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COMPOSITIONAL VARIATIONS OF THE GOLD INCLUSIONS VS HOST MINERALS IN THE SHEAR-ZONE RELATED GOLD ORES FROM SOUTH CARPATHIANS, ROMANIA

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ABSTRACT: *Valea lui Stan (Brezoi) and Costeşti (Horezu) are both shear-zone related gold mineralizations within the metamorphic rocks in South Carpathians. They are similar in respect to the mineral associations and structural setting, but are different in respect to the geochemical parageneses and the related protores. In both occurrences the gold is present as inclusions in different sulphides (arsenopyrite, chalcopyrite, pyrite, sphalerite, pyrrhotite) and quartz. Gold occurs in these minerals at different size scales. Rarely found at macroscopic scale, gold is usually present at microscopic and submicroscopic scale, as micro-, infra- and nano-inclusions. In the two mineralizations, gold is represented by a silver-rich alloy, and having subordinate amounts of Cu, Bi, Ni and Mn. At Valea lui Stan the natural alloy is usually richer in Au than at Costeşti. Some compositional differences have been observed between the gold composition in respect to the host minerals. When gold is included in arsenopyrite (in both occurrences) the Ag content is higher than the case in which is included in chalcopyrite (Valea lui Stan) or pyrrhotite (Costeşti).*

Keywords: *gold; host minerals; gold composition; shear-zone related ores; South Carpathians;*

Introduction

The metamorphic rocks in the South Carpathians host several shear-zone related gold ores/mineralizations. Two examples are: Valea lui Stan (near Brezoi) and Costeşti (near Horezu). The metamorphic host rocks belong to the Getic-Supragetic Realm, or the Median Dacides [1, 2]. The mineralizations are located in the eastern part of the Căpăţânii Mts., west of river Olt (Fig. 1). The ore bodies are both discordant and concordant to the fabric of the host rocks and consist generally of gold and sulphides in quartz lenses. In all the occurrences the gold is present as inclusions mainly in arsenopyrite, pyrite, chalcopyrite, sphalerite, pyrrhotite and quartz.

Valea lui Stan mineralized structure is located in the Eastern part of the Căpăţânii Mts., West of Olt River. The ore bodies are both discordant and concordant in relation to the fabric of the host metamorphic rocks. The mineralization occurs mainly in the metabasic rocks of the Sibisel Group, in connection with N-S brittle-ductile shear zones related to the Getic-Supragetic Alpine nappe stacking. The protore of the mineralizations is considered to be the amphibolitic sequences of the Sibisel Group, argued by the higher Au content in respect to other (similar) rocks in the area [3]. The ore paragenesis is dominated by pyrite, chalcopyrite, arsenopyrite, which are also the main host minerals for gold; quartz is the main gangue mineral. Other metallic minerals have been also described by previous authors [4.3]: pyrrhotite, sphalerite, galena, tetrahedrite-tennantite, native gold, bornite, magnetite, ilmenite, hematite; as

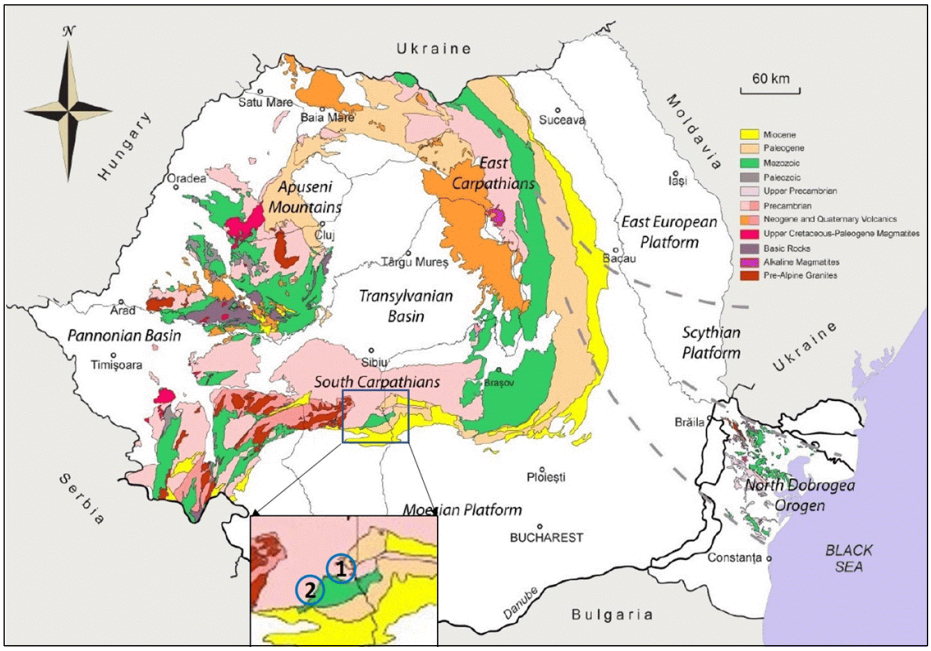


Fig. 1. Localization of the investigated areas within the South Carpathians
1 – Valea lui Stan, 2 – Costeşti. (Geological map from [5], with completions)

secondary minerals are cited: marcasite, goethite, covellite, chalcocite, malachite, azurite, anglesite, cerussite, scorodite. In the Valea lui Stan ores the native gold occurs as inclusions in arsenopyrite, chalcopyrite, pyrite, quartz, and sometimes in goethite. Possible new minerals for this occurrence have been identified by qualitative analysis – SEM [6]: Sb minerals (secondary) on the arsenopyrite cracks and a Cu-Bi-Hg-Pb-Fe-S compound in association with chalcopyrite and arsenopyrite.

Costeşti mineralized structure is located in the South-Eastern part of the Căpăţânii Mts., West of Olt River, and southwestward from the similarly featured Valea lui Stan occurrence. The ore bodies, both discordant and concordant to the fabric of the metamorphic rocks, are located in the paragneisses, micaschists and amphibolites of the Vaideeni Formation along NW-SE shear zones [7]. Here, the biotite-blastomilonites sequences are considered the protore for the mineralization, the geochemical analyses pointing out higher Au content for this kind of rocks in respect to others [8]. The mineral paragenesis of the Costeşti occurrence is larger than the one from Valea lui Stan. Here, pyrite and arsenopyrite prevail in the ore minerals association. Quartz, carbonates (calcite, ankerite) and chlorite are the main gangue minerals. Other ore minerals known in the paragenesis are as follows [7,8]: chalcopyrite, bismuthinite, tetrahedrite-tennantite, sphalerite, jamesonite, greenockite, pyrrhotite, galena, native gold, native silver, native bismuth, wittichenite, other unidentified Bi sulphosalts (containing Bi, Pb, Ag, As, S), magnetite, marcasite, arsenolite. The Au from Costeşti ores occurs mainly in arsenopyrite, sometimes associated with native Bi and Bi sulfosalts, as well as in gangue minerals (quartz). Several Au grains have been observed as inclusions in pyrrhotite [6]. New entries for the mineral association can also be cited [6]: cubanite, “Zwischenprodukt”, Ca-bearing pyrrhotite,

ikunolite (?), "schreibersite"-like minerals, "merumite" compounds.

Although similar, these occurrences are different in respect to the main geochemical association, related protores and other features [6], as follows:

(1) monophasic (Costeşti) against polyphasic (Valea lui Stan) shear-zone deformation events;
(2) protore composition: amphibolites for Valea lui Stan and biotite blastomilonites for Costeşti [4, 8];
(3) different major and minor ore elements, i.e. Au-As-Cu (major) and Cr-Ni-Pb-Zn (minor) for Valea lui Stan, and Au-As-Bi (major) and Cr-Ni-Se-Cd (minor) for Costeşti, respectively [6];
(4) quite different history: Valea lui Stan discovered at the beginning of the XXth Century and exploited until the 1940's [5], and Costeşti discovered more recently (1982-1985) and partly explored [8];
(5) higher gold grades (up to maximum 100 g/t) at Valea lui Stan and lower gold grades (up to 10-15 g/t) at Costeşti;
(6) both ore occurrences belong to the "small size shear zones" [SSSZ, acc. to 9]; however, the known size of the shear zone is bigger at Valea lui Stan (more than 3-4 km) and smaller at Costeşti (about 1.5 km).

The relative richness of the Valea lui Stan gold deposit may be theoretically explained by a combination of items (1) and (6).

The characteristics of Valea lui Stan and Costeşti mineralizing systems [6] are similar to those of the Archean lode gold deposits, compiled by Groves and Foster (1993) and McCuaig and Kerrich (1994), suggesting the similarity to this type of deposits (Table 1).

Table 1. Comparison data - Archean lode gold deposits vs. Costeşti & Valea lui Stan occurrences.

	Archean lode gold deposits (Groves & Foster, 1993; McCuaig & Kerrich, 1994)	Costeşti (Udubaşa, 2004)	Valea lui Stan (Udubaşa, 2004)
T°C	160-700 (commonly 250-400)	180-385 450-550	350-400
P_{fluid} (kbar)	0,7-5,0 (commonly 1-3)	1,8-3,8	-
Salinity (wt.% NaCl eq.)	0-35 (commonly <6)	6-21	< 20
$\delta^{34}S$ (‰)	-0,7 … +9	-0,8 … +5,8	-2,8 … +15,22
Volatiles composition	H-C-O-S-N H_2O-CO_2±CH_4±H_2S±N_2	H+C+O+N (-S) H_2O-CO_2-CH_4-N_2	similar to Costeşti
Gold enrichment factors	10^3-10^4	10^2	10^2

The gold inclusions types in sulphides

Nearly all the sulphides of the two shear-zone related gold ores contain gold, which is unequally distributed over the investigated sulphides, i.e. arsenopyrite, pyrite, chalcopyrite, sphalerite, pyrrhotite etc.

In the investigated ores the gold has been found to occur either at macroscopic level or at submicroscopic one (micro-, infra- and nano-inclusions). A first attempt to classify the solid inclusions (gold included)

in different minerals has been made by Udubaşa et al. [10]. It has been shown that there exists micro-, infra- and nano-minerals (or inclusions) as a function of their size. Gold can occur at any of these levels and the methods of investigation are specific for each type of inclusions.

The macroscopic gold is rarely found in shear-zone related ores, especially in the Valea lui Stan ores; at Costeşti the gold was seen with naked eyes but only in some heavy mineral concentrates. Microscopic inclusions of gold have been observed both in sulphides (arsenopyrite, pyrite, chalcopyrite, sphalerite) and quartz (Fig. 2). Their form and size greatly vary.

The best developed and most interesting are the gold inclusions in arsenopyrite (Fig. 3); in some cases, such inclusions are enveloped in bands of apparently gold-free arsenopyrite, non-visible under the optical microscope. Nevertheless, investigation with the electron microprobe shows the presence of gold (contents of about 0.2 ppm and less), which gradually disappears as the distance from the gold inclusion increases. This may be called "infra-gold"[11], which can be interpreted as a result of solid state diffusion of gold-bearing ores.

It is interesting to note that no cracks in arsenopyrite occur. Zoned arsenopyrite with gold inclusions and satellite fine gold inclusions were observed by Möller et al.[12], who suggested that electro-chemical processes are responsible for such distribution patterns, in relation to varying As/S ratio in arsenopyrite. Grain boundaries with variable As/S ratios give rise to formation of np-junctions, i.e. favourable sites for gold deposition.

Perhaps the most interesting and at the same time most intriguing feature of gold occurrence pattern in sulphides from the studied ores was depicted by using SEM equipped with electron diffraction (SAED). Coral-like aggregates up to 60-80 nm in size have been identified on the grain surface of sulphides (Fig. 4). This is the third level (the fourth if we take into consideration the macroscopic gold – rarely found) of gold occurrence in sulphides – "nano-gold" [11], which cannot be depicted by any other methods of investigation. Such nano-inclusions of gold may have formed also by electrochemical processes as shown by Möller et al. [12].

Variations of the gold composition as a function of host sulphides

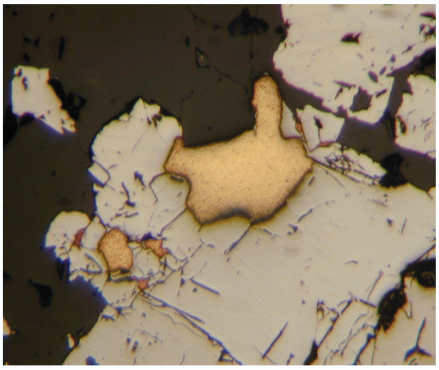
Previously observed by Udubaşa [6], the composition of gold in the shear-zone related ores at Valea lui Stan and Costeşti, South Carpathians, is a function of both the global geochemistry of ores (Cu-dominated at Valea lui Stan, As-dominated at Costeşti) and the nature of the host minerals. Further analyses have been carried out on gold from both occurrences.

The electron microprobe analyses [5], revealed that the natural alloy contains major Au and Ag, sometimes approaching the composition of the former "electrum", and subordinate amounts of Cu, Ni, Mn, Bi, Fe and As. Some selected analyses of the gold grains are given in the Table 2 and the rest of the data were plotted in ternary diagrams, Au – Ag – Cu x10, (Fig. 5).

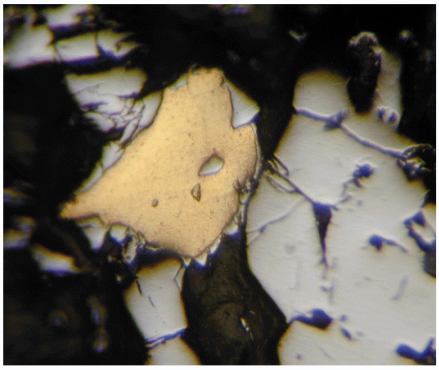
From Table 2, one can see that the natural alloys are richer in Au at Valea lui Stan (range 44.04 - 72.30 at.%; average 66.43 at.%) as compared to the Costeşti occurrence (range 40.67 - 61.21 at.%; average 45.57 at.%).

For the Valea lui Stan occurrence, the gold grains show significant Ag content ("electrum" composition) – up to aprox. 60 at.% (Tab. 2). Some other elements are present but at low contents: usually Cu, but also Bi, Ni and Mn.

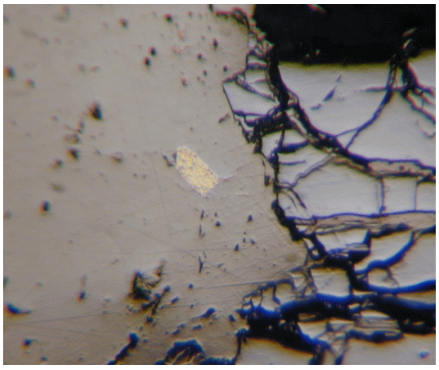
The gold fineness varies between 246.5 – 835.9 ‰. Taking into account the correlation with the host minerals (Fig. 5) it can be observed that the gold inclusions from chalcopyrite are poorer in Ag as those



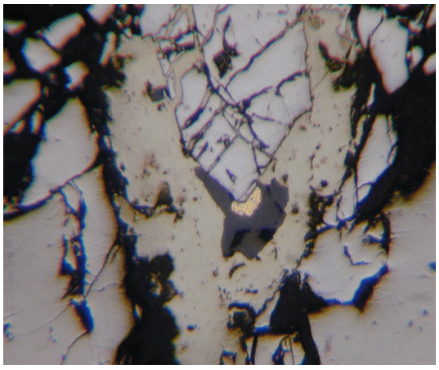
a) Gold inclusions in arsenopyrite. Valea lui Stan ores. N II, 120x magnification.



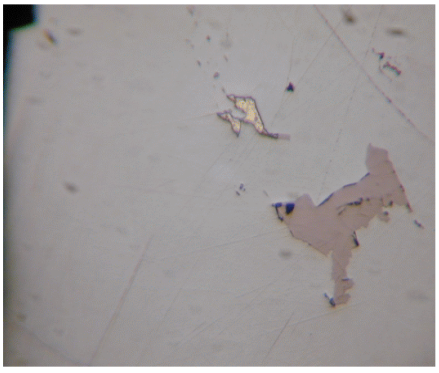
b) Gold with arsenopyrite inclusions. Valea lui Stan ores. N II, 120x magnification.



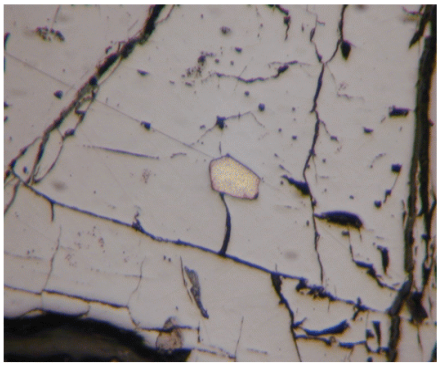
c) Gold in chalcopyrite. Valea lui Stan ores. N II, 190x magnification, oil imersion.



d) Native gold at the boundary between quartz and arsenopyrite, in chalcopyrite. Valea lui Stan ores. N II, 190x magnification, oil imersion.



e) Native gold and pyrrhotite in arsenopyrite. Costeşti ores. N II, 190x magnification, oil



f) Native gold in pyrrhotite. Costeşti ores. N II, 120x magnification.

Fig. 2. Gold inclusions in sulphides and quartz

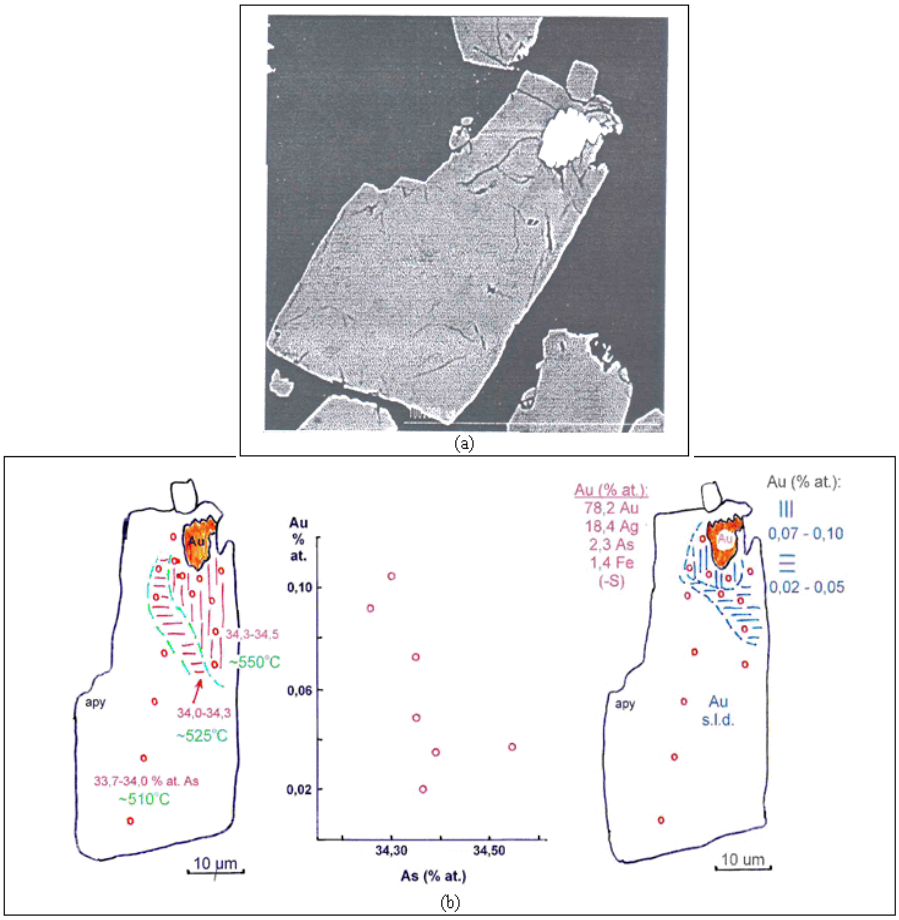


Fig. 3. Apparently homogeneous grain of arsenopyrite in BSE image (a), but with a cryptozonality of the Au and As content as revealed by quantitative analyses. Costeşti ores. Scale bar in (a) is 100 µm.

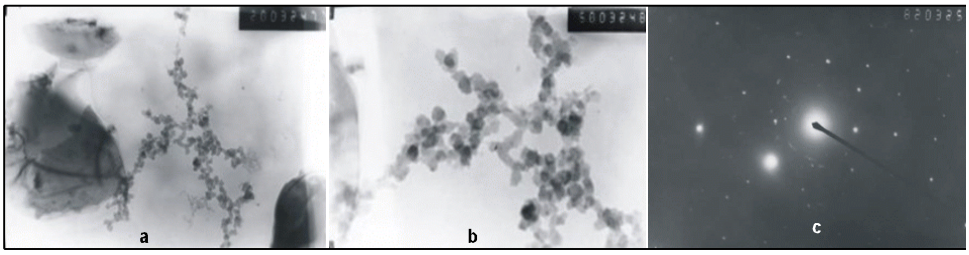


Fig. 4. TEM/SAED images of coral-like aggregates up to 60-80 nm in size on the grain surface of sulphides from Valea lui Stan ores [13].

Pyrite single crystal (left, up) with Au precipitations (usually at the edge of the crystal) and Au particles as chains ("corals") near pyrite (down, left). Average dimension of the particles: ~ 60 nm. Electron diffraction pattern of Au (down, right; analyst N. Popescu-Pogrion).

Table 2. Selected analyses of gold composition from Valea lui Stan and Costeşti (minimum and maximum contents*; at.%), the calculated empirical formulas and the range of the gold fineness

Occurrence		Au	Ag	Cu	Host minerals
Valea lui Stan	1)	44.04	53.95	1.50	chalcopyrite
	2)	72.30	25.93	1.78	chalcopyrite
	3)	47.62	41.41	-	*arsenopyrite*
	4)	57.22	41.29	1.50	*arsenopyrite*
Costeşti	5)	40.67	58.35	0.71	pyrrhotite
	6)	61.21	38.59	-	pyrrhotite
	7)	30.38	68.27	0.71	*arsenopyrite*
	8)	44.51	55.38	-	*arsenopyrite*

* Bi, Mn and Ni contents were omitted, being accidentally encountered and showing values of less than 0.3 at. % in both occurrences.

Empirical formulas:

Valea lui Stan	Costeşti
1) $Au_{0.44}Ag_{0.54}Cu_{0.01}Ni_{0.003}Mn_{0.001}$	5) $Au_{0.407}Ag_{0.583}Cu_{0.007}Ni_{0.002}Mn_{0.001}$
2) $Au_{0.72}Ag_{0.26}Cu_{0.02}$	6) $Au_{0.612}Ag_{0.386}Mn_{0.002}$
3) $Au_{0.48}Ag_{0.41}Bi_{0.11}$	7) $Au_{0.304}Ag_{0.683}Cu_{0.007}Ni_{0.003}Mn_{0.003}$
4) $Au_{0.57}Ag_{0.41}Cu_{0.02}$	8) $Au_{0.445}Ag_{0.554}Ni_{0.001}$

Range of the gold fineness

Valea lui Stan	Costeşti
246.5 – 835.9 ‰	448.3 – 743.4 ‰

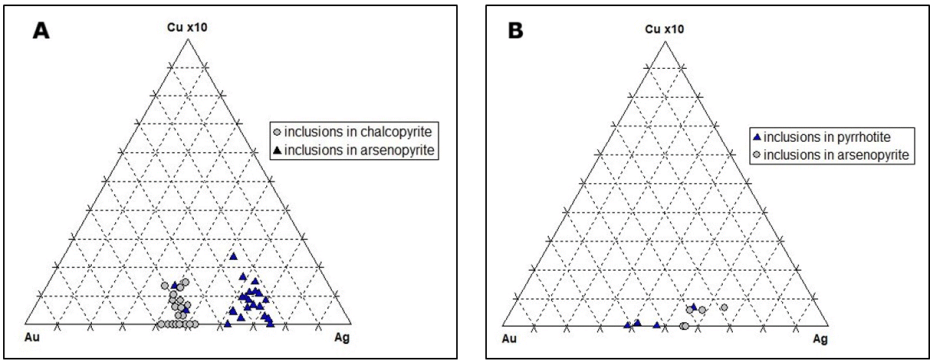


Fig. 5. Plot of the gold inclusions composition (at.%) in the ternary diagram Au – Ag – Cu x10 function of the host minerals. A – Valea lui Stan samples; B – Costeşti samples

included in arsenopyrite which are richer in Ag.

The gold grains from the Costeşti occurrence have also important contents of Ag – up to aprox. 70 at.% (Tab. 2). Other present elements are Cu, Mn and Ni. The gold fineness varies between 448.3-743.4 ‰.

The correlation of the composition with host minerals (Fig. 5) reveals that pyrrhotite hosts now the gold inclusions poorer in Ag and the arsenopyrite has gold inclusions richer in Ag.

Conclusions

Valea lui Stan (Brezoi) and Costeşti (Horezu) are both shear-zone related gold mineralizations within the metamorphic rocks in South Carpathians. They are similar in respect to the mineral associations and structural setting. In both cases the ore bodies are represented by discordant and concordant quartz lenses with gold and sulphides.

The differences between the two occurrences consist in the geochemical parageneses (Au-As-Cu at Valea lui Stan; Au-As-Bi at Costeşti) and the related protores (amphibolites at Valea lui Stan; biotite blastomilonites at Costeşti).

In both occurrences the gold is present as inclusions in different sulphides (arsenopyrite, chalcopyrite, pyrite, sphalerite, pyrrhotite) and quartz. In these minerals gold has been found to occur at different size scales. Rarely found at macroscopic scale, gold is usually present at microscopic and submicroscopic scale, as micro-, infra- and nano-inclusions [13].

In the two mineralizations, gold is represented by a silver-rich alloy, sometimes approaching the "electrum" composition, and having subordinate amounts of Cu, Bi, Ni and Mn. At Valea lui Stan the natural alloy is usually richer in Au than at Costeşti.

Some compositional differences have been observed between the gold composition in respect to the host minerals. When gold is included in arsenopyrite (in both occurrences) the Ag content is higher than the case in which is included in chalcopyrite (Valea lui Stan) or pyrrhotite (Costeşti).

For the case of high Ag-content of the gold inclusions in arsenopyrite it can be assumed that some of the gold probably enters the arsenopyrite structure, as explained by Möller et al. (1997) due to electrochemical processes (see Fig. 3b).

In the case of gold inclusions in chalcopyrite (Valea lui Stan) and pyrrhotite (Costeşti), respectively, the higher Au-Ag ratio could be explained by a possible "entrapment" of Ag in the structure of these minerals.

In order to explain in more detail the geochemistry of gold inclusions in these sulphides further analytical work will be undertaken in the near future.alloy is usually richer in Au than at Costeşti.

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