Au-Ag-Te-Se deposits

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Mineral assemblages from the vein salband at Sacarimb, Golden Quadrilateral, Romania: II. Tellurides

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Abstract: Bismuth tellurides (tetradymite, tellurobismuthite and buckhornite) are identified in salband mineralization at Sacarimb. Nagyagite is ubiquitously present, whereas other Au(Ag)-tellurides (sylvanite, petzite, hessite, stützite) and native tellurium are only locally abundant. Tellurides are mainly hosted within Sb-As-sulphosalts, textures indicate co-precipitation of sulphosalts and tellurides. A second population of the same Au(Ag)-tellurides, but now also including Bi-tellurides, relates to fluids introduced during vein reopening. The observations indicate that tellurides account for much of the 1-2g/t gold in the salband ore.

Key words: Sacarimb, Romania, Epithermal Au-Te mineralization, Bi-tellurides

Introduction

Sacarimb (formerly Nagyag) is the type locality for several telluride species, including nagyagite, krennerite, petzite and stützite. The deposit is known for its diverse telluride mineralogy. Pilsenite, Bi_4Te_3 and aleksite, $PbBi_2Te_2S_2$ have been reported from the deposit (Simon and Alderton, 1995; Shimizu et al., 1999), but the presence of Bi-tellurides has otherwise not been reported until now.

Tellurides are known from 19 of the 64 deposits/prospects within the Neogene Golden Quadrilateral (GQ), Romania, but Sacarimb is the only true Au-telluride deposit in this magmatic province of calc-alkaline signature (Cook et al., 2004). As in other epithermal Au-Ag deposits, some 50% of the Au at Sacarimb was contained as tellurides, but contrasting with more typical cases, the main component in

the Sacarimb ore was nagyagite, a Au-telluride with a highly complex chemistry: $[(Pb_3(Pb,Sb, As)_3)S_6][(Au,Te_2)_3].$

Mineralization is formed in a lowsulphidation epithermal system that comprises some 230 veins centred upon a volcanic neck (CN; Fig. 1). The bulk of telluride-rich ore was exploited from an intermediate interval of the veins, between Carol and Ferdinand levels (e.g., Brana, 1958), that have a total vertical extent of some 600m.

Characterisation of the main telluride ore representative for this interval was given in a previous contribution (Ciobanu et al., 2004). The sample suite (Table 1 of Ciobanu et al., this volume) is representative of the vein margins across the main mineralised interval and upper levels of the system (Fig. 1). The salband of main veins in the upper part of the deposit (from Bernat down to the Ferdinand

level) was recently investigated by Deva Gold S.A., who defined a 10 Mt ore reserve with1-2 g/t Au. The salband ores reported here are representative of this reserve.



Fig. 1. Geological sketch map of the Sacarimb area, after Udubasa et al. (1992)

Sample description

Characterisation of the main mineral associations in the present sample suite, i.e., sulphides and sulphosalts, is given in Ciobanu et al. (this volume). Here, we present only the data pertaining to the tellurides that were found in 9 out of the 11 studied samples. Nagyagite is the main telluride, and is present in all samples with the exception of S7.11. Sylvanite, petzite, hessite, stützite, tetradymite and telluro bismuthite are found in only some of the samples. Coloradoite, buckhornite and two Pb-Bi-Te-S phases, saddlebackite $(Pb_3Bi_2Te_2S_3)$ and Pb₃BiTeS₄ were rarely observed; native tellurium was also identified in two cases.

The two Bi-tellurides, tetradymite and tellurobismuthite, are observed for the first time at Sacarimb. They are found in particular abundance in one sample (7.5) that also contains the majority of the Bi-sulphosalts (Ciobanu et al., this volume). This sample includes also relatively abundant nagyagite. The sample differs from the others in the fact

that the association consists chiefly of pyrite and fahlore. Although a second sample (7.9) has a similar composition and also includes minor Bi-sulphosalts, no Bi-tellurides were identified. However, this second sample is the richest and most diverse in Au(Ag)-tellurides (nagyagite, sylvanite, petzite, and hessite). The other Bi-bearing tellurides, i.e., Pb-Bi-Te-S phases and buckhornite are not exclusively found in the above mentioned associations.

Telluride associations and textures

Tellurides are mainly hosted within Sb-(As)sulphosalts, although they may also occur within any of the sulphides (except alabandite). It is interesting to note that, in any given sample, there is a strong tendency for most telluride grains to be hosted in only a single type of sulphosalt, rarely also in one of the sulphides in the association. Secondly, tellurides were observed to be associated with episode(s) of brecciation (Fig. 2A), especially in the two samples of pyrite-fahlore ore mentioned above. Most often, nagyagite is found enclosed within fahlore. The lamella in Fig. 2B is positioned along a narrow band of Td₄₈, As-richer than the rest of the enclosing sulphosalt (Td₆₉). This contrasts to the trend seen when nagyagite is placed within bournonite, which shows a prominent Sb-rich composition (Bnn₈₇; Fig. 2C). Instead of wellshaped lamellae, lobate, exsolution-like bodies of nagyagite are typically observed in intermediate members of the jordanite-geocronite series (Jord₃₂₋₄₂; Fig. 2D, E). In the same areas, blebs of galena may also be present. One of the blebs in such areas (Fig. 2E) is identified as buckhornite. Although the bleb has a width of only a few µm, it is still possible to identify a small droplet of sylvanite and a narrow area with the composition of saddlebackite along the margins of the buckhornite. In rare cases, nagyagite lamellae in sphalerite with 'step-like' borders marked by galena (Fig. 2G) strongly resemble characteristic aspects observed in the main telluride ore (Ciobanu et al., 2004). However, we note that, in the main ore, it is altaite (PbTe) and not galena that forms such

borders; altaite is lacking from the salband associations. In the same sample, nagyagite is found at grain boundaries between fahlore and pyrite, crosscutting zonation patterns in the latter (Fig. 2G). We note that the zoning is otherwise marked by exsolved blebs of bournonite. Coarse grains of native tellurium were also observed in fahlore from Sb-richer parts of the sulphosalt (Fig. 2H). In this case, nagyagite is present in the adjacent galena.

The other Au(Ag)-tellurides may also be hosted by bournonite with zoned composition (Fig. 2I). We note the association between stützite and sylvanite in this case, and the conspicuous lack of nagyagite. However, Au(Ag)-tellurides are found together with nagyagite in another sample (7.9). Hessitepetzite, sylvanite-petzite and hessite-sylvanite pairs were observed in some 5-10 µm blebs (Fig. 2J-L). The telluride blebs may be in direct contact with nagyagite lamellae, forming the tip of a junction boundary between nagyagite and bournonite (Fig. 2J). Such blebs are hosted mainly within fahlore and, interestingly, tend to commonly associate with exsolved sphalerite (Fig. 2A, L). All tellurides in this sample are, however, associated with brecciation features, and are found along trails that crosscut preexisting mineral boundaries (Fig. 2A).

Similarly, the Bi-tellurides are located within dilational sites formed during brecciation. In Fig. 3A, the tellurobismuthite grain is placed in a pressure shadow between pyrite and rhodochrosite; the latter also shows a porous marginal overgrowth. Fringes of Bi-tellurides are also located along compositional zones of fahlore, indicating reworking during brecciation (Fig. 3B). Nagyagite, as well as Bitellurides, exploiting porosity induced during brecciation, clustering exsolution bodies of pyrite (Fig. 3C).

Tellurobismuthite may form single idiomorphic grains (Fig. 3D) or appear as irregular blebs (Fig. 3E), depending on the shape of the pores and stress-induced field during brecciation. More rarely, both tetradymite and tellurobismuthite occur in the same bleb (Fig. 3F). Coloradoite was observed at the margin of one of the tetradymite grains (Fig. 3G). The bleb-shaped morphology of the coarser tetradymite, paralleled by trails of inclusions in fahlore, is strongly indicative of shear-assisted brecciation (Fig. 3H). Most interestingly, tetradymite and nagyagite may be associated within common blebs (Fig. 3I), some of which include also jordanite (Fig. 3J). Jordanite, nagyagite and galena also form typical exsolution blebs in fahlore (Fig. 3K). More rarely, nagyagite lamellae were observed within rare bournonite (Fig. 3L); we again note a prominent Sb-rich composition (Bnn₆₈) of bournonite in such cases.

Buckhornite and/or Pb-Bi-Te-S phases were observed within Bi-sulphosalts (Figure 2C, G in Ciobanu et al., this volume).

Mineral chemistry

Nagyagite and other Au-(Ag) tellurides

Hessite, stützite, sylvanite and other Au-(Ag) tellurides are all essentially stoichiometric (Table 1).

Nagyagite compositions (Table 2) show significant variation, particularly with respect to Pb/(Pb+Sb+As), with some grains displaying

Table 1. Composition of Au-(Ag) tellurides and native tellurium, salband mineralization, Sacarimb

	Ag	Au	Fe	Bi	Sb	As	Te	Se	S	Total	Formula
Sylvanite											
S7.9 (mean of 3)	11.46	25.55	-	-	-	-	61.25	-	-	98.27	(Au _{1.09} Ag _{0.89}) _{1.98} Te _{4.02}
Stützite											
\$7.11.2	56.09	-	-	-	-	-	40.45	0.62	-	97.16	Ag _{4.92} Te _{3.00} Se _{0.08}
Native tellurium											
S7.3.8	0.15	-	-	-	0.31	-	99.07	0.05	-	99.58	



Fig. 2. Back-scattered electron images illustrating the occurrence of Au-(Ag)-tellurides in salband ores from Sacarimb. Samples: 7.9 (A, B, J, K, L); 7.6 (C); 7.8 (D, E); 7.1 (F, G); 7.3 (H); 7.11 (I). Arrows in A represent tellurides. See text and Table 1 in Ciobanu et al. (this volume) for additional description and explanation. All scale bars 5 μ m, except (A): 50 μ m. Abbreviations: Bnn – bournonite, Buck – buckhornite, Gn – galena, Hs - hessite, Jord – jordanite, Nag – nagyagite, Py – pyrite, Pz – petzite, Qz – quartz, Sdl – saddlebackite, Sp – sphalerite, Stz – stützite, Syl – sylvanite, Td – tetrahedrite, Te – native tellurium

Table 2. Composition of nagyagite, salband mineralization, Sacarimb

	Au	Pb	Bi	Sb	As	Te	Se	S	Total	Formula
'Normal'- nagyagite										
\$7.b5.51	9.11	52.13	2.17*	8.52	0.28	16.98	0.28	9.99	99.46	$Pb_{3}(Pb_{1.60}Sb_{1.28}As_{0.07})_{2.95}S_{5.70}Au_{0.85}Te_{2.44}Se_{0.06}$
\$7.1.1	8.95	54.94	-	7.76	-	15.75	1.28	10.89	99.57	$Pb_{3}(Pb_{1.66}Sb_{1.12})_{2.78}S_{5.97}Au_{0.80}Te_{2.17}Se_{0.28}$
\$7.b5.42	10.37	56.51	-	6.14	0.35	15.97	-	10.90	100.24	$Pb_{3}(Pb_{1.84}Sb_{0.89}As_{0.08})_{2.81}S_{6.03}Au_{0.93}Te_{2.22}$
\$7.1.7	9.18	53.42	-	8.86	-	15.92	-	11.12	98.50	$Pb_{3}(Pb_{1.56}Sb_{1.29})_{2.85}S_{6.13}Au_{0.82}Te_{2.20}$
As-bearing, lo	w-Pb na	gyagite								
S7.8.23	11.33	41.77	-	10.12	2.55	20.58	-	10.25	97.53	$Pb_{3}(Pb_{0.40}Sb_{1.40}As_{0.55})_{2.35}S_{5.95}Au_{0.97}Te_{2.72}$
\$7.8.5	11.31	44.72	1.08*	8.75	2.32	19.52	-	11.31	99.01	$Pb_{3}(Pb_{0.67}Sb_{1.22}As_{0.53})_{2.42}S_{6.00}Au_{0.98}Te_{2.60}$

characteristic 'low-Pb' compositions, as well in variable Au/(Au+Te) ratios. Unlike nagyagite investigated in vein fillings (Ciobanu et al., 2004), no significant amounts of As are noted.

Bi-tellurides

Tetradymite (Bi_2Te_2S) and *tellurobismuthite* (Bi_2Te_3) are both close to stoichiometric in composition (Table 3; Fig. 4a); no Se-substitution is seen in tetradymite. Interestingly, both species display substantial substitution by Sb (Fig. 4b). Tellurobismuthite-telluroantimony solid solution has widely documented elsewhere, but this is not the case for Bi_2Te_2S -

 Sb_2Te_2S . The data for the fine-grained phases in the Pb-Bi-Te-S phases is less easy to ascribe to individual minerals.

Saddlebackite, $Pb_3Bi_2Te_2S_3$, is recognised, but several other grains tend to give compositions close to ~ Pb_3BiTeS_4 – which corresponds to no known natural mineral or synthetic compound.

Compositions resembling *buckhornite* are noted (Table 4), but differ from stoichiometric buckhornite, [Pb₂BiS₃][AuTe₂], by the exceptionally low Au contents, and in some grains, by significant contents of Sb, beyond those previously reported.

Table 3. Compositional data for Bi-telluride minerals. Brackets indicate mean (n)

	Pb	Bi	Sb	Te	Se	S	Total	Formula		
Tetradymite, Bi2Te2S										
S7.b5 gr b2 (5)	3.65	48.74	4.97	37.50	0.52	4.74	100.13	$(Bi_{1.58}Pb_{0.12}Sb_{0.28})_{1.98}Te_{1.99}Se_{0.04}S_{1.00}$		
S7.b5 gr b3 (5)	2.60	46.80	7.93	37.90	0.56	4.51	100.27	$(Bi_{1.50}Pb_{0.08}Sb_{0.44})_{2.02}Te_{1.99}Se_{0.05}S_{0.94}$		
S7.b5 gr b4	-	57.07	1.58	37.99	0.15	4.26	101.05	$Bi_{1.90}Sb_{0.09})_{1.99}Te_{2.07}Se_{0.01}S_{0.92}$		
S7.b5 gr b6	3.88	54.88	-	38.40	-	3.61	100.77	$(Bi_{1.89}Pb_{0.13})_{2.02}Te_{2.17}S_{0.81}$		
S7.b5 gr b6* (3)	2.48	53.49	2.59	38.49	0.06	3.68	100.76	$(Bi_{1.81}Pb_{0.08}Sb_{0.15})_{2.05}Te_{2.13}Se_{0.01}S_{0.81}$		
S7.b5 gr b7	-	50.32	5.61	40.83	-	3.64	100.43	$(Bi_{1.67}Sb_{0.32})_{1.99}Te_{2.22}S_{0.79}$		
S7.b5 gr b8 (3)	1.59	51.64	5.02	38.40	0.17	3.82	100.64	$(Bi_{1.72}Pb_{0.05}Sb_{0.29})_{2.06}Te_{2.09}Se_{0.02}S_{0.83}$		
S7.b5 gr b9*	-	55.06	2.69	38.64	0.18	4.28	100.85	$Bi_{1.82}Sb_{0.15})_{1.97}Te_{2.09}Se_{0.02}S_{0.92}$		
S7.b5 gr b10 (3)	2.65	51.38	3.30	38.60	0.09	3.98	100.01	$(Bi_{1.72}Pb_{0.09}Sb_{0.19})_{2.00}Te_{2.12}Se_{0.01}S_{0.87}$		
S7.b5 gr b11 (4)	2.66	52.86	2.68	37.65	0.24	3.94	100.02	$(Bi_{1.78}Pb_{0.09}Sb_{0.16})_{2.03}Te_{2.08}Se_{0.02}S_{0.87}$		
S7.b5 gr b13 (2)	-	53.38	3.02	36.35	0.27	5.09	100.12	$(Bi_{1.80}Sb_{0.17})_{1.97}Te_{1.93}Se_{0.02}S_{1.08}$		
\$7.5.3	4.82	52.06	-	35.61	-	4.38	96.86	$(Bi_{1.81}Pb_{0.17})_{1.98}Te_{2.03}S_{0.99}$		
\$7.5.4	4.68	52.52	0.66	35.49	-	3.71	97.05	$(Bi_{1.87}Pb_{0.17}Sb_{0.04})_{2.07}Te_{2.07}S_{0.86}$		
S7.a5.18	6.35	52.40	1.16	36.09	-	3.14	99.15	$(Bi_{1.87}Pb_{0.23}Sb_{0.07})_{2.17}Te_{2.11}S_{0.73}$		
Tellurobismuthite										
S7.b5 gr b1 (7)	0.38	42.15	5.78	49.63	0.10	0.12	98.15	$(Bi_{1.56}Pb_{0.01}Sb_{0.37})_{1.95}Te_{3.02}Se_{0.01}S_{0.03}$		
S7.b5 gr b5 (6)	0.99	45.34	3.74	49.23	0.20	0.15	99.65	$(Bi_{1.68}Pb_{0.04}Sb_{0.24})_{1.96}Te_{2.99}Se_{0.02}S_{0.04}$		
S7.b5 gr b6*	-	46.86	3.57	49.00	0.32	-	99.75	(Bi1.75Sb0.23)1.98Te2.99Se0.03		
S7.b5 gr b9 (2)	-	42.16	5.74	51.05	0.24	0.25	99.43	$(Bi_{1.53}Sb_{0.36})_{1.89}Te_{3.03}Se_{0.02}S_{0.06}$		
(?) Pb-Bi-Te-S phase ~Pb ₃ BiTeS ₄										
\$7.5.b5.130	52.67	17.59	0.88	12.41	1.15	12.74	97.43	$Pb_{2.68}Bi_{0.89}Sb_{0.08}Te_{1.02}S_{4.18}Se_{0.15}$		
Saddlebackite, Pb3Bi2	$\Gamma e_2 S_3$									
S7.8.14	33.61	25.91	3.63	22.32	2.08	7.72	95.26	$Pb_{1.93}Bi_{1.47}Sb_{0.35}Te_{2.08}S_{286}Se_{0.31}$		



Fig. 3. Back-scattered electron images illustrating the occurrence of Bi-tellurides in salband ores from Sacarimb. (sample 7.5). See text and Table 1 in Ciobanu et al. (this volume) for additional description and explanation. All scale bars 5 μ m, except (A): 50 μ m, (B) and (C) 10 μ m. Abbreviations: Bnn – bournonite, Col – coloradoite, Jord - jordanite, Nag – nagyagite, Py – pyrite, Rdc – rhodochrosite, Sp – sphalerite, Tbs – tellurobismuthite, Td – tetrahedrite, Ttd – tetradymite

Table 4. Compositional data for the buckhornite-like phase. Brackets indicate mean (n)

	Pb	Bi	Sb	Au	Te	Se	S	Total	Formula
S7.b5 (5)	42.20	16.29	0.42	6.97	18.52	0.58	12.56	97.54	$Pb_{2.12}Bi_{1.06}Sb_{0.04}S_{4.08}(Au_{0.37}Te_{1.51}Se_{0.08})$
S7.8.3	42.70	11.72	6.07	6.40	21.82	-	7.90	96.60	$Pb_{2.43}Bi_{0.91}Sb_{0.59}S_{2.91}(Au_{0.38}Te_{2.02})$
S7.8.12	48.55	5.82	6.93	6.89	18.23	-	8.81	98.00	$Pb_{2.65}Bi_{0.45}Sb_{0.64}S_{3.11}(Au_{0.40}Te_{1.77})$

Discussion

Tellurides are present as inclusions, mainly in sulphosalts, within the Sacarimb salband ore. Nagyagite is mostly the 'normal' Sb-rich variety. The correlation between end-member Sb-nagyagite and the Sb>As character of the Sb-As-sulphosalts is observed only for bournonite. This strongly implies co-precipitation of this mineral pair, a trend also observed in the main telluride ore. Nagyagite is



Fig. 4. Compositional data for Bi-tellurides. (A) Ternary diagram in a portion of the Bi_2S_3 - Bi_2Te_3 - Bi_2Se_3 system. (B) Plot illustrating Sb substitution in tellurobismuthite (circles) and tetradymite (diamonds) in terms of Sb vs. (Bi+Pb), each analysis calculated to 5 atoms

observed as exsolution blebs rather than wellshaped lamellae in jordanite suggesting that this was incorporated within the latter by solidsolution mechanisms. The relationship between nagyagite and host fahlore is more difficult to interpret in genetic terms because of the overprinting of primary zonation patterns in the latter. We can nonetheless consider tellurides as part of the precipitates during the entire deposition sequence, from early pyrite-fahlore, to sphalerite-bournonite, and lastly galenajordanite. The occurrence of native tellurium indicates that fluids are close to Te saturation, as in the main telluride ore, although restricted to a narrower interval of fS_2 values implied by the lack of altaite (log $fS_2 > -10$).

The associations between tetradymite and other tellurides, such as nagyagite or coloradoite, within common blebs, suggest that the limited occurrence of Bi-tellurides does not necessary imply a separate source of fluids from the one that is responsible for the bulk telluride association. This is further stressed by the observed Sb content in both tellurobismuthite and tetradymite.

Based upon textural relationships, we recognise, however, that the Bi-tellurides, as well as a second generation of the same Au(Ag)-tellurides, were formed from fluids introduced during vein reopening associated with shear-assisted brecciation (see Ciobanu et al., this volume). This second population is more significant than the first population and may represent higher ore grades than 1-2 g/t. Although this event is recognised for the salband mineralization in general, deposition of this second population of tellurides is restricted to discrete areas along the veins, also identified as those where the main assemblage is chiefly composed of pyrite and fahlore (lacking the more polymetallic character). Further investigation is however necessary to interpret the observed facts.

Conclusions

- 1. Nagyagite and several other Au(Ag) tellurides account for the majority, if not all, of the gold in the salband ore.
- 2. Bi-tellurides (tetradymite, tellurobismuthite) are identified in salband mineralization.
- 3. Further study is needed to confirm the presence of rare buckhornite and the Pb-Bi-Te-S phases in the Sacarimb deposit.
- 4. Two populations of tellurides are recognised. They share the Au(Ag)-tellurides but not the
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main Bi-tellurides (tetradymite and tellurobismuthite).

References

- Brana, V. 1958. Zacamintele Metalifere ale Subsoliduui Rominesc. Ed. Stintifica, Bucuresti, 261 p.
- Ciobanu, C.L., Cook, N.J., Damian, G., Damian, F., Buia, G. 2004. Telluride and sulphosalt associations at Sacarimb. In: N.J. Cook, C.J. Cionanu (Eds.), Gold-Silver Telluride Deposits of the Golden Quadrilateral, South Apuseni Mts., Romania. IAGOD Guidebook Series 12, 145-186.
- Cook, N.J., Ciobanu, C.L., Damian, G., Damian, F. 2004. Tellurides and sulphosalts from deposits in the Golden Quadrilateral. In: N.J. Cook, C.J. Ciobanu (Eds.), *Gold-Silver Telluride Deposits*

of the Golden Quadrilateral, South Apuseni Mts., Romania. IAGOD Guidebook Series 12, 111-144.

- Shimizu, M., Shimizu, M., Cioflica, G., Shimazaki, H., Kovacs, M., Lupulescu, M., Petrusan, G.S., Feigel, M., Popa, G., Refec, I., Pânzan, I. 1999. New informations on opaque minerals from Neogene ore deposits in Romania. *International Symposium 'Mineralogy in the System of Earth Sciences'*, Abstract vol., Univ. Bucharest, p. 101.
- Simon, G., Alderton, D.H.M. 1995. Pilsenite, Bi₄Te₃ from the Săcărâmb gold-telluride deposit, Metaliferi Mts: First occurrence in Romania. *Romanian Journal of Mineral Deposits*, **76**, 111-113.
- Udubaşa, G., Strusievicz, R.O., Dafin, E., Verdeş, G. 1992. Mineral occurrences in the Metaliferi Mts., Romania. *Romanian Journal of Mineral Deposits*, **75** (suppl. 2), 1-35.