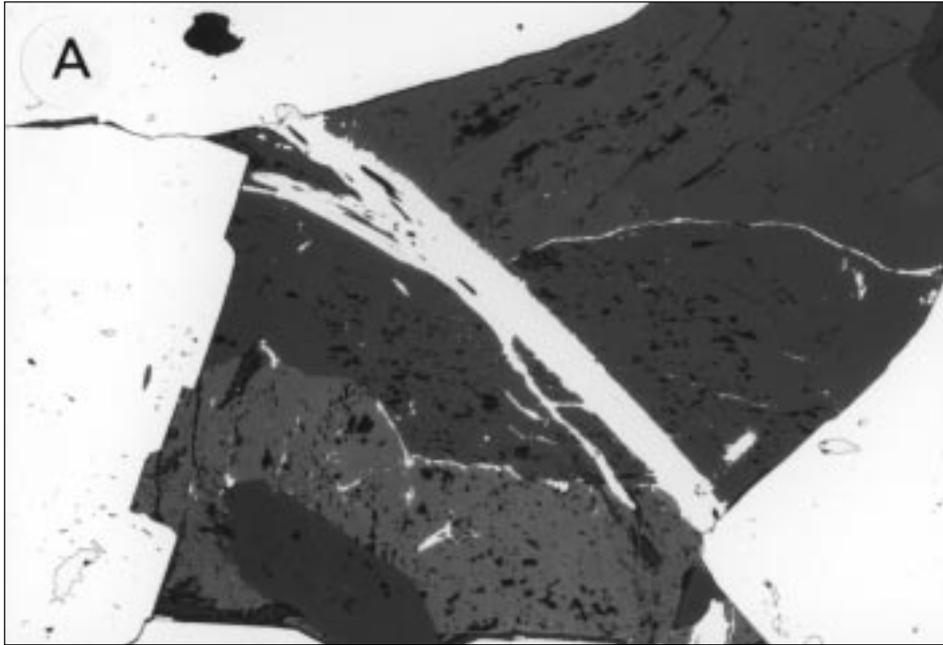


Fig. 2a
Acicular grain of lillianite (Ili) enclosed within the siderite gangue matrix to pyrite ore. „Caterina“ vein, Toroioaga Mine, Baia Borha. Horizontal field of view: 370 μm . Photomicrograph in reflected light.

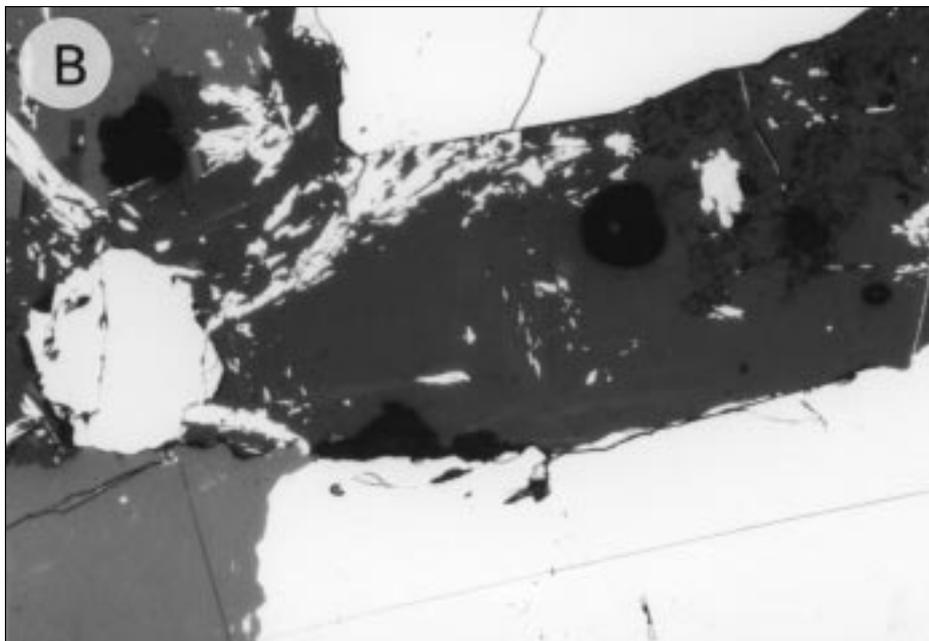
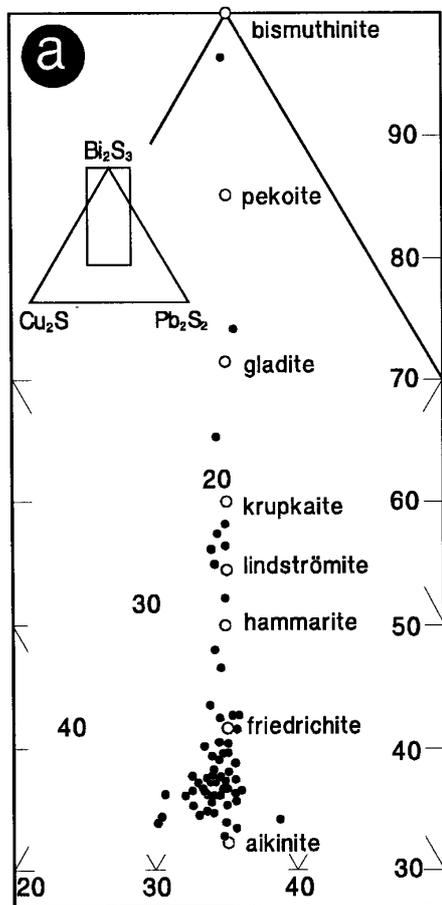


Fig. 2b
Scattered aggregates of lillianite and „schirmerite“ at the margins of, and enclosed within pyrite and chalcopyrite. „Caterina“ vein, Toroioaga Mine, Baia Borha. Horizontal field of view: 625 μm . Photomicrograph in reflected light.



Bismuthinite Derivatives:

A broad scatter covering the full compositional range in Cu_2S - PbS - Bi_2S_3 space (Fig. 3a) is observed, in which compositions clustering towards aikinite-friedrichite are the most abundant. The array of compositional variation shows no particular distribution centred around the eight known members of the series (aikinite, friedrichite, hammarite, lindströmite, krupkaite, gladite, pekoite, and bismuthinite). Instead, a more or less continuous compositional range between individual derivatives is observed, best explained in terms of disordering (PRING, 1989).

Fig. 3a
Compositional variation among Bi-sulphosalts from the Torioaga occurrence.
Bismuthinite derivatives in Bi_2S_3 - Cu_2S - Pb_2S_2 space

Lillianite Homologous Series:

Several distinct groups of compositions are identified which match to phases within the lillianite homologous series (MAKOVICKY & KARUPMØLLER, 1977a, b), indicated in Fig. 3b:

- (i) Compositions along the lillianite-gustavite join ($N = 4$)
- (ii) Compositions along the heyrovskýite solid solution join ($N = 7$)
- (iii) Compositions falling within the field of „schirmerite“ ($4 < N < 7$)

The latter are compositions which plot in the „schirmerite“ field (MAKOVICKY & KARUPMØLLER (1977b), between the lillianite-gustavite and heyrovskýite joins. They may, however, in part, represent other lillianite homologues with similar compositions, e.g. vikingite.

Cosalite:

Cosalite displays a range of compositions, from close to ideal $\text{Pb}_2(\text{Bi,Sb})_2\text{S}_5$, to varieties containing more than 2 wt. % $(\text{Cu}+\text{Ag})$, as shown in Fig. 3b.

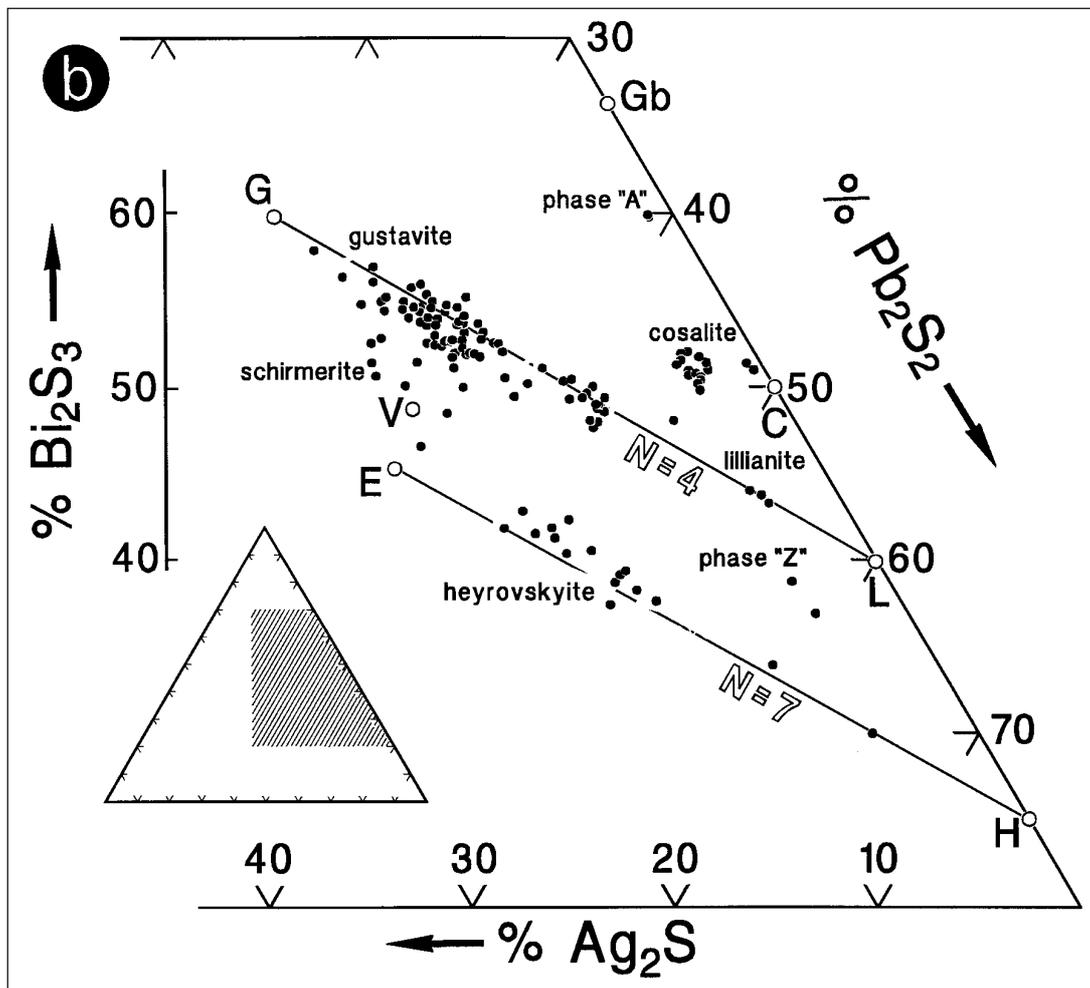


Fig. 3b
 Compositional variation among Bi-sulphosalts from the Torioaga occurrence.
 Lillianite homologues and related minerals in Pb_2S_2 - Ag_2S - Bi_2S_3 space.
 C: cosalite, L: lillianite, G: gustavite, V: vikingite, E: eskimoite.

Izoklakeite-giessenite:

A broad compositional range is observed, $Cu_{1.56-2.07}Ag_{2.08-2.62}Fe_{0.35-1.22}Pb_{21.05-21.99}(Bi_{9.96-15.99}Sb_{6.31-12.09})_{21.78-22.51}S_{55.30-56.10}Se_{0-0.23}Te_{0-0.22}$. This is well within the limits observed in other occurrences summarised by MOËLO et al. (1995), except that Cu contents commonly exceed 2 atoms p.f.u.. Substitution mechanisms for this remain unclear.

Nuffieldite:

Compositions fall close to those from other occurrences (MOZGOVA et al., 1994), conforming to the general formula, $Cu_{1-x}Pb_2(Pb_yBi_{1-y-z}Sb_z)Bi_2S_{7-y}$, where $x = y$ and $0.2 < y < 0.55$. It has been shown (MAUREL & MOËLO, 1990) that Sb is an essential component of nuffieldite. Again, (Cu+Ag+Fe) is in relative excess.

Berryite:

Always associated with aikinite-friedrichite, berryite shows a very limited compositional range; mean, $(\text{Cu,Ag,Fe})_{5.5}\text{Pb}_3\text{Bi}_7\text{S}_{16}$. Such compositions agree well with previously published data (e.g. BORTNIKOV et al., 1985), and suggest the compositional range for berryite to be narrower than for many of the other Bi-sulphosalts.

Phase „A“ (= Eclarite?):

This mineral falls between cosalite and galenobismuthite in Ag_2S - PbS - Bi_2S_3 space (Fig. 3b). The composition, $(\text{Cu}_{1.1}\text{Ag}_{0.27}\text{Fe}_{0.59})_{2.03}\text{Pb}_{7.82}(\text{Bi}_{11.36}\text{Sb}_{0.79})_{12.15}\text{S}_{27.34}$, corresponds closely to that of the rare mineral eclarite, known only from its' type locality with the composition, $(\text{Cu}_{0.73}\text{Ag}_{0.21}\text{Fe}_{0.67})_{1.61}\text{Pb}_{8.56}(\text{Bi}_{11.19}\text{Sb}_{0.62})_{11.81}\text{S}_{27.99}$ (PAAR et al., 1983). If an extended degree of $\text{Pb} \rightleftharpoons (\text{Ag,Cu})$ substitution is accepted, the fit to eclarite is very close. Although microprobe data alone are insufficient to characterise phase „A“ the microanalytical data suggest that this might represent a second occurrence of eclarite.

Not only have these minerals been observed for the first time in this area, but the compositions of several species are worthy of attention, since they display significant substitution of Sb for Bi. Sulphosalts containing both essential Sb and Bi and Sb-rich varieties of Bi-sulphosalts are known from only a small handful of localities worldwide (e.g. MOZGOVA et al., 1987 for lillianite-gustavite; ERTL et al., 1994 for heyrovskýite; LEE et al., 1993 for cosalite). The new occurrence therefore represents a valuable additional natural occurrence of minerals in the Ag_2S - Cu_2S - PbS - Bi_2S_3 - Sb_2S_3 system, and provides new information on compositional ranges and paragenetic relationships for this phase system.

Lillianite-gustavite, heyrovskýite, „schirmerite“ and cosalite all display significant substitution of Sb for Bi:

	mol. % Sb/(Sb+Bi)
Lillianite-gustavite	2.6 - 33.7
Heyrovskýite	2.0 - 27.4
„Schirmerite“	3.4 - 43.1
Cosalite	4.6 - 17.0
Izoklakeite-giessenite	28.3 - 54.6
Nuffieldite	14 - 18

Such high values are consistent with experimental data for the Ag_2S - PbS - Bi_2S_3 phase system (CHANG et al., 1980). Izoklakeite-giessenite and nuffieldite contain essential Bi and Sb. The bismuthinite derivatives and berryite do not show Sb substitution above levels of approx. 1 mol. %.

THE BĂIUȚ OCCURRENCE

The epithermal Pb-Zn-Cu-Au-Ag deposits in the Băiuț area (BORCOȘ & GHEORGHITĂ, 1976) are situated in the easternmost part of the Gutâi Mts, east of the city of Baia Mare. Four individual vein ore deposits are recognised (Breiner, Văratec, Cisma, and Coasta Urșului), but the orefield also contains a mineralised breccia pipe (Rotunda-Kelemen). A single metallogenetic phase at around 9.0 Ma is proposed for the deposits which display strongly geochemical zonation (VALDMANN, 1997, in press). Five distinct mineralisation types are observed in the Băiuț district, which are rarely found together; 1. Au-Ag; 2. Cu-Zn-Pb-Au-Ag; 3. Cu (only); 4. Cu-Au; 5. Zn-Pb-Cu. Little paragenetic data is available to date on the component ore minerals in any of the deposits in the Băiuț orefield.

The veins which constitute the Văratec deposit (BORCOȘ & GHEORGHITĂ, 1976) are hosted within Pontian pyroxene andesites, pyroclastics and sedimentary rocks. The deposit is dominantly Pb-rich, although it contains mineralisation types 1, 2, 3 and 5 and displays a relatively well-developed vertical zonation, with increasing Cu at depth. The deposit is also characterised by abundant magnetite and other Fe- and Mn oxides. Relatively high temperatures (360°C) have been suggested by earlier workers. This is fully consistent with the observed mineralogy, including the Bi-sulphosalts.

In this study, all samples containing Bi-sulphosalts are from the Văratec deposit. Investigation of numerous samples from Rotunda-Kelemen has, thus far, not indicated the presence of any Bi-sulphosalts.

Bismuth sulphosalts

Bismuth sulphosalts are widely distributed in pyrite-chalcopyrite ores from Băiuț-Văratec, which are similar in petrographic appearance to those from Toroioaga. Both galena and sphalerite are subordinate to chalcopyrite and pyrrhotite is absent. Quartz and siderite are the main gangue phases. Various Fe-oxides are abundant within the investigated samples.

Lillianite homologues are the most abundant Bi-sulphosalts in the investigated sample suite, with lillianite-gustavite, heyrovskýite and „schirmerite“ all identified. Bismuthinite derivatives are represented by pekoite and bismuthinite. Also noted are matildite and related compositions along the PbS-AgBiS₂ join, berryite, wittichenite and a small number of extremely Ag-rich sulphosalts which are tentatively allocated to the pavonite homologous series.

Bismuthinite derivatives:

These occur as euhedral grains, between 5 and 50 μm in size, enclosed, in descending order of abundance, within chalcopyrite, pyrite, iron oxides (Fig. 2c) and gangue. Associated phases include both galena, containing up to 8 % AgBiS₂, and matildite (discussed below). Bismuthinite derivatives are never observed in grain contact with lillianite homologues, yet are generally present within the same polished sections (c.f. the Toroioaga occurrence). Also in sharp contrast to Toroioaga, only Cu-Pb poor varieties towards the bismuthinite end of the series are observed.

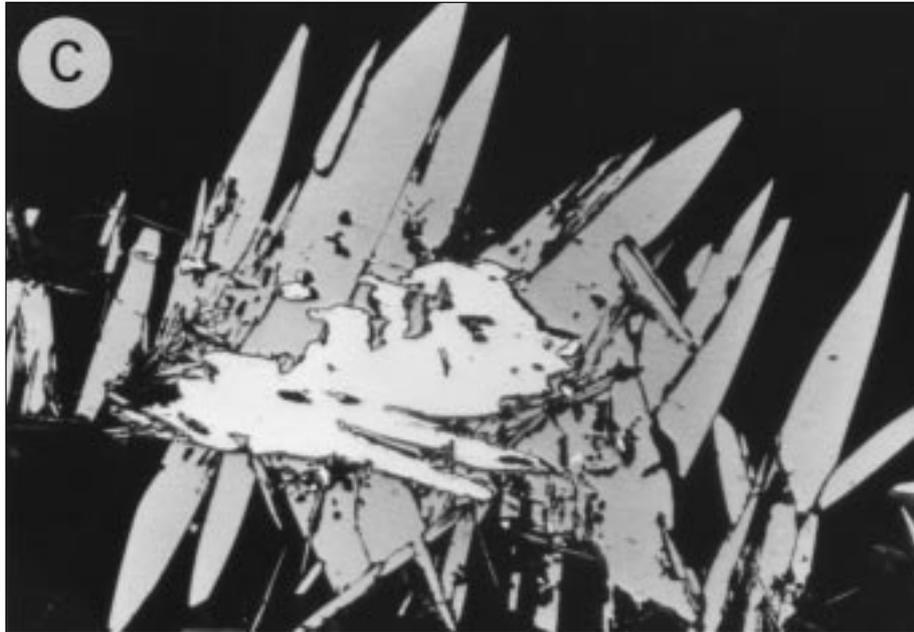


Fig. 2c

Patchy, partly corroded grain of bismuthinite (white) overgrown by acicular Fe-oxide (grey) within siderite matrix. horizontal field of view. 360 μm . Photomicrograph in reflected light.

	(1)	(2)	(3)	(4)	(5)
Analysis:	2543.9/1	100.4/2	226-2.13	100.1	2543.8/1
Wt. %					
Cu	0.53	1.03	1.44	1.16	1.15
Ag	0	0	0	0	0
Fe	0	0	0.44	0.17	0.18
Pb	1.81	2.07	1.62	1.39	1.93
Bi	76.72	76.78	77.09	76.86	77.32
Sb	0.08	0	0.10	0.08	0.25
S	18.01	17.52	17.98	18.06	17.87
Se	1.82	1.33	0.96	1.66	1.19
Te	0.08	0	0	0	0
Total	99.05	98.73	99.63	99.38	99.89
n_a	4.8	6.9	9.9	7.3	7.9
Formulae calculated to $(\text{Cu}+\text{Pb})/2+\text{Bi} = 8$:					
(1) $\text{Cu}_{0.18}\text{Pb}_{0.19}\text{Bi}_{7.81}(\text{S}_{11.94}\text{Se}_{0.49})_{12.45}$					
(2) $\text{Cu}_{0.34}\text{Pb}_{0.21}\text{Bi}_{7.73}(\text{S}_{11.49}\text{Se}_{0.35})_{11.84}$					
(3) $\text{Cu}_{0.47}\text{Fe}_{0.16}\text{Pb}_{0.16}\text{Bi}_{7.59}(\text{S}_{11.54}\text{Se}_{0.25})_{11.79}$					
(4) $\text{Cu}_{0.37}\text{Fe}_{0.07}\text{Pb}_{0.22}\text{Bi}_{7.67}(\text{S}_{11.71}\text{Se}_{0.34})_{12.04}$					
(5) $\text{Cu}_{0.37}\text{Fe}_{0.07}\text{Pb}_{0.19}\text{Bi}_{7.64}(\text{S}_{11.51}\text{Se}_{0.31})_{11.82}$					

Back scattered electron imaging has not indicated the presence of intergrown derivatives with distinct compositions. Analysed grains (Table 1) occupy the compositional field between pekoite and bismuthinite with no compositional gap between. Using the classification of MAKOVICKY & MAKOVICKY (1978), n_a values lie between 4.3 and 12.4. Such compositions intermediate between the two superstructures are attributed to disordering induced by rapid crystallisation. A characteristic feature of bismuthinite derivatives from Băiuț is that they contain significant Se, up to 1.82 wt. %.

Tab. 1

Representative electron probe microanalyses of bismuthinite.

Lillianite homologues:

Acicular grains of up to 200 μm in length occur enclosed within chalcopyrite, at the grain boundaries between chalcopyrite, pyrite and gangue (Fig. 2d), enclosed within quartz-side-rite gangue (Fig. 4a) and associated with Fe-oxides (Fig. 4b). More rarely, they are encountered fully enclosed within pyrite. A common feature of the Băiut samples, in contrast to Toroioaga, is the occurrence of mosaic-like intergrowths of individual lillianite homologues (e.g. gustavite, heyrovskyite) within the acicular grains, as can be seen clearly under partly-crossed nicols in Fig. 4a. Electron probe microanalysis has shown, however, that not all grains are aggregates of individual homologues, but that many of the grains are compositionally more or less homogeneous. Widespread twinning, however, may give the impression of mosaic-like intergrowths under crossed nicols.

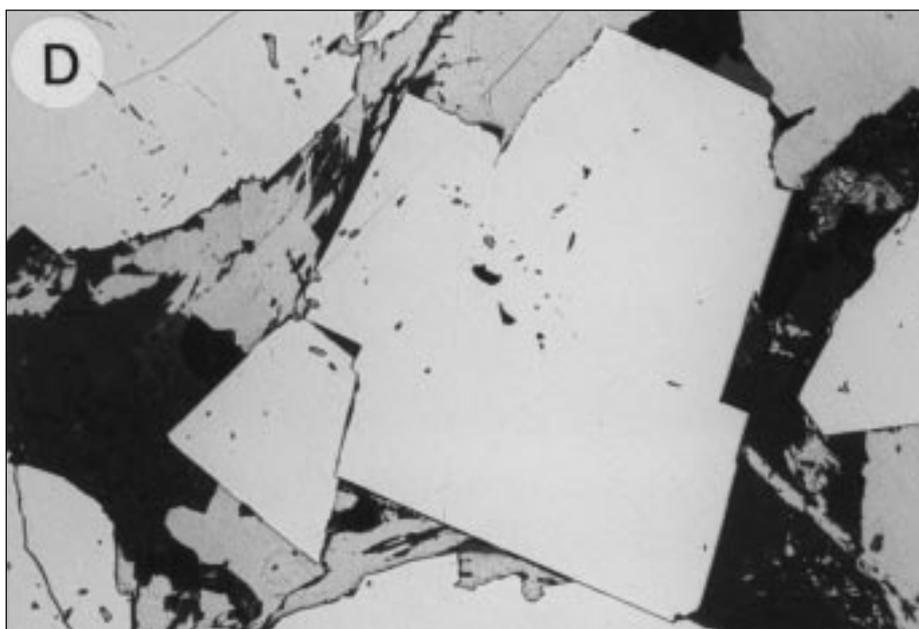


Fig. 2d

Grains of various lillianite homologues (gustavite, „schirmerite“ and heyrovskyite) filling the matrix between pyrite (py), chalcopyrite (cp) and siderite gangue (black). Horizontal field of view: 350 μm . Photomicrograph in reflected light.

Compositions along the lillianite-gustavite join (Table 2) are by far the most widespread and define relatively tight clusters in $\text{Ag}_2\text{S} - \text{Bi}_2\text{S}_3 - \text{Pb}_2\text{S}_2$ space at approx. Gu_{60-70} with a smaller number of analyses close to end member gustavite (Fig. 5). Calculated N values range between 3.77 and 4.60, with most close to ideal 4.0.

All analysed lillianite-gustavite grains display significant concentrations of Se, ranging between 1.03 and 2.70 wt. %. This maximum Se concentration corresponds to a atom. $\text{Se}/(\text{S}+\text{Se}+\text{Te})$ ratio of 0.07. HUIFANG LIU & CHANG (1994) have experimentally examined the phase relationships of Pb-Bi chalcogenides and showed that lillianite-gustavite, in contrast to heyrovskyite, does not form a complete solid solution with the seleniferous analogue, but rather breaks down to two terminal solid solutions. The $\text{Se}/(\text{S}+\text{Se}+\text{Te})$ ratios of rather less than 10 % determined here are thus in full accordance with these experimental results.

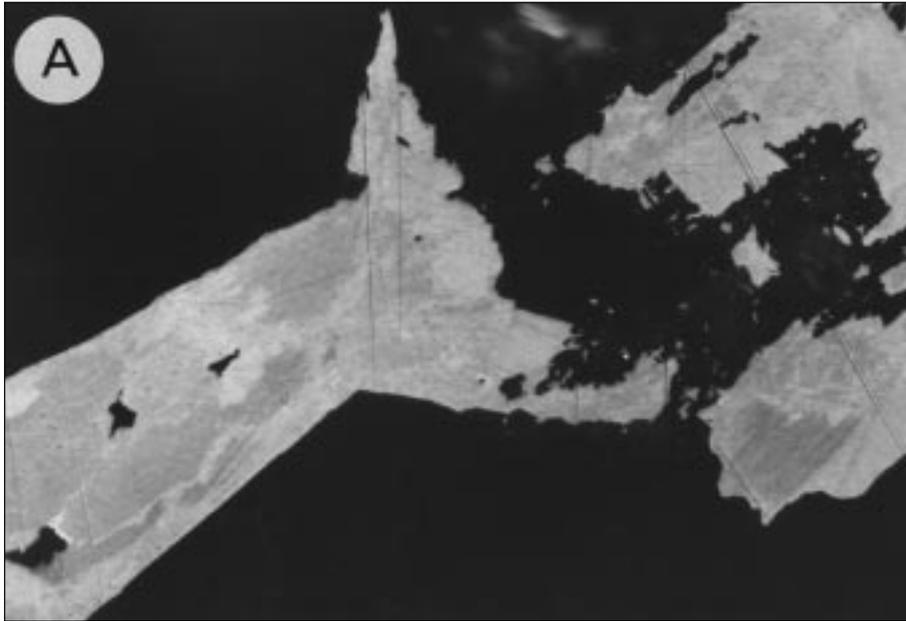


Fig. 4a
Lath-shaped grains of lillianite minerals in siderite matrix viewed under partly crossed nicols. Microscopically visible intergrowths of gustavite with heyrovskýite (and possibly other lillianite homologues?) are clearly visible. Horizontal field of view: 310 μm . Photomicrograph in reflected light.

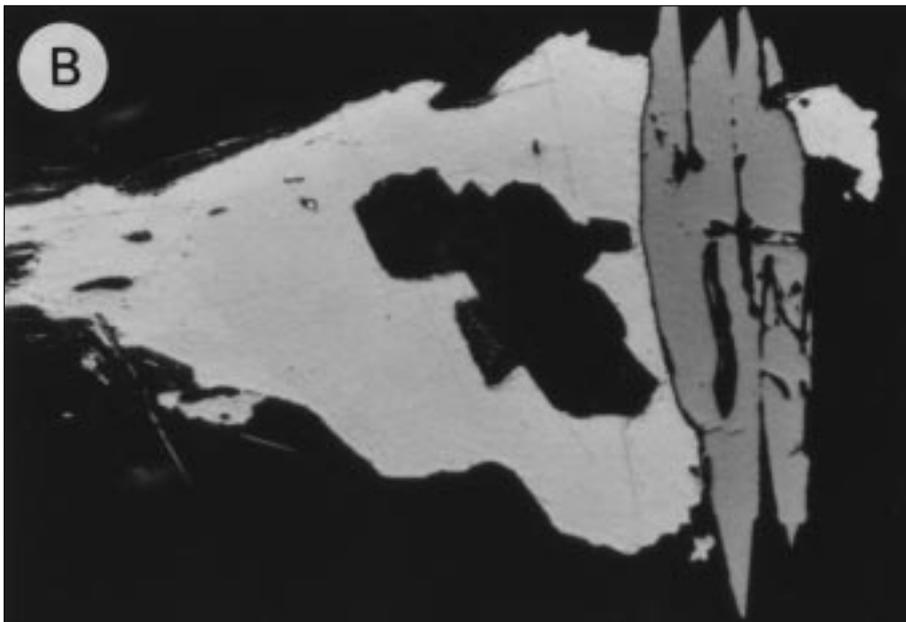


Fig. 4b
Compositionally homogeneous gustavite grain (pale grey) overgrown by Fe-oxide (darker grey), within siderite gangue. Horizontal field of view: 360 μm . Photomicrograph in reflected light.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
Analysis:	2543.14	2543.24	226-2.9	100.3/2	2543.2/3	2543.1/2	2543.6/1	2543.5/3	2543.2/4	2543.8/6	2543.7/4	2543.5/2	2543.8/4	2543.27	2543.4/3	2543.6	2543.6/4
Wt. %																	
Cu	0.36	0.31	0.49	1.01	0.60	0.21	0.27	0	0	0	0.18	0.20	0.20	0	0.14	0.49	0.17
Ag	5.74	5.55	8.23	5.88	6.14	6.40	6.11	6.42	5.72	11.09	12.41	6.56	7.13	7.80	8.77	10.30	10.75
Fe	0	0.14	0.16	0	0.12	0	0.18	0	0.14	0	0	0.18	0.29	0.26	0.18	0.22	0.12
Pb	31.34	31.59	22.50	28.10	30.82	30.64	32.32	41.90	44.28	25.60	23.38	31.06	31.91	28.16	24.83	24.70	26.60
Bi	44.46	44.73	49.13	46.77	44.44	44.69	44.90	33.99	31.59	45.21	46.89	43.78	42.09	45.52	47.68	45.50	45.29
Sb	0.08	0.14	0	0	0.10	0	0.08	0.05	0	0	0.06	0.12	0	0	0.13	0.14	0.06
S	15.06	14.99	16.37	15.48	15.40	15.75	15.89	14.96	14.47	15.56	15.46	15.21	15.07	15.13	15.69	15.50	15.62
Se	2.35	2.58	1.42	2.18	1.95	1.36	1.32	1.97	2.01	1.42	1.81	2.35	1.99	2.58	1.64	1.92	0.98
Te	0.17	0.17	0	0	0	0.06	0.08	0.15	0	0	0.13	0.22	0	0	0	0.11	0
Total	99.56	100.20	98.30	99.42	99.57	99.11	101.07	99.44	98.21	98.88	100.32	99.68	98.68	99.45	99.06	98.88	99.59
Formulae (to 5 Cu+Ag+Fe+Pb+Sb+Bi):																	
Cu	0.07	0.06	0.09	0.19	0.11	0.04	0.05	0	0	0	0.03	0.04	0.04	0	0.03	0.09	0.03
Ag	0.63	0.60	0.89	0.63	0.66	0.70	0.65	0.70	0.63	1.16	1.26	0.71	0.77	0.84	0.93	1.07	1.11
Fe	0	0.03	0.03	0	0.03	0	0.04	0	0.03	0	0	0.04	0.06	0.05	0.04	0.04	0.02
Pb	1.79	1.79	1.26	1.58	1.73	1.74	1.79	2.38	2.54	1.40	1.24	1.75	1.79	1.58	1.38	1.34	1.43
Bi	2.51	2.51	2.73	2.60	2.47	2.52	2.46	1.91	1.80	2.44	2.46	2.45	2.34	2.53	2.62	2.45	2.41
Sb	0.01	0.01	0	0	0.01	0	0.01	0.01	0	0	0.01	0.01	0	0	0.01	0.01	0.01
(Bi+Sb)	2.52	2.52	2.73	2.60	2.48	2.52	2.47	1.92	1.80	2.44	2.47	2.46	2.34	2.53	2.63	2.46	2.42
S	5.54	5.48	5.93	5.62	5.58	5.79	5.69	5.49	5.37	5.48	5.29	5.55	5.47	5.48	5.62	5.43	5.41
Se	0.35	0.38	0.21	0.32	0.29	0.20	0.19	0.29	0.30	0.20	0.25	0.35	0.29	0.38	0.24	0.27	0.14
Te	0.02	0.02	0	0	0	0.01	0	0.01	0	0	0.01	0.02	0	0	0	0.01	0
(S+Se+Te)	5.91	5.88	6.14	5.94	5.86	6.00	5.88	5.80	5.67	5.68	5.56	5.92	5.76	5.86	5.85	5.71	5.55
N (calc.)	4.22	4.12	4.29	3.89	4.35	4.45	4.39	7.21	7.52	6.80	7.25	4.63	5.23	4.86	4.82	6.03	6.58

Tab. 2

Representative electron probe microanalyses of lillianite homologues (1-7: lillianite-gustavite; 8-11: heyrovskite; 12-17: „schirmerite“)

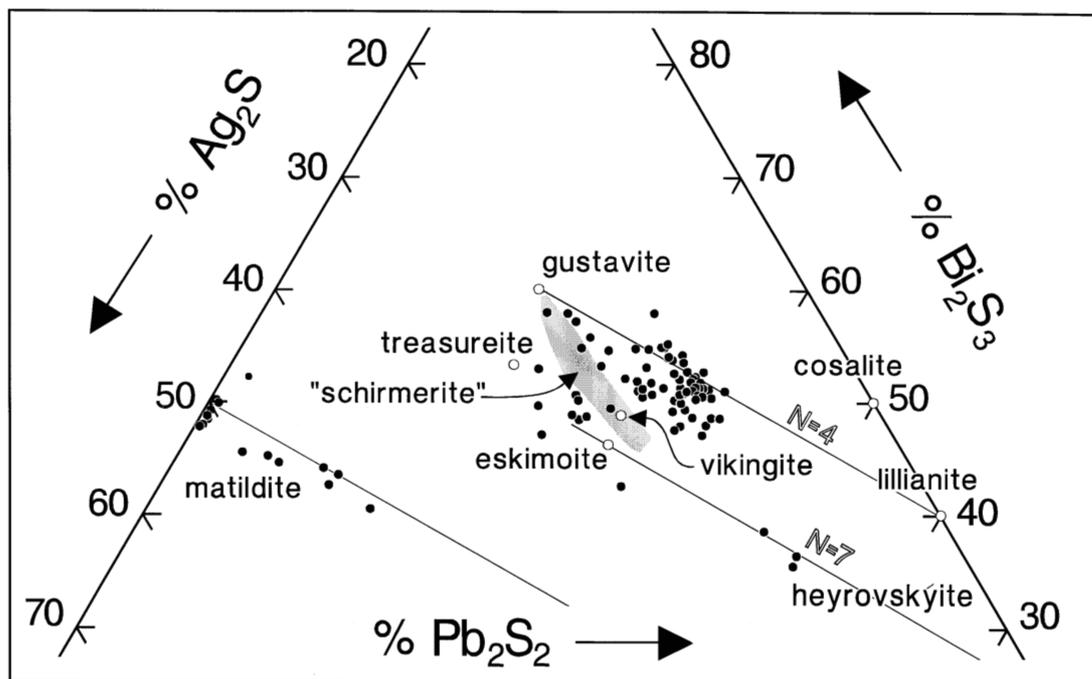


Fig. 5
Compositional variation among lillianite homologues and matildite from Bâiut- Vârteci, presented in Pb_2S_2 - Ag_2S - Bi_2S_3 space. See text for discussion.

Many lillianite-gustavites also contain levels of Te above the detection limit (typically 0.10 to 0.15, but as high as 0.40 wt. % in some cases). Concentrations of Sb substituting for Bi are, without exception, less than 1.0 mol. %.

The second most abundant species of lillianite homologue corresponds to compositions richer in Ag (Table 2) which fill a broad compositional field between gustavite and a point on the $N = 7$ join. The appearance of these grains under the microscope is very similar to that of gustavite, with which they are intimately intergrown, commonly occurring in fine-grained aggregates. The compositions of many grains of this group fall close to, but not within, the field of „schirmerite“. In the absence of other diagnostic data, it is difficult to provide a more accurate identity. It is noted that many of these compositions plot well to the right of the „schirmerite“ field and may actually represent sub-microscopic intergrowths of different homologues, e.g. gustavite and heyrovskýite (in effect, mixture analyses). Several analysed compositions are also close to the plotting positions of both eskimoite and vikingite. Calculated N values range between 4.71 to 6.73, effectively forming an Ag-enriched extension of the compositional field displayed by gustavite. The „schirmerite“ compositions also contain appreciable Se, up to 2.2 wt. %.

A smaller number of analyses have N values clustering around 7 (6.5 to 8.2) and are therefore regarded as members of the heyrovskýite solid solution series. All analysed heyrovskýite grains were observed as intergrowths with lillianite-gustavite and/or „schirmerite“ (e.g. Fig. 4a).

Matildite¹:

AgBiS_2 is a common constituent of the Bi-sulphosalt intergrowths, occurring as small inclusions in the common sulphides and within the Bi-sulphosalts themselves. Coarser grains of matildite are enclosed within the gangue matrix and commonly show an enclosing rim of wittichenite (Fig. 4c).

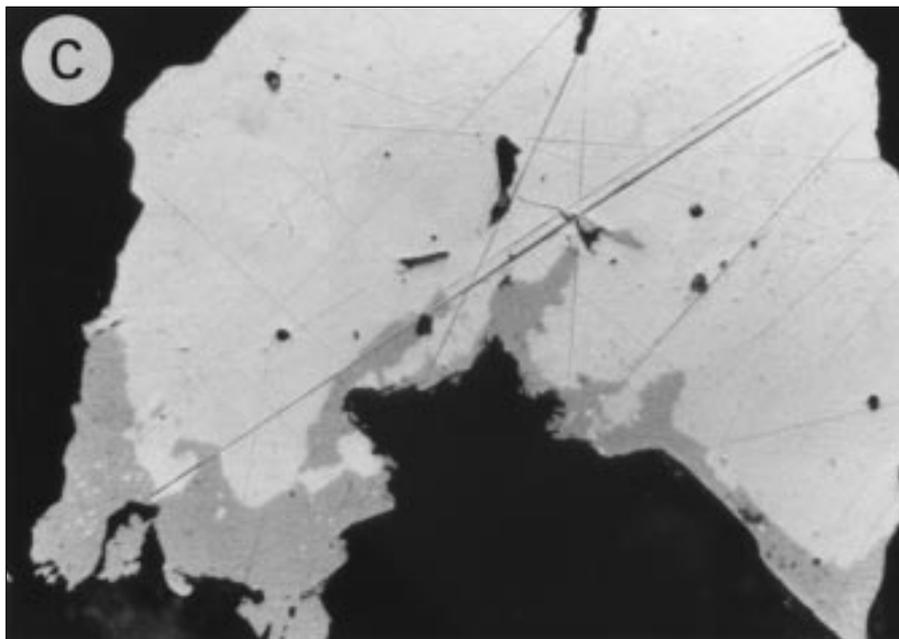


Fig. 4c

Coarse grain of matildite (light), bordered by wittichenite (light grey). Brighter grains within wittichenite have a composition similar to berryite. Horizontal field of view: 160 μm . Photomicrograph in reflected light.

Two distinct compositional groups are present among the matildite analytical data (Table 3). The first compositional group clusters around end-member matildite, while the second group contain significant quantities (4.4 to 15.6 wt. %) of Pb. This latter group plots on the AgBiS_2 - PbS join in Ag_2S - Bi_2S_3 - Pb_2S_2 space (Fig. 5), and can be regarded as solid solution compositions between galena and matildite. The most Pb-rich grain analysed, with the composition $\text{Ag}_{0.87}\text{Bi}_{0.83}\text{Pb}_{0.34}\text{S}_2$, corresponds to 16.5 mol % PbS in matildite. It is noted that this composition is very close to $\text{Ag}_5\text{Bi}_5\text{Pb}_2\text{S}_{12}$, which KOVALENKER et al. (1993) reported from veins of the Štiavnica-Hodruša orefield, Slovakia, and chose to regard as one of a number of distinct phases along the galena-matildite join. Like other Bi-minerals from Băiut, matildite is also Se-bearing, with concentrations of up to 1.71 wt. % having been determined.

Wittichenite:

Present as alteration rims surrounding matildite, wittichenite can be confirmed from Băiut. Analytical data (Table 4) indicate the presence of minor Ag (to 1.6 wt. %) and Se (to 0.60 wt. %).

¹The name matildite is used in preference to schapbachite for all minerals with the composition AgBiS_2 , following more common international usage.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Analysis:	226-2.6a	100.1/2a	226-2.16	226-2.11	2543.8/1	2543.8/2	2543.6/3	226-2.7
Wt. %								
Cu	0.50	0.49	0.21	0.29	0	0	0.10	0.70
Ag	28.15	27.72	27.13	25.51	23.80	24.15	23.60	22.74
Fe	0.19	0.03	0	0.27	0	0.10	0	0.86
Pb	0	0.42	4.63	7.67	11.75	13.17	13.44	16.87
Bi	54.06	53.11	48.26	46.94	45.53	44.45	45.21	42.24
Sb	0	0	0.13	0	0.12	0.07	0.13	0
S	16.63	16.07	15.72	15.65	15.13	14.94	15.72	15.54
Se	0.94	0.83	1.71	1.10	2.10	2.10	1.02	1.22
Te	0	0.04	0	0	0.06	0.08	0.04	0.10
Total	100.47	98.71	97.79	97.43	98.49	99.06	99.26	100.27
Formulae:								
(1)	$\text{Cu}_{0.03}\text{Fe}_{0.01}\text{Ag}_{0.98}\text{Bi}_{0.97}(\text{S}_{1.95}\text{Se}_{0.05})_{2.00}$							
(2)	$\text{Cu}_{0.03}\text{Ag}_{0.99}\text{Pb}_{0.01}\text{Bi}_{0.98}(\text{S}_{1.92}\text{Se}_{0.04})_{1.96}$							
(3)	$\text{Cu}_{0.01}\text{Ag}_{0.98}\text{Pb}_{0.09}\text{Bi}_{0.91}(\text{S}_{1.92}\text{Se}_{0.09})_{2.01}$							
(4)	$\text{Cu}_{0.02}\text{Fe}_{0.02}\text{Ag}_{0.93}\text{Pb}_{0.15}\text{Bi}_{0.88}(\text{S}_{1.92}\text{Se}_{0.06})_{1.98}$							
(5)	$\text{Ag}_{0.89}\text{Pb}_{0.23}\text{Bi}_{0.88}(\text{S}_{1.90}\text{Se}_{0.11})_{2.01}$							
(6)	$\text{Fe}_{0.01}\text{Ag}_{0.89}\text{Pb}_{0.25}\text{Bi}_{0.85}(\text{S}_{1.86}\text{Se}_{0.11})_{1.96}$							
(7)	$\text{Cu}_{0.01}\text{Ag}_{0.87}\text{Pb}_{0.26}\text{Bi}_{0.86}(\text{S}_{1.95}\text{Se}_{0.05})_{2.00}$							
(8)	$\text{Cu}_{0.04}\text{Fe}_{0.06}\text{Ag}_{0.81}\text{Pb}_{0.31}\text{Bi}_{0.77}(\text{S}_{1.86}\text{Se}_{0.06})_{1.92}$							

Tab. 3
Representative electron probe microanalyses of matildite.

Berryite:

This mineral has only been observed in a single sample, in which it is a widespread phase, intergrown with various lillianite homologues and forming a myrmekitic intergrowth with wittichenite and matildite (Fig. 4d). Microprobe analyses calculated on the basis of 15 (Ag+Cu+Pb+Bi+Sb) (Table 4) show reasonable accordance with the generalised formula $(\text{Cu,Ag})_5\text{Pb}_3\text{Bi}_7\text{S}_{16}$ (NUFFIELD & HARRIS, 1966).

Similar to the berryite within the Toroioaga occurrence, the analyses of material from Băiuț also display an slight excess of (Cu+Ag) beyond 5 atoms per formula unit; analyses averaging 5.2 (Cu+Ag) p.f.u. (Fig. 6). However, this would appear to be compensated for by a small deficiency in Bi below 7 atoms p.f.u., although no particularly strong negative correlation is noted. As noted previously (COOK, 1997), the compositional limits for berryite, both in terms of Cu/(Cu+Ag) and (Cu+Ag) \Leftrightarrow Bi exchange (?) remain poorly constrained. Berryite from Băiuț has an Ag/(Ag+Cu) ratio of consistently less than 0.5, in contrast to the same mineral from Toroioaga, in which Ag > Cu. Consistent with other Bi-sulphosalts from Băiuț, berryite contains up to 2.2 wt. % Se.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Analysis:	100.2/2	100.5/3	100.11/1	100.2/2	100.2/5	226-2.4	226-2.4a	100-2.4
Wt. %								
Cu	6.81	6.03	5.80	6.83	7.45	1.20	1.18	37.22
Ag	5.63	7.14	8.54	6.96	7.45	12.95	13.39	0.56
Fe	0.26	0.11	0	0.26	0.25	0.65	0.60	0.12
Pb	21.29	20.79	19.30	20.50	19.68	5.52	5.17	0
Bi	46.47	46.74	48.39	47.37	46.68	61.57	59.97	41.69
Sb	0	0.12	0.06	0	0	0	0	0
S	16.02	15.93	16.11	16.42	16.39	16.76	16.77	18.91
Se	2.13	2.22	1.95	1.88	1.78	1.35	1.61	0.22
Te	0.19	0.11	0.12	0	0	0.15	0	0.08
Total	98.80	99.19	100.27	100.22	99.81	100.15	98.69	98.80
Formulae:	(15 valency cations)					(18 valency cations)		(4 cations)
Cu	3.29	2.92	2.77	3.21	3.45	0.32	0.32	2.96
Ag	1.60	2.04	2.40	1.93	2.03	2.01	2.12	0.03
Fe	0.14	0.06	0	0.14	0.13	0.20	0.18	0.01
Pb	3.15	3.09	2.82	2.96	2.80	0.45	0.43	0
Bi	6.82	6.89	7.02	6.77	6.59	4.93	4.90	1.01
Sb	0	0.03	0.02	0	0	0	0	0
(Bi+Sb)	6.02	6.92	7.04	6.77	6.59	4.93	4.90	1.01
S	15.32	15.30	15.22	15.30	15.04	8.75	8.94	2.98
Se	0.83	0.87	0.75	0.71	0.66	0.29	0.35	0.01
Te	0.05	0.03	0.03	0	0	0.02	0	0
(S+Se+Te)	16.20	16.20	16.00	16.01	15.71	9.05	9.29	2.99

Tab. 4
Representative EPMA data on berryite (1-5), Ag-Bi-Pb-S phase (6,7) and wittichenite (8).

Silver-rich Bi-sulphosalts:

This distinct compositional groups (Table 4) are represented by acicular grains, up to 80 μm in length and no more than 5 μm in width, which occur together with lillianite-gustavite and „schirmerite“ (Fig. 4e). This conspicuous morphology allowed acceptable EPMA analyses to be made on only two grains. Calculated to 18 valency cations, this gives the mean formula: $\text{Cu}_{0.32}\text{Ag}_{2.06}\text{Fe}_{0.19}\text{Pb}_{0.43}\text{Bi}_{4.91}(\text{S}_{8.84}\text{Se}_{0.31}\text{Te}_{0.01})_{9.17}$. An unambiguous identification for these grains is difficult on the basis of electron probe microanalysis alone, given the difficulties in calculating mineral formulae in this portion of the $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3-\text{PbS}$ system, especially where Cu may substitute for both Ag and Bi (c.f. KARUP-MØLLER & MAKOVICKY, 1979). Such a composition would fit reasonably well to a member of the pavonite homologous series (MAKOVICKY et al., 1977; MUMME, 1990; KARUP-MØLLER & MAKOVICKY, 1992; ŽÁK et al., 1994), although crystallographic characterisation is generally required in order to identify pavonite homologues with any certainty. The ratio of cations to sulphur is close to Me_5S_6 , suggesting this may be the ^7P homologue, benjaminite (ideally $\text{Ag}_{1.5}\text{Bi}_{3.5}\text{S}_6$, or in substituted form, $\text{Cu}_a\text{Pb}_b\text{Ag}_{1.5-y}\text{Bi}_{3.5-y}\text{S}_6$, where $a + b \geq 2y$). The high Ag/Cu ratio of the analysed grains and the moderate Pb substitution are fully concordant with previously reported benjaminite compositions (e.g. KARUP-MØLLER & MAKOVICKY, 1979), in sharp contrast to the ^8P homologue, mummeite, the next closest fit on the basis of Me:S ratio.

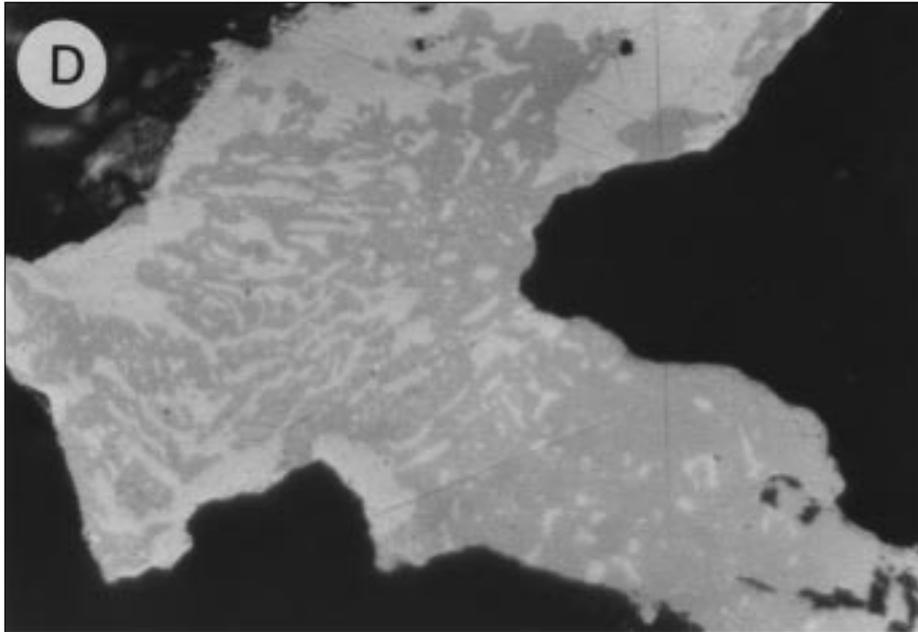


Fig. 4d
Myrmeketic intergrowth of wittichenite (dark) with berryite (light). Both wittichenite and berryite contain sub-microscopic intergrowths of matildite. Horizontal field of view: 120 μm . Photomicrograph in reflected light.

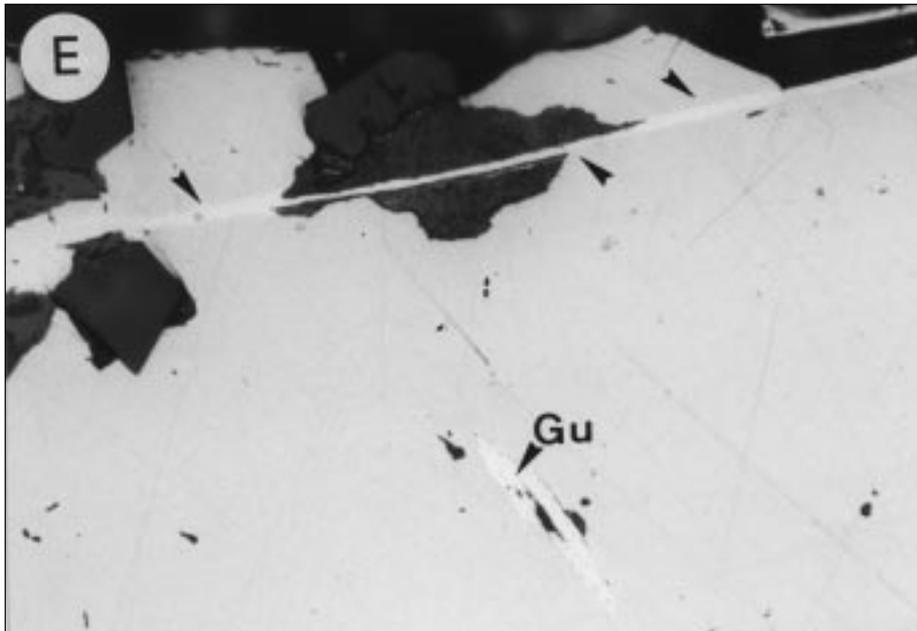


Fig. 4e
Acicular grain of unidentified Ag-Bi-(Pb) sulphosalt, possibly benjaminite? (arrowed). Horizontal field of view: 350 μm . cp: chalcopyrite; gu: gustavite. Photomicrograph in reflected light.

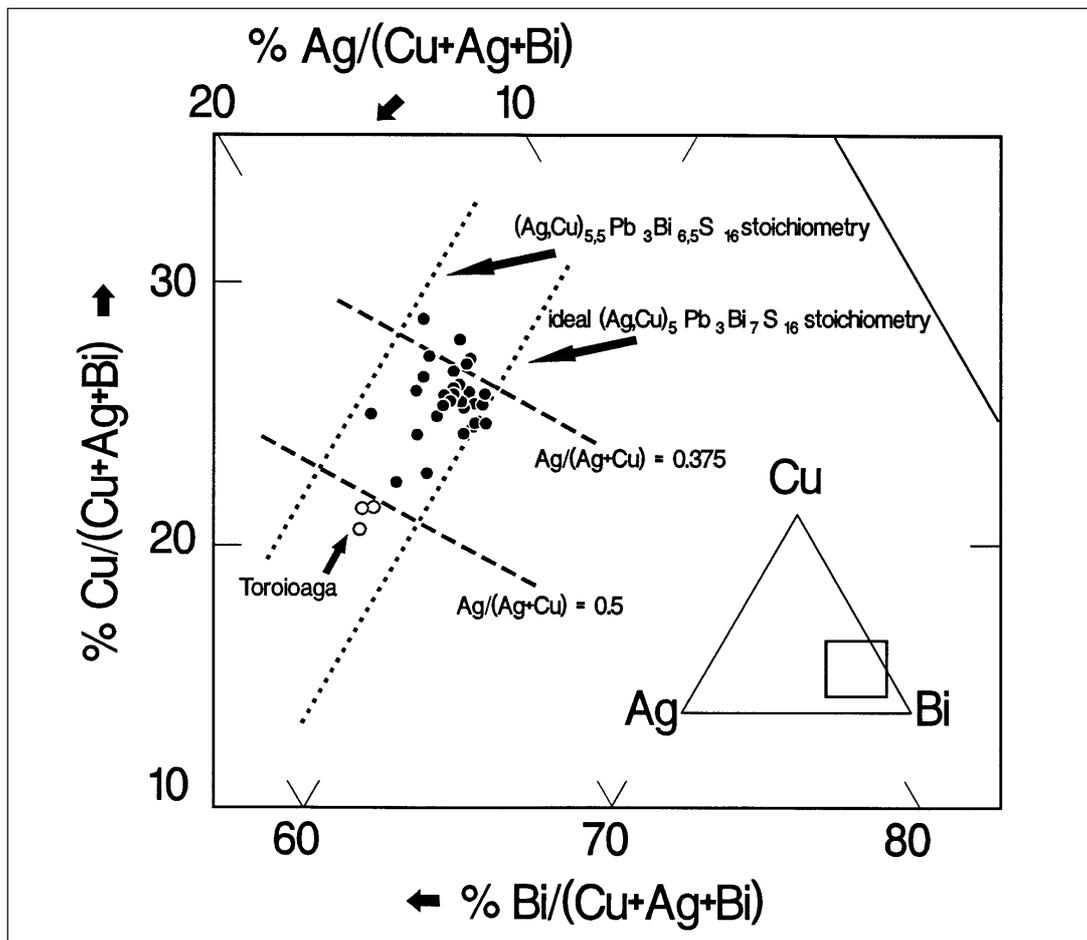


Fig. 6
Compositional variation among analysed grains of berrylite from Băiut - Văratec, expressed in terms of atomic Ag, Cu and Bi. Berrylite compositions from the Toroioaga veins are shown for comparison.

Discussion and conclusion

The Ag-Pb-Bi and Cu-Pb-Bi sulphosalts are identified in a distinct and readily characterised type of ore in both the Toroioaga and Băiut-Văratec deposits. These ores, containing mostly pyrite and chalcopyrite with minor galena are in sharp mineralogical contrast with the vein assemblages carrying Zn and Pb minerals and associated Pb-Sb sulphosalts, from which no Bi-sulphosalts have been observed. The Cu-Bi ores clearly represent a temporally distinct type of mineralisation.

In the Toroioaga deposit, the Cu-rich mineralising event has been interpreted as later than that responsible for the polymetallic sulphides. A working hypothesis, invoking an as-yet-undiscovered Cu ± Au porphyry body at depth has been adopted by many workers in the area. Such a model is strengthened by the presence of Cu ± Bi ± Au mineralisation above the proposed porphyry body.

In the case of the Toroioaga deposit, the overprinting by a Cu-Bi enriched higher sulphidation event onto a pre-existing Pb-Zn-(Sb) mineralisation could have produced the distinctive and compositionally unusual array of Bi-sulphosalt assemblages. These include the extensive compositional variation along the entire span of the aikinite-bismuthinite series, the high levels of Sb in various lillianite homologues and the presence of minerals such as izoklakeite and nuffieldite, which are only stabilised by Sb. The situation for Băiuț-Văratec can be viewed in simpler terms; the Bi-Sb sulphosalts are absent because of the absence of Sb in earlier-deposited mineral assemblages.

COOK (1997) cautiously suggested relatively high formation temperatures ($> 350^{\circ}\text{C}$) for the Bi-sulphosalt bearing assemblages at Toroioaga. This was based on S isotope distributions among pyrite-galena pairs and available experimental data on the $\text{PbS} - \text{Ag}_2\text{S} - \text{Bi}_2\text{S}_3 - \text{Sb}_2\text{S}_3$ system (CHANG et al., 1980). The latter suggests that significant levels of Sb can be built into lillianite, heyrovskýite or cosalite only at temperatures exceeding 350°C . More precise temperature constraints are difficult to give, given the paucity of relevant experimental studies, but comparison with investigations of comparable assemblages elsewhere favours temperatures in the $300 - 400^{\circ}\text{C}$ range.

The absence of native Bi in either deposit is in accord with high $f\text{S}_2$ in the hydrothermal solutions. In the Băiuț occurrence, the dominance of Ag-Bi-rich phases (gustavite, bismuthite and particularly, matildite) suggests relatively low Cu activity at the time of mineralisation. However, the presence of berryite and wittichenite in close association, the latter mineral clearly the latest in the paragenetic sequence, provides evidence for a rise in Cu/Ag of the fluid towards the end of the hydrothermal episode.

Modern paragenetic studies on Neogene vein systems in N.W. Romania are at a relatively early stage and many of the ideas expressed above are only working hypotheses although, in the case of the Toroioaga deposit, they are backed up by solid geochemical data (CHIOREANU, 1996). More quantitative data on all stages of mineralisation is urgently required. Mineral compositional data should be augmented by more precise geothermometric, and ideally also chronological data on distinct mineralising events and should also highlight the distribution of individual mineral assemblages across the vein systems. Furthermore, the presence and extent of Bi-sulphosalt bearing assemblages should be sought and confirmed in other deposits within the Neogene metallogenic area. In this regard, it is worth reporting that their presence in ores of the Nistru deposit has recently been confirmed (Fl. DAMIAN, unpubl. data).

The Bi-sulphosalts may also represent valuable indicators of gold mineralisation and the mineralogical and geochemical correlation between Bi and Au deserves to be tested further. The role of Ag-Bi-Pb sulphosalts, such as gustavite, as potentially important Ag-carriers should also be addressed. If these minerals are as widely distributed as is suggested from the samples investigated to date, they should probably not be ignored in ore processing considerations .

Most importantly, this type of study serves to illustrate how essential it is that future genetic models for the Neogene deposits in N.W. Romania encompass a wider spectrum of hydrothermal mineralisation styles beyond the classic vein style of mineralisation. Geochemistry and ore mineralogy can play a pivotal role in the development of those models. This process, involving the application of new analytical techniques and the re-evaluation of older data, is already leading to exciting developments in mineral exploration in the area as „non-traditional“ types of deposit are prospected for.

Acknowledgments

Special thanks are due to Gh. DAMIAN (University of Baia Mare) for providing the samples from Băiut-Văratec used in this study and for considerable discussion. The assistance of K.-P. KELBER with the photomicrographs and P. SPÄTHE for preparation of excellent polished sections is also gratefully appreciated. This investigation forms part of a project financed by the Deutsche Forschungsgemeinschaft.

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