SILVER SULFOTELLURIDES AND OTHER Te-SULFOSALTS IN ALABANDITE-BEARING VEINS FROM SĂCĂRÂMB Au-Ag-Te ORE DEPOSIT, METALIFERI MOUNTAINS, ROMANIA

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Abstract. This paper addresses Ag-sulfotellurides and Te-sulfosalts occurring in Săcărâmb epithermal Au-Ag-Te ore deposit, Metaliferi Mountains, Romania. Cervelleite-like minerals were identified in close association with galena, sylvanite, bournonite and native tellurium. It is optically isotropic, it has a blue-grey colour and a chemical composition of $Ag_{2.1}Te_1S_{2.8}$ (stoichiometric Ag_2TeS_3 from EDS analyses of three grains). Benleonardite associated with tennantite, bournonite, galena and jordanite was found in two samples, with the composition $Ag_{16.1}(Sb_{0.9}As_{1.5})_{2.4}S_{7.3}Te_{3.3}$ The chemical composition of one grain shows a high concentration of Cu with a calculated empyrical formula of $(Ag_{12}Au_{0.3}Cu_{3.8})_{15.9}(As_{0.3}Sb_{1.4})_{1.7}Te_{9.2}S_{2.2,}$ which indicates a substitution between Ag and Cu. Two goldfieldite grains were found in association with bournonite, galena and tellurides. One grain has the chemical composition $Cu_{10.2}Ag_{1.5}Sb_{1.3}As_{0.6}Te_{1.8}S_{11.5}$ and the second goldfieldite is Bi-bearing with the chemical composition $Cu_{11.5}Ag_{0.2}Bi_{0.8}Te_{2.55}S_{12.}$ Sulfotellurides are an indicator for low $f Te_{2,}$ this indicates that at Săcărâmb the Te/S ratio varied in the alabandite rich veins. The Ag-Te-S system is still poorly studied despite it's significant scientific and economic importance.

Keywords: sulfotellurides, sulfosalts, alabandite, cervelleite, benleonardite, goldfieldite, Săcărâmb

Introduction

Natural compounds of silver containing both sulfur and tellurium are known as two main groups: cervelleite-like compounds and sulfosalts like benleonardite $Ag_8(Sb,As)Te_2S_3$. Cervelleite was found in Romania by Cook and Ciobanu (2003) at Băița Bihor and Ocna de Fier skarn deposits. Te bearing sulfosalts are more widespread in the Gold Quadrilater. The most important Te-sulfosalt is nagyagite discovered at Săcărâmb Au-Ag-Te ore deposit. Other Te-sulfosalts found at Săcărâmb are: museumite (Bindi and Cipriani, 2004), aleksite (Shimizu, 2003), tetradymite (Posepny, 1868) and goldfieldite (Udubasa et al., 2002). Recently, at Roșia Montană Au-Ag deposit were discovered two Te-sulfosalts: alburnite-*locus tipicus* (Tămaș et al., 2014) and Ge-bearing benleonardite (Sabău et al., 2016). In this study, it is reported a new occurrence of benleonardite, Cu-Au bearing benleonardite, cervelleite, Bi-bearing goldfieldite and an unknown cervelleite-like minerals.

Geological Setting

The Săcărâmb Au-Ag-Te ore deposit is located in the Metaliferi Mountains in Romania.;it is the largest telluride mineral accumulation in Europe with a total of 14 minerals containing Te, Au and Ag. The ore mineralization has a Miocene-Pliocene age (14.7-7.4 Ma) and is related to the Neocene volcanic activity in the region, being part of the Alpine-Carpathian-Dinaride area (Udubașa et al. 1992). The ore mineralization is of hydrothermal origin, Săcărâmb is classified as a low-sulphidation Au-Ag-Te epithermal deposit (Ciobanu et al. 2005). The host of the mineralization is an andesitic neck with about 230 veins in a 1000 m^2 area with a 600 m vertical extent. The vein fields include four vein groups perpendicularly oriented, disposed as: Magdalena-Carolina and Nepomuc groups, having a NE-SW direction while Longhin-Antelonghin and Ertzbau groups have a NW-SE orientation (Ianovici et al. 1976) The majority of the veins are rich in Au-Ag tellurides. What constitutes its uniqueness from other Au-Ag-Te deposits is the widespread presence of alabandite.

Materials and methods

Over 50 polished sections were studied from ore samples found in two waste dumps (Sector 2 and Sector 3). Microscopic observations were carried out on a Leitz Wetzlar reflected light microscope and the images were taken using a PANPHOT Leitz Wetzlar reflected light microscope equipped with a Nikon Eclipse E-400 camera. Chemical analyses and SEM images were realized with a Zeiss Merlin GEMINI II SEM-EDS spectrometer, with a working regime: accelerating voltage ranging between 15-20 kV, beam current ranging between 1-2 nA, background time 20 s and a beam diameter that varies depending of the scale.

Telluride assemblages

The first association observed was in the form of: krennerite, hessite (Ag_2Te) and nagyagite inclusions in alabandite however in some cases sulfosalts were present as well (Fig. 1). The second type of association identified was the presence of native tellurium, sylvanite hessite and krennerite in the secondary rhodochrosite veins that crosscut the massive alabandite (Fig. 1). In this occurrence tellurides are usually associated with these sulfosalts: tetrahedrite, jordanite ($Pb_{14}(As,Sb)_6S_{23}$), dufrenoysite ($Pb_2As_2S_5$) and bournonite. A third assemblage was discovered with native tellurium, sylvanite, hessite, nagyagite, goldfieldite, benleonardite and an unknown silver sulfotelluride (Fig 1). All of the tellurides from this assemblage are included in a sulfosalt-sulfide association comprised of bournonite, tetrahedrite-tennantite, galena, sphalerite and alabandite.

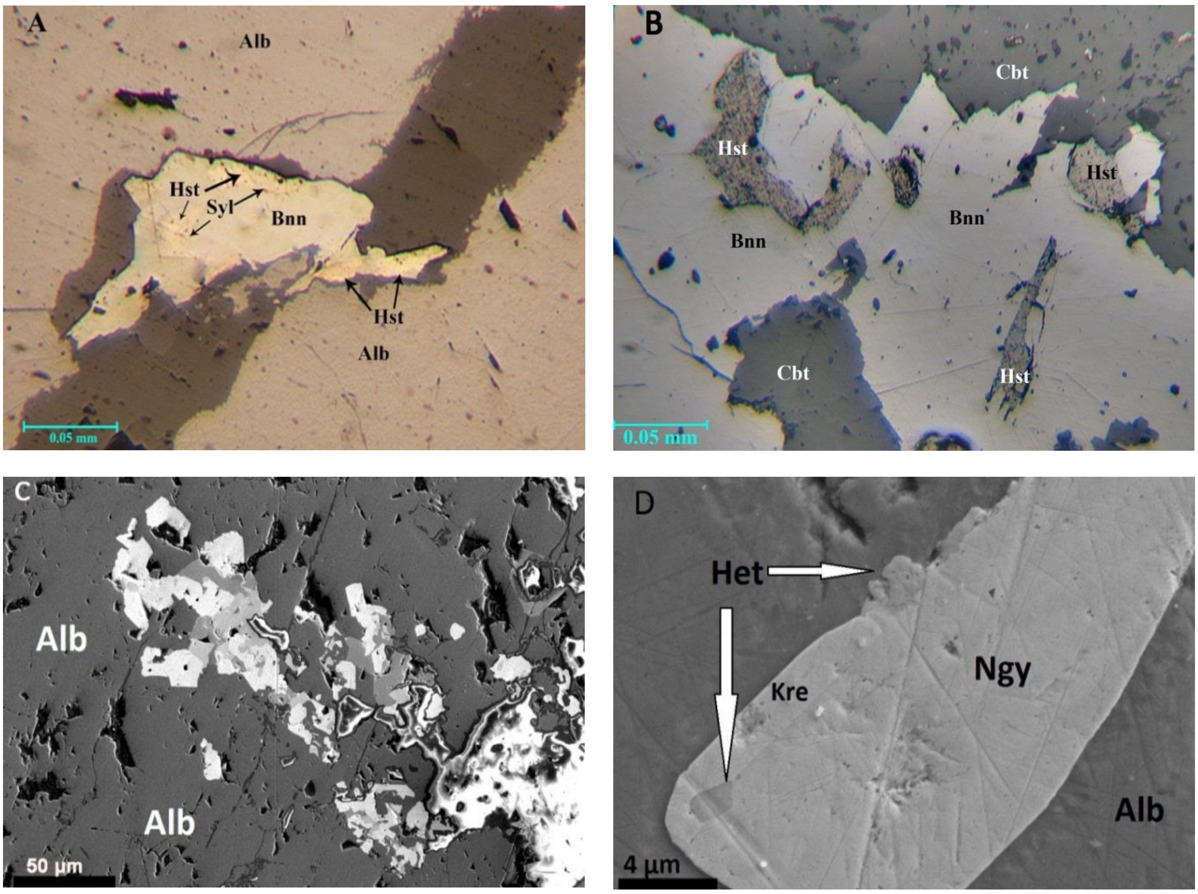

Fig. 1. Examples of tellurides and sulfosalt associations from Săcărâmb: A) association of hessite and sylvanite in bournonite with alabandite (parallel polarized light) B) hessite crystals included in bournonite (parallel polarized light) C) SEM image of a complex association of galena-sulfosalts-sulfotellurides and tellurides included in alabandite D) SEM image of nagyagite crystal with krennerite inclusion and on the margin heteromorphite $Pb_7Sb_8S_{19}$, all included in alabandite. Hst- hessite, Syl- sylvanite, Ngy- nagyagite, Alb- alabandite, Bnn- bournonite, Kre-krennerite, Het-heteromorphite and Cbt- carbonate.

Sulfotellurides

Cervelleite-like minerals were found in 3 polished sections. The grain size of this mineral phases varies between 1 to 10 µm. Under the microscope, these phases are isotropic and bluish grey. The Ag sulfotellurides coexist with hessite and sylvanite, presenting a replacement texture (Fig. 2). The tellurides and sulfotellurides appear as inclusions in tetrahedrite and bournonite associations, or in carbonate veins. The chemical compositions of cervelleite is presented in Table 1. After the calculation based on 6 total number of atoms, the empirical formula of Săcărâmb cervelleite is ($Ag_{3.8}Te_{0.6}S_{1.6}$). The unknown Ag-sulfotellurides have an empirical formula of ($Ag_{2.1}Te_{1}S_{2.8}$) calculated based on 6 total number of atoms, it is possible that this phase has a simplified formula of Ag_2TeS_3.

Table 1. Representative EDS chemical analyses of cervelleite and cervelleite-like minerals from Săcărâmb. The analyses were corrected to 100Wt% by the AZtecEnergy EDS analysis software.

Element Wt%	S3K2 cervelleite	S3K4 Unknown mineral	S3K4 Unknown mineral	S3K2 Unknown mineral
Ag	76.53	51.52	50.89	57.54
S	9.66	20.31	20.61	17.90
Te	13.81	28.17	28.5	24.57
Total	100	100	100	100
At%	Chemical formula based on sum of 6 atoms			
Ag	3.80	2.15	2.12	2.49
S	1.61	2.85	2.88	2.60
Te	0.58	0.99	1.00	0.90

Benleonardite, $Ag_8(Sb,As)Te_2S_3$, was identified in two polished sections in association with bournonite, jordanite, tetrahedrite and galena (Fig. 2). It has a bluish grey colour and a moderate anisotropy. The empirical formula was calculated using 29 atoms per formula unit: $Ag_{16.1}(Sb_{0.9}As_{1.5})_2S_{7.3}Te_{3.3}$. To calculate the empirical formula, it was used the chemical data of benleonardite from Bindi et al. (2015), in which benleonardite is considered a member of the pearceite-polybasite group. In the material from Săcărâmb, it was discovered a Cu-bearing benleonardite which indicates a clear substitution of Ag by Cu, indicating the possibility of a Cu homologue of benleonardite. This hypothesis is sustained by the new data regarding the crystal-chemical formula of benleonardite ($Ag_{15}Cu(Sb,As)_2S_7Te_4$) and the membership in the pearceite-polybasite group Bindi et al. (2015). Cu enrichment of benleonardite relates to the association with tennantite.

Goldfieldite appears in two polished sections in association with bournonite, galena, jordanite and tellurides (Fig. 2). The chemical composition of Săcărâmb goldfieldite is varied (Table 2), in one probe goldfieldite is rich in Ag, with an empirical formula of $Cu_{11}Ag_{1.7}Sb_{1.4}As_{0.6}Te_2S_{12.3.}$ The calculation was based on 29 atoms, for minerals with 2 or less Te a.p.f.u. after the chemical study of golfieldite by Trudu and Knittel (1998). The second goldfieldite is Bi-bearing with concentrations above 10 Wt%. The calculated empirical formula for Bi-bearing goldfieldite is $Cu_{11.5}Ag_{0.2}Bi_{0.8}Te_{2.55}S_{12}$ (based on 27 atoms). It is the first known presence of Bi-bearing goldfieldite at Săcărâmb ore deposit. Bismuth is known to be found in tennantite and tetrahedrite commonly known as „annivite” and it has the same position as As and Sb in the crystal-chemical formula Gołębiowska et al. (2012).

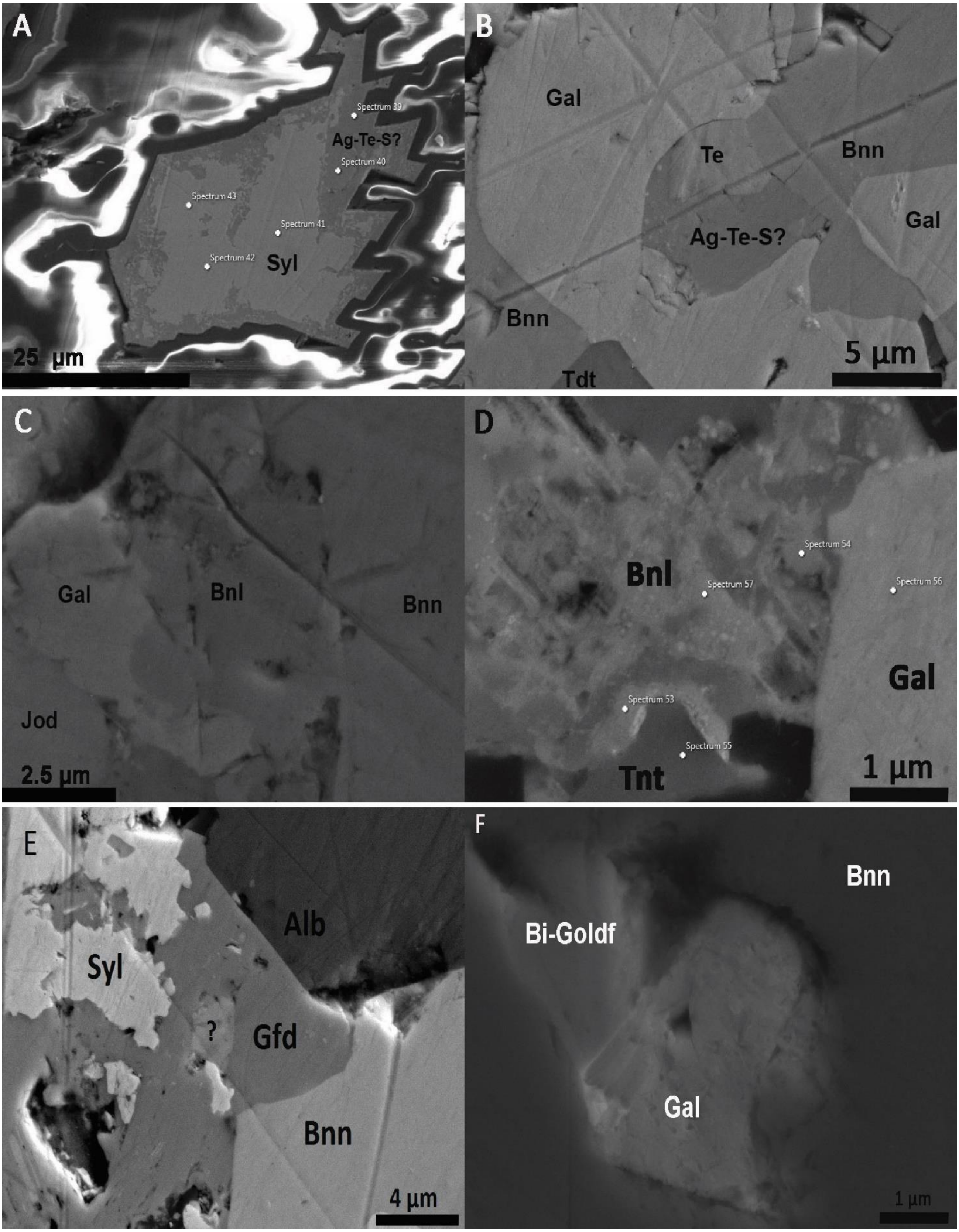

Fig. 2. SEM images of sulfotellurides and Te-bearing sulfosalts found at Săcărâmb: A- unknown silver sulfotelluride replacing a sylvanite crystal, B –silver sulfotelluride with native tellurium, galena, tetrahedrite and bournonite, C- benleonardite crystal between galena and bournonite in association with jordanite, D- benleonardite replacing tennantite, E- sylvanite with an unidentified sulfotelluride in goldfieldite, associated with bournonite and alabandite F – inclusions of galena bismuth-bearing goldfieldite in bournonite. Alb-alabandite, Syl-sylvanite, Gfd-goldfieldite, Bi-Goldf- bismuth bearing goldfieldite, Bnl-benleonardite, Bnn-bournonite, Jod-jordanite, Tnt-tennantite, Te-native tellurium Ag-Te-S?- unknown sulfotelluride

Table 2. Representative EDS chemical analyses of benleonardite and goldfieldite from Săcărâmb. The analyses were corrected to 100Wt% by the AZtecEnergy EDS analysis software.

Element Wt%	S3K2	S3K2	S3K4	S3K4	S3C1	S3C1	S3K4	S3K4
benleonardite			Cu-benleonardite		Bi-goldfieldite		Ag-goldfieldite	
Au	0	0	3.61	1.68	-	-	-	-
Ag	66.87	66.67	55.94	53.33	1.44	1.42	10.02	10.02
Cu	0	0	7.41	13.1	45.05	45.17	40.22	40.74
Sb	4.15	3.83	8.55	6.04	-	-	10.66	9.14
As	4.31	3.99	0	2.28	-	-	2.87	2.59
S	9.05	8.9	11.6	11.72	23.41	23.69	22.93	22.60
Te	15.62	16.62	12.89	11.83	19.71	19.61	13.29	14.91
Bi	-	-	-	-	10.38	10.1	-	-
Total	100	100	100	100	100	100	100	100
At%	sum of 29 atoms				sum of 27 atoms		sum of 29 atoms	
Au			0.4	0.2	-	-	-	-
Ag	16.1	16.1	12.7	11.5	0.22	0.2	1.61	1.62
Cu	0	0	2.8	4.8	11.5	11.5	10.98	11.16
Sb	0.9	0.8	1.7	1.2	-	-	1.52	1.3
As	1.5	1.4	0.0	0.7	-	-	0.66	0.6
S	7.3	7.3	8.8	8.5	11.9	12	12.4	12.3
Te	3.2	3.4	2.5	2.2	2.5	2.5	1.8	2
Bi	-	-	-	-	0.8	0.8	-	-

Conclusions

An interesting fact about these associations is that Au-tellurides in alabandite are much rarer than Ag-tellurides and native tellurium, furthermore an abundance of Au-tellurides are found in the secondary carbonate veins with sulfosalts. This indicates that the first telluride phase was rich in Ag and Pb and the second one that came with sulfosalts was rich in As, Sb and Au. The discovery of Bi-goldfieldite, indicates the existence of another member of the tetrahedrite group and a possible series between goldfieldite and a Bi homologue. Formation of the sulfotellurides indicates relative low $f\ Te_2$ in some areas of the hydrothermal system. Numerous finds of unusual and poorly characterized telluride compositions in low-sulfidation epithermal veins reveal the still incomplete knowledge of the Ag-Te-S system and consequently deficient exploration and economic significance.

Acknowledgments

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