STUDIA UNIVERSITATIS BABEŞ-BOLYAI, GEOLOGIA, XLVIII, 1, 2003, 45-54

COMPOSITIONAL DATA ON BOURNONITE – $CuPbSbS_3$ FROM VĂRATEC ORE DEPOSIT, BĂIUȚ MINE FIELD, EASTERN CARPATHIANS, ROMANIA

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ABSTRACT. Mineralogical features and compositional data on bournonite from epithermal vein deposit of Văratec, Băiuț mine field in the Baia Mare district, Romania are presented. Bournonite is disposed in quartz matrix or it is associated with chalcopyrite and tetrahedrite. SEM images demonstrate the absence of intergrown derivates with distinct compositions. Variations of chemical composition of bournonit have been recorded using electron probe microanalyses. The negative correlation of Sb – As contents indicates a substitution process between the two elements and the presence of limited solid solution towards seligmanite.

Keywords: epithermal, bournonite, mineral assemblage, chemical composition, solid solution, Sb-As substitution

INTRODUCTION

The Baia Mare district is famous for the presence of numerous species of sulphosalts. Different mineral deposits of the district are the type locality for several sulphosalts (Udubaşa et al., 1992): Baia Sprie for andorite ($PbAgSb_3S_6$) and semseyite ($Pb_9Sb_8S_{21}$), Herja for fizelyite ($Pb_{14}Ag_5Sb_{21}S_{48}$), Dealul Crucii for füllöpite ($Pb_3Sb_8S_{15}$). Alongside Pb-Sb sulphosalts, the mineralizations also contains abundant silver sulphosalts, copper sulphosalts and small quantities of Pb-Bi sulphosalts.

Among copper sulphosalts, different members of tetrahedrite-tennantite series ($(Cu,Ag)_{10}(Fe,Zn,Cu)_2(Sb,As)_4S_{13}$) were reported frequently in all mineral deposits of Baia Mare district. Bournonite ($CuPbSbS_3$) was mentioned in many mineral deposits (Ilba, Săsar, Herja, Baia Sprie, Cavnic, Băiuț), but in smaller quantities than tetrahedrite-tennantite. Although the bournonit is relatively abundant, it has not been studied in detail. Only mineralogical descriptions of the associations containing bournonite are available, and few data regarding the composition of bournonite from Herja (Cook & Damian, 1997), Baia Sprie (Tămaş & Bailly, 1999) and Breiner Băiuț (Damian & Costin, 1999 b).

In this paper, our aim is to present the mineralogical characteristics and compositional data of bournonite from Văratec ore deposit, Băiuț mine field. Our study is based on reflected light microscopy, scanning electron microscopy and electron probe microanalyses, performed on samples collected from recently open parts of the mine.

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GEOLOGICAL SETTING

The ore deposits in the Băiuț area (Borcoş & Gheorghiță, 1976) are situated in the easternmost part of the Gutâi Mountains, est of the city of Baia Mare (Fig. 1). Three main ore deposits (Breiner, Văratec, Cisma-Coasta Ursului) are recognized in this orefield. The Văratec deposit (Borcoş et al., 1977) consists of three major groups of veins along NE-SV, ENE-VSV, NNE-SSV oriented fractures, hosted within Pontian pyroxene andesites, pyroclastics and sedimentary rocks (Fig. 2). These formations are pierced by subvolcanic porphyry dioritic bodies. The veins have lengths of 80-1200 m, thickness about 5-6 m and depths more than 350 m.

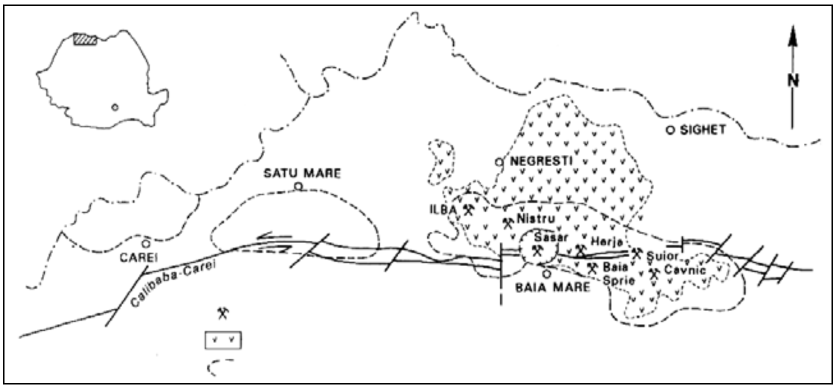

Fig. 1. *Simplified geological map of the Baia Mare district, showing the location of Băiuț area (after Bailly et al., 1998).*

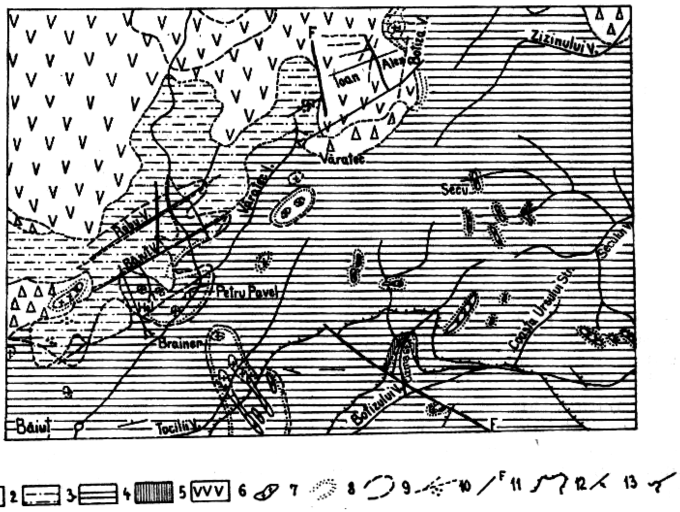

Fig. 2. *Geological sketch map of the Băiuț mine field (from Borcoş & Gheorghiță, 1976).* *1, Quaternary; 2, Neogene dedimentary rocks; 3, Paleogene sedimentary rocks; 4, Upper Cretaceous sedimentary rocks; 5, Pontian pyroxene andesite; 6, Pontian pyroxene ± biotite andesite body; 7, thermal metamorphism; 8, hydrometasomatic metamorphism; 9, vein and impregnation; 10, fault; 11, overthrust; 12, position of beds; 13, gallery.*

The epithermal mineralization is characterized by the geochemical signature Pb-Zn-Cu-Au-Ag, with significant contents of Co, Ni, V, Cr, Ti, Sb, As, Bi, and W. Borcoş et al. (1977) recognized a monoascending character of mineralization, and the presence of four metallic and gangue mineral associations: (1) quartz + iron oxides, (2) quartz + iron oxides + pyrite ± chalcopyrite ± siderite, (3) quartz + iron oxides + sulphides + adularia + siderite + kaolinite, (4) quartz + carbonates + marcasite. The homogenisation temperatures of the primary inclusions from quartz crystals allowed to estimate an interval from 230°C to 360°C for the temperature of mineralization (Borcoş & Gheorghiță, 1976; Manilici & Kalmar, 1992).

Detailed mineralogical data of Văratec Băiuț mineral deposit, especially on different species of sulphosalts, have recently been presented by Cook (1998), Damian & Costin (1999 a) and Damian et al. (2000).

MINERALOGICAL FEATURES

Mineralogical analyses have been made on samples representing fragments of banded ore, collected from Alexandru vein and Botiza IV vein. This banded texture resulted from rhythmic deposition of different types of sulphides bands and gangue minerals bands. The thickness of the bands ranges from few mm up to 2-3 cm.

Polished sections made from this type of ore, have been investigated in detail by reflected light microscope. The mineral assemblage characteristic for these samples is formed by main minerals such as pyrite, chalcopyrite, sphalerite, galena, smaller amounts of Cu sulphosalts (tetrahedrite and bournonite), and gangue minerals (quartz and carbonates). Textural evidences and mineralogical compositions indicate that the samples belong to mineral association nr. 3.

Pyrite occurs as large (up to 1 mm) euhedral to subhedral grains in quartz and small (50-100 μm) rounded inclusions in chalcopyrite. Large euhedral crystals of galena are associated with smaller anhedral grains of sphalerite. Subhedral to rounded grains of sphalerite present frequently oriented chalcopyrite inclusions (chalcopyrite disease). Coarse-grained chalcopyrite enclose the earliest sulphides and contains sphalerite inclusions. Tetrahedrite forms more or less wider rims on chalcopyrite or it is intergrown with subhedral chalcopyrite crystals.

The ore microscopy revealed the presence of coarse grains of bournonite (up to 200 μm in length) enclosed in the gangue matrix or disposed at the pyrite crystals boundaries (Plate I, Fig. 1). Small grains of bournonite (about 30 μm in length) occur as inclusions in chalcopyrite or they are disposed on the rim of tetrahedrite (Plate I, Fig. 2). Bournonite has a clear greyish colour with a distinct bluish green tint and a medium reflectivity. Most of the bournonite grains show its characteristic polysynthetic twinning – "parquet-twinning" type (Ixer & Duller, 1998). The weak bireflectance and the distinct anisotropy are visible.

CHEMICAL COMPOSITION

In order to determine the chemical composition of bournonite, scanning electron microscopy (SEM) investigations and electron probe microanalyses (EPMA) were performed. An electron microscope HITACHI S-2500 (Nancy I University, Microanalyses Centre) was used for acquisition of energy dispersive X-ray spectra and backscattered electrons images. The electron probe microanalyses were carried out on the CAMECA SX-50 instrument (Nancy I University, Microanalyses Centre). The following standards and radiations were used: $CuFeS_2$ (Cu-Kα, Fe-Kα, S-Kα), ZnS (Zn-Kα), AsGa (As-Lα), PbSe (Se-Lα), metallic Ag (Ag-Lα), Sb_2S_3 (Sb-Lα), PbS (Pb-Mα), metallic Bi (Bi-Mα). An accelerating voltage of 20 kV and a beam current of 10 nA for S, Cu, As, Sb, Pb, Bi, respectively 30 nA for Fe, Zn, Se, Ag were used. Minimum detection limits are ca. 0.1 wt. % for all elements. The errors of the measurements are: S ±0.5 wt. %; Cu ±0.25 wt. %; As ±0.12 wt. %; Sb ±0.5 wt. %; Pb ±1.0 wt. %; Bi ±1.4 wt. %; Fe ±0.07 wt. %; Zn ±0.18 wt. %; Se 0.08 wt. %; Ag ±0.24 wt. %.

The energy dispersive X-ray spectra (Fig. 3) collected during SEM analyses revealed the presence of Pb, Cu, Sb, As, and S. The backscattered electrons images (Plate II, Figs. 1,2) showed the homogeneous character of the bournonite grains (i.e. any part of the grain has the same value of average atomic number) and the absence of intergrown derivates with distinct compositions.

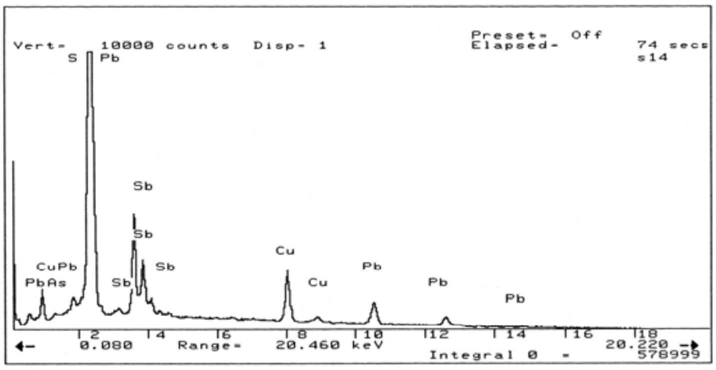

Fig. 3. *Energy dispersive X-ray spectra of bournonite.*

Electron probe microanalyses indicate small variations of bournonite chemical composition (Table 1). We note the relatively constant content of S (19.2-20.1 wt. %). The highest values of Cu content and the presence of small amounts of Fe are specific to the bournonite grains enclosed in chalcopyrite and associated with tetrahedrite (Plate I, Fig. 2). These grains are further characterized by more variable and smaller amounts of Pb than the grains disposed in gangue matrix.

The Sb content ranges between 21.3 wt. % and 25.1 wt. %. In all samples, small amounts of As were detected (0.8-2.9 wt. %). Higher As content tend to correlate negatively with lower Sb content, indicating a substitution process between the two elements.

Table 1

Electron probe microanalyses (in wt. %) of bournonite.

Points	S	Fe	Cu	As	Sb	Pb	Total
650-1	20.0	0.7	14.4	0.9	24.6	40.0	100.6
650-2	20.0	0.7	14.9	0.8	24.7	38.4	99.5
650-3	19.5	0.5	14.2	0.8	24.9	40.3	100.2
650-4	19.5	0.6	14.1	1.9	24.1	39.8	100
650-5	19.8	0.6	14.6	2.9	21.3	41.3	100.5
651-1	19.5	0	13.0	1.2	23.5	42.6	99.8
651-2	19.2	0	13.0	1.0	25.1	41.7	100
651-3	19.2	0	12.9	1.0	24.9	41.3	99.3
651-4	19.6	0	12.8	1.1	24.9	41.7	100.1
651-5	19.2	0	13.1	2.4	22.0	42.7	99.4

Table 2

Structural formula of bournonite to S=3.

Points	Formula
650-1	$Cu_{1.09}Pb_{0.93}(Sb_{0.97}As_{0.06})_{1.03}S_3$
650-2	$Cu_{1.13}Pb_{0.89}(Sb_{0.97}As_{0.05})_{1.02}S_3$
650-3	$Cu_{1.10}Pb_{0.96}(Sb_{1.01}As_{0.05})_{1.07}S_3$
650-4	$Cu_{1.10}Pb_{0.95}(Sb_{0.98}As_{0.12})_{1.10}S_3$
650-5	$Cu_{1.12}Pb_{0.97}(Sb_{0.85}As_{0.19})_{1.04}S_3$
651-1	$Cu_{1.01}Pb_{1.01}(Sb_{0.95}As_{0.08})_{1.03}S_3$
651-2	$Cu_{1.03}Pb_{1.01}(Sb_{1.03}As_{0.06})_{1.09}S_3$
651-3	$Cu_{1.02}Pb_{1.00}(Sb_{1.03}As_{0.06})_{1.09}S_3$
651-4	$Cu_{0.99}Pb_{0.99}(Sb_{1.00}As_{0.07})_{1.07}S_3$
651-5	$Cu_{1.03}Pb_{1.03}(Sb_{0.91}As_{0.16})_{1.07}S_3$

The structural formula of bournonite from all analyses calculated to 3 S atoms are given in the Table 2. Formula very close to stoichiometry characterize the larger grains of bournonite which occur enclosed in gangue minerals. The analyses of the grains associated with chalcopyrite and tetrahedrite show a slight excess in Cu over 1 atom per formula unit and a slight deficiency in Pb below 1 atom per formula unit. An excess in (Sb+As) beyond 1 atom per formula unit is observed for all analyses.

DISCUSSION

Bournonite – $CuPbSbS_3$ belongs to bournonite isoseries from Cu(Ag)-rich sulphosalts group (Moëlo, 1997); other minerals related to this isoseries are seligmanite – $CuPbAsS_3$ and soucekite – $CuPbBi(S,Se)_3$. The mineral structures of the phases classified in this isoseries are “derived” by 2 Å shear from aikinite $CuPbBiS_3$ (Makovicky, 1989). Despite his presence in many types of mineral deposits, only few data about crystal structure and chemical compositions of bournonite are available. Wu & Birnie (1977) postulated that As substitutes for Sb in bournonite to at least an As/(As+Sb) value (atomic) = 0.54 and they suspected the existence of a complete solid solution between bournonite and seligmanite.

Chemical compositions of bournonite from Văratec ore deposit are similar with those of bournonite from Breiner ore deposit, located in the same mine field (Damian & Costin, 1999 b). Very limited solid solutions towards the As end-member, seligmanite were noted for both occurrences, but some analyses from Breiner Băiuț has greater values of As (Fig. 4). Arsenic richer members of bournonite were reported by Tămaş & Bailly (1999) in samples collected from Baia Sprie mineral deposit (Fig. 4), indicating a more extended solid solution between bournonite and seligmanite. Cook & Damian (1997) presented compositional data of the bournonite from Herja mineral deposit with typical low content of As (Fig. 4).

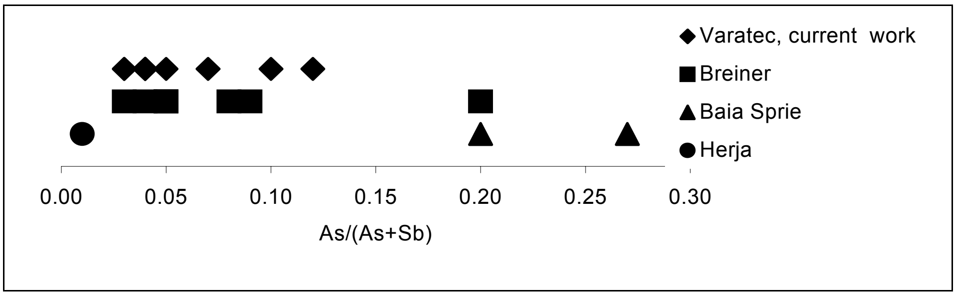

Fig. 4. *Plot of As/(As+Sb) values for bournonite from different mineral deposits of Baia Mare district.*

CONCLUSIONS

Bournonite it's not a major mineralogical component of Văratec ore deposit, but alongside the tetrahedrite, they represent the mains Cu sulphosalts. Microscopic analyses show the association of bournonite grains with minerals related to third stage of paragenetic sequence. Based on mineralogical evidence, we consider that the deposition of bournonite took place towards the end of this stage, to a temperature around 280 – 260°C (Borcoş & Gheorghiță, 1976).

Electron probe microanalyses demonstrate the presence of As-bearing bournonite in Văratec ore deposit. Similar chemical compositions were reported in Breiner ore deposit, suggesting similarities of ore fluids responsible for mineral assemblages formation. As-richer members are specific for Baia Sprie ore deposit, while members with very low As content are present in Herja mineralizations.

This paper represents a first stage in the study of bournonite composition in the Văratec ore deposit. In order to demonstrate the metalogenetic importance of its occurrence in this mineral deposit, further microscopic analyses and compositional data are required.

Acknowledgements. Special thanks are due to Prof. Jean Claude Samama (Ecole Nationale Supérieure de Géologie Nancy, Institut National Polytechnique Lorrain) for opportunity to perform the SEM and electron probe microanalyses.

REFERENCES

Bailly, L., Milesi, J-P, Leroy, J. & Marcoux, E. 1998, Les minéralizations épithermales à Au-Cu-Zn-Sb du district de Baia Mare (Nord Roumanie): nouvelles données minéralogiques et microthermométriques. C. R. Acad. Sci. Paris, série II, tome 327, N° 6, fascicule a, pp. 385 – 390.

Borcoş, M. & Gheorghiță, I. 1976, Neogene hydrothermal ore deposits in the volcanic Gutâi Mountains. IV. Băiuț - Văratec - Botiza metallogenic field. *Rev. Roum. Geol., Geophys. et Geogr., Geologie*, 20, 2, pp. 197 – 209.

Borcoş, M., Gheorghiță, I., Mândroiu, V. & Volanschi, E. 1977, Considerații privind procesele metalogenetice desfăşurate în extremitatea estică a munților Gutâi (zăcământul Băiuț - Văratec). *Studii tehnice şi economice*, Geologie economică, seria A, 11, pp. 53 – 96.

Cook, N. J. & Damian, G. Ş. 1997, New data on "Plumosite" and other sulphosalt minerals from Herja hydrothermal ore deposit, Baia Mare district, Romania. *Geologica Carpatica*, 48, 6, pp. 387 – 399.

Cook, N. J. 1998, Bismuth sulfphosalts from hydrothermal vein deposits of Neogene age, N.W. Romania. *Mitt. Österr. Miner. Ges.*, 143, pp. 19 – 39.

Damian, F., Damian G. & Costin, D. 2000, Bismuth sulphosalts in the Neogene hydrothermal vein ores from the Baia Mare Ore District. *Acta Mineralogica – Petrographica*, Tomus XLI, Suppl. (Abstracts), pp. 27, Szeged, Hungaria.

Damian, G. & Costin, D. 1999 a, New data about the bismuth sulphosalts from the hydrothermal mineralisations from Văratec-Băiuț, Baia Mare District. *Rom. J. of Mineralogy*, Vol. 79, Suppl. 1 (Abstract volume), pp. 28, Bucureşti.

Damian, G. & Costin, D. 1999 b, Tetrahedrite – bournonite in Breiner – Băiuț mineralization (Gutâi Mts., Eastern Carpathians). *Studia Universitatis Babeş – Bolyai, Geologia*, XLIV, 1, pp. 137 – 149.

Ixer, R. A. & Duller, P. R. 1998, *Virtual Atlas of Opaque and Ore Minerals in their Associations*. The Society for Mining, Metallurgy, and Exploration (SME), http://www.smenet.org/opaque-ore/.

Makovicky, E. 1989, Modular classification of sulphosalts – current status. Definition and application of homologous series. *N. Jb. Miner. Abh.*, 160, pp. 269 – 297.

Manilici, V. & Kalmar, I. 1992, Asupra compoziției mineralogice şi a temperaturilor de cristalizare a mineralelor din zăcămintele Băiuț, Văratec şi Cizma - Coasta Ursului. *St. cerc. Geologie*, 37, pp. 17 – 28.

Moëlo, Y. 1997, Sulfosalt systematic. *Commission on Ore Mineralogy (I.M.A.), Short Course on Ore and Environmental Mineralogy,* IGM Porto, 15 p.

Tămaş, C. G. & Bailly, L. 1999, Microprobe data regarding the bournonite – $PbCuSbS_3$ from Baia de Arieş, Apuseni Mts, Romania. *Studia Universitatis Babeş – Bolyai, Geologia*, XLIV, 1, pp. 23 – 30.

Udubaşa, G., Ilinca, G., Marincea, Ş., Sabău, S. & Rădan, Ş. 1992, Minerals in Romania: the state of the art 1991. *Rom. J. Mineralogy*, 75, pp. 1 – 51.

Wu, I.J. & Birnie, R.W. 1977, The bournonite – seligmanite solid solution. *Am. Mineral.*, 62, 1097 – 1100.

Plate I. Photomicrographs in plane polarized reflected light

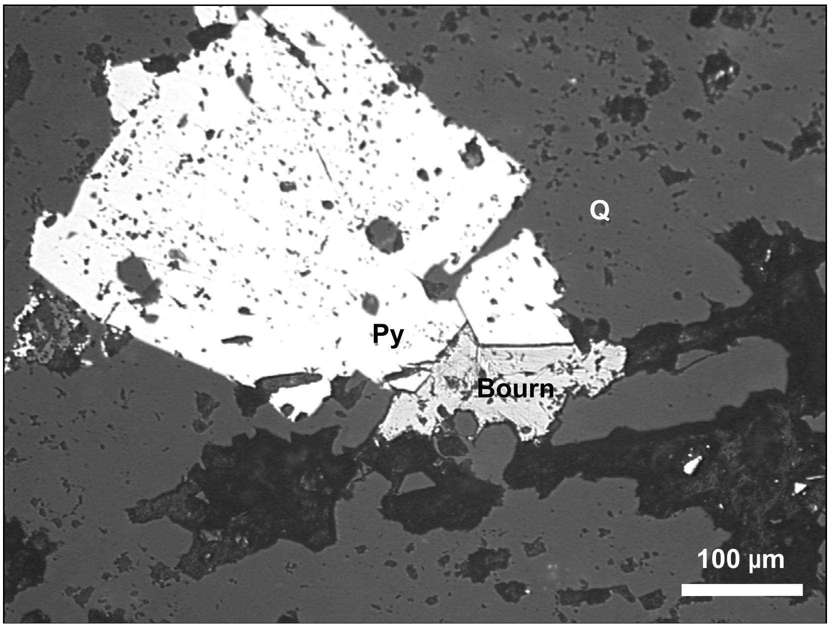

Fig. 1. *Bournonite grain (Bourn) and pyrite crystals (Py) in quartz matrix (Q).*

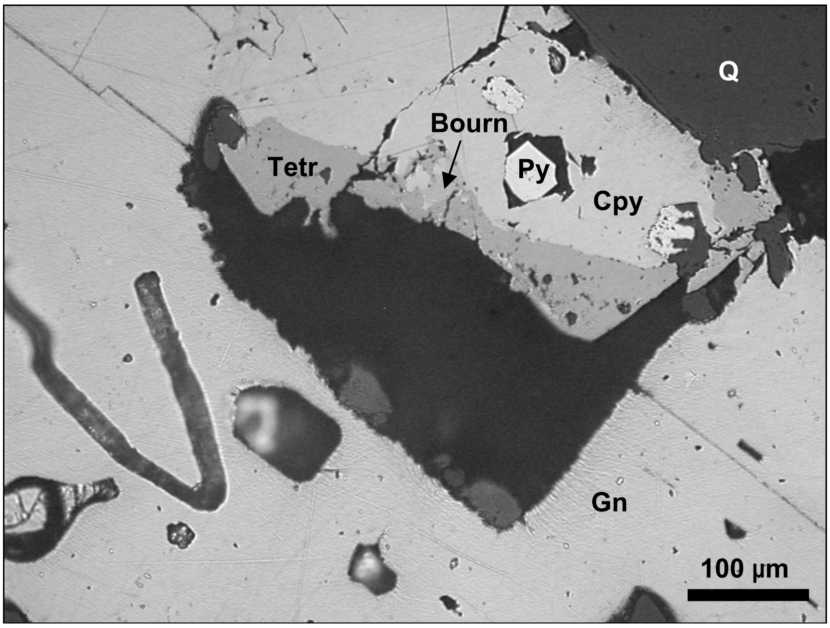

Fig. 2. *Inclusions of bournonite (Bourn) in chalcopyrite (Cpy) and tetrahedrite (Tetr). Py-pyrite, Gn-galena, Q-quartz.*

Plate II Backscattered electron images

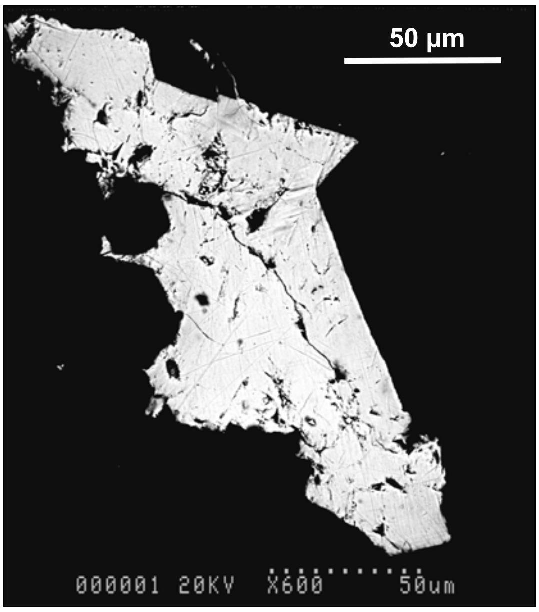

Fig. 1. *Bournonite showing homogeneous chemical composition.*

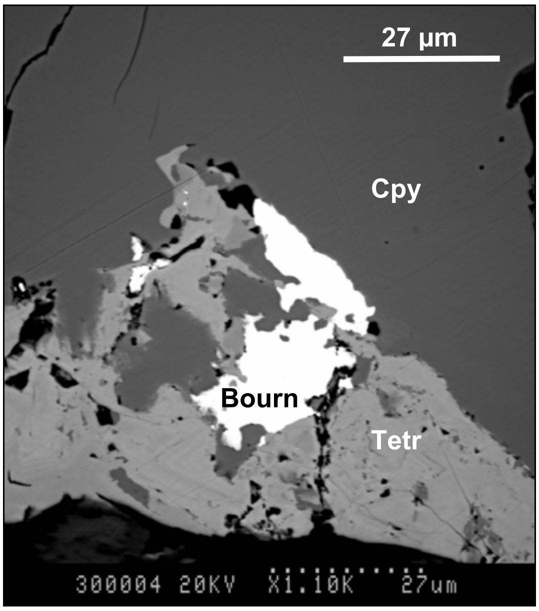

Fig. 2. *Bournonite (Bourn) associated with chalcopyrite (Cpy) and tetrahedrite (Tetr).*