Preliminary data on two tin-sulfosalts (canfieldite and pirquitasite) from Roşia Montană

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Abstract: During the re-assessment of the collection of ore minerals ''N. Petrulian'' from the Department of Mineralogy of the University of Bucharest, one sample from Roşia Montană was investigated by micro-Synchrotron Radiation X-Ray Fluorescence (SR-XRF). The results, correlated with microscope study revealed, for the first time at Roşia Montană, the presence of two tin sulfosalts (canfieldite si pirquitasite), and of two types of gold (Ag-rich and Ag-poor). Such differences in gold composition are related to temperature and sequence of formation, as suggested by mineral relations. The Ag-rich gold formed earlier, at higher temperature, while the Ag-poor gold was generated subsequently, at lower temperature.

***Keywords**:* Roşia Montană, gold, canfieldite, pirquitasite

1. Introduction

Roşia Montană is one of the most famous gold ore deposit in the Neogene Province of the Apuseni Mts., and also one of the oldest historical sources of gold in Romania and in Europe. Archaeological research places the origins of this deposit at least in the times of the Roman Empire if not earlier (Cauuet et al., 2003). Together with Roşia Poieni porphyry copper ore deposit, it forms a real metallogenetic knot (Fig. 1). The fame of this deposit has been reactivated during the last years, mainly due to the mining project of the Canadian Company *Gabriel Resources Ltd*., developed by its Romanian branch, the *Roşia Montană Gold Corporation*.

2. Previous research

The mineralogy of Roşia Montană ore deposit is comparatively less known with respect to other gold ore deposits in the Metaliferi Mts. e.g. Săcărâmb, Stănija, Baia de Aries, all of which are type localities for several minerals. Yet, native gold and beautiful, large mineral samples from Roşia Montană are famous exhibits in various mineralogical museums around the world.

The mineralogical investigations carried out during last decade, especially using scanning electron microscopy (SEM) and electron probe microanalysis (EPMA), have revealed numerous metallic minerals in the Roşia Montană ore deposit. Newly described minerals such as *stephanite, polyargyrite, achantite, tennantite* and also *proustite-pirargyrite, miargyrite* and *argyrodite* (Tămaş et al., 2004), were added to the minerals already mentioned by Petrulian (1934) e.g. *argentite, proustite, pearceite, polybasite*.

Tămaş et al. (2006) mentioned several new tellurium mineral occurrences from Roşia Montană: *altaite, hessite, sylvanite, cervelleite, petzite* which added to the already rich telluride inventory of the Metaliferi Mts.

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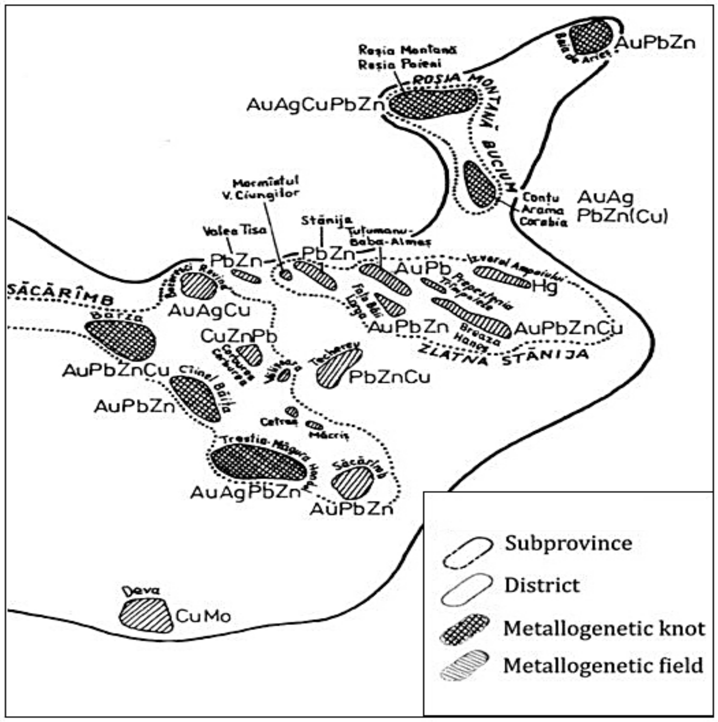

Fig.1. The metallogenetic Neogene Subprovince in the South Apuseni Mts. (after Popescu, 1986)

Chemical micro-analyses suggesting the presence of *tellurium-argyrodite* have also been mentioned. During the last two years, a series of new investigations of native gold from classical occurrences in Romania have been carried out in co-operation with physicists from the Nuclear Physics and Engineering Institute in Bucharest, in order to identify the sources of gold used for ancient jewelry artifacts.

The origin of gold in various artifacts was seen as crucial for clarifying some debates among archaeologists and geologists on different possible gold sources within the Romanian territory. For example, Constantinescu et al. (2008) found traces of Sn in several gold bracelets of a Dacian treasure, a feature interpreted as an indicator of an alluvial origin of gold, which was mixed with some cassiterite grains during the panning. Nevertheless, the authors mentioned trace amounts of Sn in the primary gold extracted from Roşia Montană and Valea Morii deposits.

3. Sample description

Following the research mentioned above, a polished section of native gold from Roşia Montană (Petrulian Collection, Department of Mineralogy, Faculty of Geology and Geophysics, University of Bucharest) was chosen for mineralogical and geochemical investigations.

The investigated sample originates from a vein-type ore, which is relatively rare at Roşia Montană, where the gold ore is commonly located in breccias. Most likely, the sample was taken from the Cârnic body, which is the part of the deposit studied by Professor Petrulian in the 1930s. The sample represents a typical example of symmetrical banded texture, where the oldest bands (Fig. 3a - band 1) are disposed in an outer position, while the youngest are located in the center (Fig. 3a - band 4). In the present, similar banded texture can be found at Roşia Montană in the Mn carbonate-rich veinlets that cross the *black breccia'*.

4. Methods

The sample was first investigated by micro-Synchrotron Radiation X-Ray Fluorescence (SR-XRF) at the FLUO-beam and XRF analyze with a XGT-7000 X-ray Analytical Microscope (Simon et al., 2003) at ANKA/ISR in Karlsruhe, we performed 2-dimensional scans with the beam focused to 7-10 µm2 (Vasilescu et al., 2003). The scan area could be visualized with an optical microscope and recorded with a camera. The detector used was an HPGe crystal. The maximum excitation energy of the X-rays at both sites was 32.5 keV. The samples were mounted in air on a dedicated frame, put on a motorized xyz stage and positioned at an angle of 45◦ to the primary X-ray beam. The identification of the peaks and the off-line data analysis was performed with AXIL software. Relative concentrations of minor and trace elements were determined using a procedure based on various standards and fundamental parameter calculations.

To clarify the distribution of the chemical elements have been done some more detailed XRF analyze with a XGT-7000 X-ray Analytical Microscope at the University of Bucharest, Faculty of Geology and Geophysics.

The acquisition characteristics set on XGT-7000 were: time - 263 [s], X-ray tube vol. - 30.00 [kV], Current - 1.000 [mA], XGT Diameter - 10 [µm]. The element maps are generated by showing X-ray intensity between a specific energy ranges (corresponding to the particular XRF lines of an element). Each pixel of the element map shows the X-ray intensity at that position.

Subsequently, we have re-examined the sample by means of reflected light microscopy in order to identify the minerals that can accommodate the elements indicated by the XRF results.

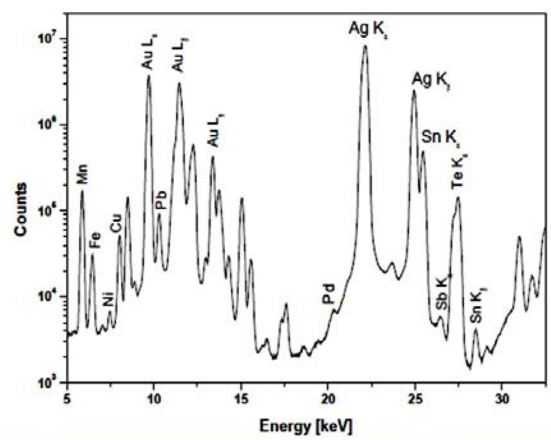

Fig. 2. The XRF surface analysis on an area of approx 1 mm by 1 mm of the investigated polished section from Roşia Montană. Maxima for Au, Ag, Sn, Te, Cu, Pb, Fe are visible in the spectrum (analyzed by Angela Vasilescu, from IFIN-HH Bucharest).

5. Results and discussions

The XRF spectrum of the investigated sample revealed the presence of Sn and other less common elements (Fig. 2). Following this indication, we examined the sample with the chalcographic microscope and we identified two tin-sulfosalts intergrown with gold.

A first Sn-phase was the relatively easily recognizable *canfieldite* (Ag_8SnS_6), a member of the isomorphic series with *argyrodite* (Ag_8GeS_6), already identified in Roşia Montană.

Canfieldite is always associated with gold and has a light-gray color with a weak creamy tint, which becomes brown-reddish due to the oxidizing processes and to the alteration caused by the light. Canfieldite cross-cuts or partially replaces gold grains (Fig. 4, a-d).

The presence of tellurium, identified by the XRF-analysis in the same sample, can indicate the Te-rich composition of canfieldite; this is supported by the absence of any other tellurium-bearing minerals in the polished section and is consistent with the presence of tellurium-argyrodite in Roşia Montană (Tămaş et al. 2004). There are places in the world where tellurium-canfieldite has been identified e.g. Revelstoke - Canada, Belukhinskoe - Russia, Tsumo, Kuga and Nakatatsu - Japan, Zlata Bana - Slovakia, Cirotan - Indonezia, some authors (e.g., Harris & Owens, 1971) indicating $Ag_8Sn(S,Te)_6$ as the chemical formula.

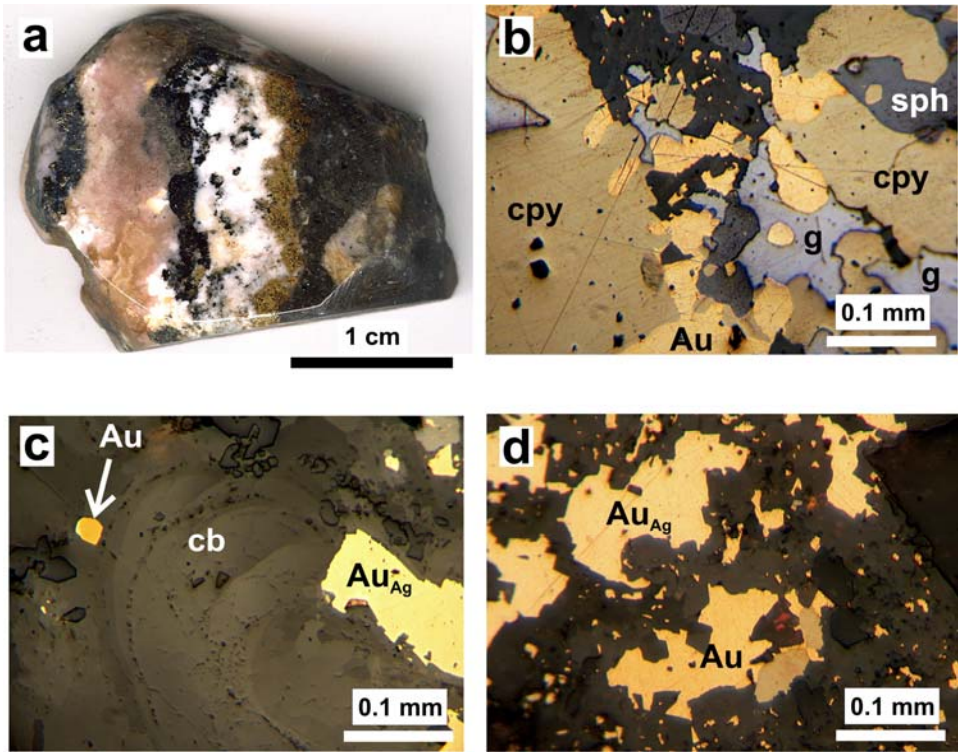

Fig. 3. Gold associations in zoned gold ore, Roşia Montană ore deposit. **a**. Polished section (The „Petrulian Collection") through the parallel-textured gold ore from Roşia Montană 1. gold zone; 2. quartz and carbonate zone; 3. sulfides and gold zone; 4. manganese carbonate zone. **b.** gold (Au) associated with sulfides: chalcopyrite (cpy) appears yellowish-green in comparison with the bright yellow gold; g = galena (parallel nicols). **c** and **d.** (parallel nicols): Silver-rich gold (Au_{Ag}) is light yellow whereas pure gold is dark yellow; image **c** presents the association between native gold and carbonates with a collophorm texture (cb).

Another discovery is an extremely rare mineral found in the intergrowth area between gold and quartz-carbonate gangue. This is a member of *pirquitasite* (Ag_2ZnSnS_4) – *hocartite* (Ag_2FeSnS_4) series. It appears as clear pleochroic grains, with brown-gray tints (Fig. 5a,b), with a strong anisotropy in various colors: brown-reddish-gray to brilliant green (Fig. 5c,d). We believe the optical properties can be assigned to *pirquitasite*, an observation sustained also by the frequent red internal reflections and by the presence of Zn in the XRF spectral analysis.

In the same gold band, closely associated with quartz and carbonate gangue where canfieldite appears, *achantite (argentite)* - Ag_2S and *polybasite* $(Ag,Cu)_{16}Sb_2S_{11}$ – *pearceite* $(Ag,Cu)_{16}As_2S_{11}$ were identified. *Argentite* may be distinctly observed, in quasi-euhedral gray-green grains, strongly affected by light and without any anisotropy (Fig. 4a, d). All observations sustain the occurrence of argentite, signifying a higher temperature phase (179^{o} C). The central parts of argentite grains, have a purple tint, are intensely altered by light, and may represent *jalpaite* (Ag_3CuS_2) – which is also sustained by the presence of copper in the XRF analysis. As far as *polybasite-pearceite* is concerned, the optical characteristics and the presence of Sb in the XRF analyses sustain mainly the first term of the series (Fig. 5a, b).

Reflected-light microscopy has revealed another peculiar characteristic, that is the existence of two types of gold in the analyzed polish section (Fig. 3, a): the prevalent gold-type is a light yellow silver–rich variety (Fig. 3, d) which is intergrown with all the minerals of the „gold–related zone". The second gold type has a clear yellow color, is less frequent, and associated with carbonate minerals (see Fig. 3, d).

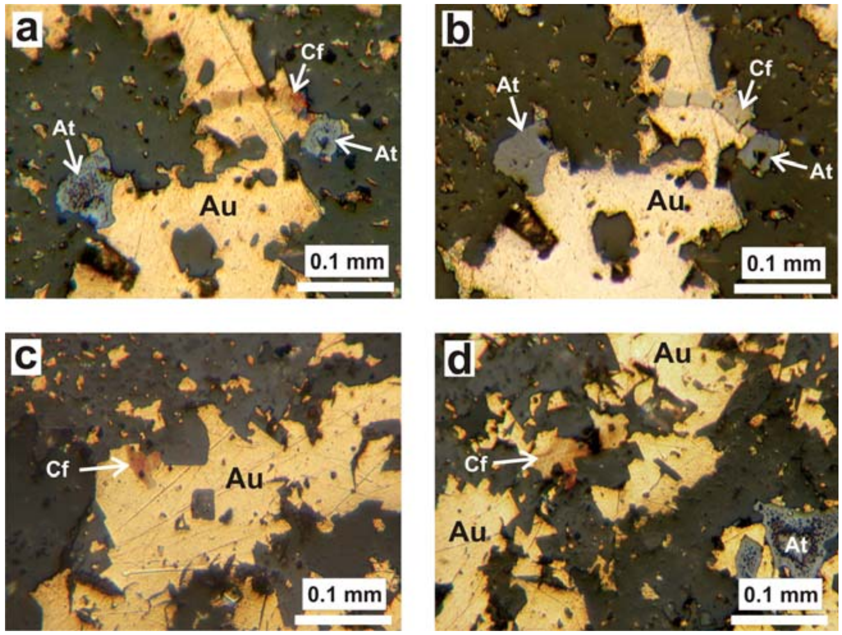

Fig. 4. Silver-rich gold with canfieldite and argentite. Polished section, parallel nicols; **a.** Tarnished polished section. Brownish canfieldite (Cf) is cross-cutting a gold grain; zoned argentite (At) is also present. **b.** The image of the same visual field after the tarnish was polished away. It is of note the light gray color with creamy tints of canfieldite and the white-yellowish color of silver-rich gold. **c** and **d.** Tarnished polished section. Gold grain (Au) including canfieldite (Cf). Zoned argentite (At) occurs in image d.

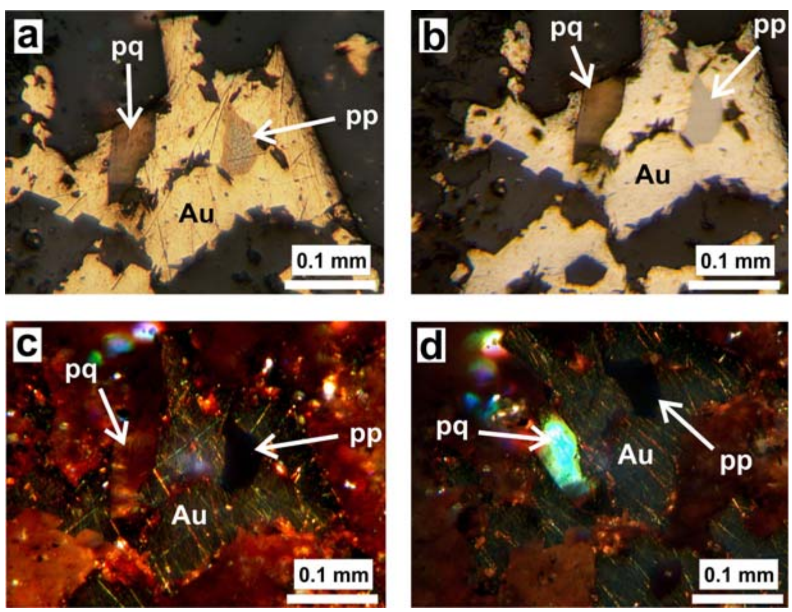

Fig. 5. Silver-rich gold (Au) with pirquitasite (pq) and polybasite-pearceite (pp). Reflected light. a and b: parallel nicols; c and d: crossed nicols. Microscopic images of intergrowths between silver-rich gold, pirquitasite and polybasite-pearceite. **a.** brown-gray colored pirquitasite and zoned polybasite-pearceite (more tarnished in the central part of grain); a weak-brownish tint can be seen towards the margins, probably where the pearceitic term occurs. **b.** The same visual field after a fresh polish: the light color of silver-bearing gold and the clear brown color of pirquitasite are visible, polybasite-pearceite are recognized by a standard gray color with a weak creamy tint. **c.** Pirquitasite with brown-reddish color and many internal reflections. **d.** The same view with partially crossed nicols, showing a green color of pirquitasite with local reddish internal reflections.

The paragenetic relationship suggests that the first gold type is of older generation, in association with pyrite, polybasite, argentite, canfieldite, quartz and „adularia" gangue, whereas the second type is younger, associated only with collophorm carbonates (Fig. 3, c).

6. Conclusions

For the time being, the preliminary data referring to the genesis of this association are the following:

- The mineral assemblage of Roşia Montană probably contains two new tin-sulfosalts: *canfieldite* and *pirquitasite*; the later one is now mentioned for the first time in Romania.
- The described minerals occur in parallel-zoned texture, exclusively together with an intergrowth between gold and quartz - „adularia" gangue. These are probably generated in an earlier, higher temperature mineralization phase.
- Gold intergrown with carbonates represents a late phase, the latter being newer than quartz. No tin minerals were found in the sulfide and native gold band of the investigated polished section; only silver-rich gold, galena, chalcopyrite, sphalerite, tetrahedrite and pyrite occur in that band suggesting a distinct phase of mineralization.
- These data may prove useful for the archaeological research, suggesting that the existence of tin may not be an irrefutable evidence for the provenance of gold from placer-type deposits, as inferred by Constantinescu et al. (2008). The presence of canfieldite suggests the primary deposits of the Apuseni Mts. as another possible source. This would imply that the Dacian gold was not necessarily obtained by panning, but also by mining.

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