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THE GEOCHEMICAL SIGNATURE OF NATIVE GOLD FROM ROŞIA MONTANĂ AND MUSARIU ORE DEPOSITS METALIFERI MTS. (ROMANIA); PRELIMINARY DATA

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Abstract: The main components of gold alloys (Au-Ag-Cu) as well as related trace elements (Sn, Te, Sb, Hg, Pb, Platinum Group Elements - PGE) are very important to authenticate archaeological gold artifacts. In order to find the provenance of ancient gold artifacts found on the Romanian territory we attempted to understand if a chemical-elemental signature exists for Romanian gold. Several analytical methods were used to investigate gold ores and gold artifacts, such as the electron microprobe, scanning electron microscopy (SEM), micro synchrotron radiation induced X-ray fluorescence (micro-SR-XRF). Among the goals of the study was to demonstrate that micro particle induced X-ray emission (micro-PIXE) could be a useful tool in establishing the origin of gold ancient artifacts.

Key words: gold artifacts, micro-PIXE, Roşia Montană, Musariu, polished samples, maps.

1. INTRODUCTION

Native gold is rarely pure, as it often contains closely related metals such as silver and copper, especially. Other elements which are detected in minor amounts in native gold are the PGE and elements contained in the minerals associated with gold within the hydrothermal ores, i.e. Pb, Zn, Sb, Hg, Te, Bi, As, etc. By now the research indicates a topomineral or even a local specificity of gold composition, mainly concerning the Au/Ag or Au/Ag/Cu ratios. For example, the silver content in gold increases with depth; in the case of copper, the contents depend on the metallogenetic context. There are significant contents for copper in gold within the sulfur ore deposits in the southern part of the Ural Mts. and also in the Norilsk type ore deposits, (Petrovskaia, 1973).

As for Romania, only scarce data on the silver, copper and other elements in native gold are available. The existing analytical data are mainly from the processing activity, where a preoccupation for gold and silver refining exists. This is expressed by fineness; ad expresses a goal to reduce impurities to below the specification limits allowed for the two metals (Davey, 1985 in Gasparrini, 1993). For example, gold from Săsar ore - Baia Mare district is rich in silver, with Au/Ag ratio from 1/5 to 1/100; in Dealu Crucii ore deposit the gold fineness is about $650^{0}/_{00}$. The fineness of the native gold is homogeneous for all the vein fields of the Săsar area: Aurum $725^{0}/_{00}$, Sofia $675^{0}/_{00}$, Valea Roşie 610 – $755^{0}/_{00}$, Adam – Cremenea 725 – $750^{0}/_{00}$, Wilhelm 705 – $745^{0}/_{00}$, Borzaş 730 – $785^{0}/_{00}$, (Damian et al., 1996).

It seems that in the Metaliferi Mts. gold has larger fineness: in the Musariu ore deposit, the gold fineness in Ana vein is about $800^{0}/_{00}$, in Brădişor ore deposit is $800^{0}/_{00}$ too and in Stănija ore deposit is $900^{0}/_{00}$. In the South Carpathians the gold fineness is about $905^{0}/_{00}$ for the occurrences Valea lui Stan and Pianu de Sus, (Brana, 1958).

We strongly emphasize that these data are too general to be important for estimating the origin of gold sources from the archaeological sites in Romania.

Data concerning to the specificity of gold composition, is also poor especially in terms of variation, both at ore deposit and vein scales. A good example in this respect is the Roşia Montană ore deposit.

2. GEOLOGICAL REMARKS

In Romania there are two sources of ancient native gold: the Apuseni Mts. and the South Carpathians. We now present some preliminary data referring to the geochemical signature of native gold from Roşia Montană and Musariu ore deposits.

Native gold accounts for the majority of the Au-Ag ore deposits in the Metaliferi Mts., Romania. The most important and renowned metallogenetic unit of Romania is the Neogene province of Apuseni Mts., also known as morphological unit of the “Metaliferi Mountains” or, form a geographical-metaphoric point of view – the “Golden Quadrilateral”.

By now there is only a general knowledge of the elements that may be contained in native gold, especially Ag and Cu. The most common way to mention this is the fineness, expressed in parts per thousand. In order to establish a particular feature of gold, our study investigates also other chemical elements occurring in gold. Samples from Roşia Montană and Musariu ore deposits (Metaliferi Mts., Romania) were investigated for Ag, Cu, Te, Sb, Zn, Fe, Mn contents. These deposits yielded the most significant amounts of gold in the Metaliferi Mts.

Tămaş et al., (2006) carried out a SEM and back-scattered-electron (BSE) study on Au-Ag alloys from Cârnic massif – Roşia Montană where compositions around $Au_{0.76}Ag_{0.23}$ were obtained.

Gold and silver were found by SEM and electron microprobe in the samples from Roşia Montană (Orlea gallery +755m and in Racoşi gallery, Cetate open pit). Both samples were found as electrum, with Au>Ag and Ag>Au respectively. In association with sphalerite, electrum has a higher gold content: $Au_{0.6718/}Ag_{0.3038}$ and in association with chalcopyrite, electrum presents different Au/Ag ratios: $Au_{0.7369/}Ag_{0.2661}$

but also $Au_{0.40}/Ag_{0.60}$ (Luisa Iatan, unpublished data).

The gold artifacts recovered from archaeological sites could be authenticated based on the ratios between the three main components of gold alloys (Au-Ag-Cu) and on the trace elements (Sn, Te, Sb, Hg, Pb, Platinum Group Elements - PGE). In order to find the provenance of ancient gold artifacts found on the Romanian territory we attempted to understand whether an elemental signature exists for Romanian gold.

Several conditions are necessary to authenticate and to study the provenance of gold artifacts:

1. The composition of a gold source remained unchanged in time.
2. It is possible that some gold to other elements ratios could change depending on the analytical techniques used for the determination of gold in ores. For example, the assay of gold ores was used by Romans and was further improved during the middle Ages. The fire assay method is applied today in the determination of silver, gold, PGE, lead, copper, tin and mercury. There is a good agreement between the data obtained through microanalytical studies and those of the fire assay, but there are exceptions too, (Bugbee, 1981 in Gasparrini, 1993).
3. In the processes of gold extraction, the ratios between gold and other original components of the primary ore could change. So, the question is whether other indicators exist, that are less prone to be modified during gold processing.
4. The techniques should be sensitive and non-destructive in order to analyze the trace elements and to study the gold artifacts.

3. NEW PHYSICO–CHEMICAL METHODS APPLIED IN ARCHAEOLOGICAL STUDIES

Several analytical methods were used to investigate gold ores and gold artifacts, like the electron microprobe, scanning electron microscopy (SEM), micro Synchrotron Radiation induced X-Ray Fluorescence (micro-SR-XRF) and micro Particle Induced X-Ray Emission (micro-PIXE).

Constantinescu et al., 2008 investigated several fragments of the so called “Transylvanian gold” using micro-SR-XRF and micro-PIXE. The results obtained for native gold were later used to authenticate five spiraled gold Dacian bracelets. The elemental analyses performed on Transylvanian native gold by micro-PIXE and also micro-SR-XRF show 8-35% Ag, 6200 ppm Cu, 200-600 ppm (μg/g) Sn, 100-250 ppm (μg/g) Sb and 600-800 ppm (μg/g) Te.

For the present work micro-PIXE on Roşia Montană and Musariu polished samples were performed at the AN2000 accelerator of Laboratori Nazionali di Legnaro, INFN, Italy. The experiment was carried out with a 2 MeV proton microbeam (9 μm^2 beam area), maximum beam current ~ 400 pA. The characteristic X-rays were measured with a Canberra HPGe detector (with 180 eV FWHM at 5.9 keV). A Mylar filter (52 μm thickness, 11% hole) in front of the X-ray detector was used to reduce the intensity of the peaks in the low spectral region (below 4 keV). 1mm x 1mm maps and point (20 μm diameter) spectra were acquired. The quantitative analysis of the X-ray spectra was performed using GUPIXWIN software. More details about the AN2000 micro-PIXE experimental facility are given in Boccaccio et al. (1996).

PLATE I

GOLD FEATURES IN ROŞIA MONTANĂ ORE DEPOSIT

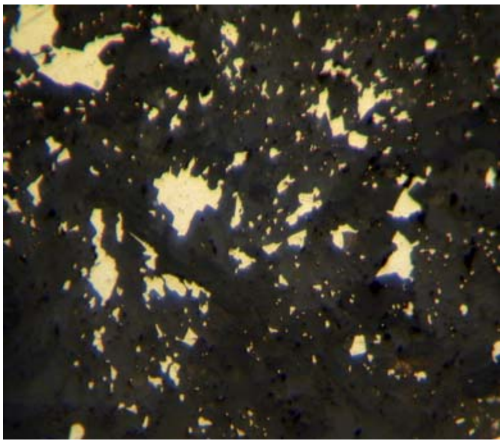


Figure 1. Native gold associated with carbonate minerals

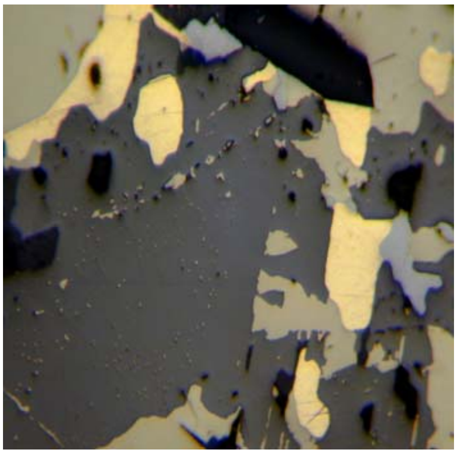


Figure 2.

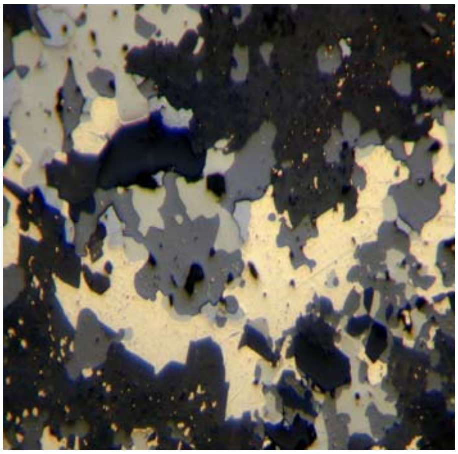


Figure 3.

Figure 2, 3. Native gold with galena, chalcopyrite and quartz (two examples)

Microscopic images, NII, 40X (*Panphot Leitzer, Nikon Eclipse*)

PLATE II

GOLD FEATURES IN MUSARIU ORE DEPOSIT

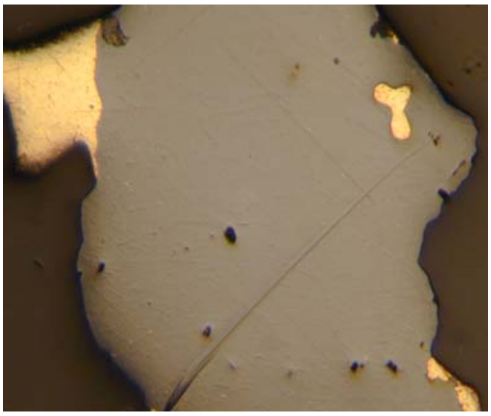


Figure 1. Native gold enclosed and bordered of sphalerite

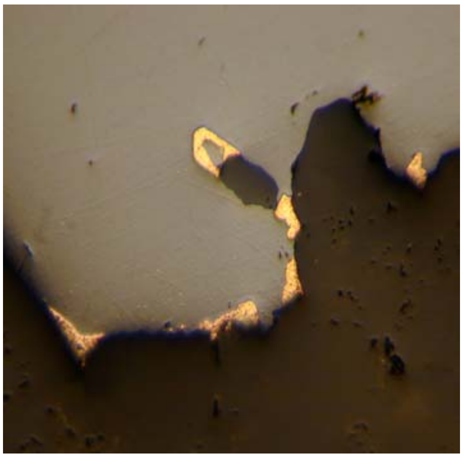


Figure 2. Native gold at the border of sphalerite and quartz

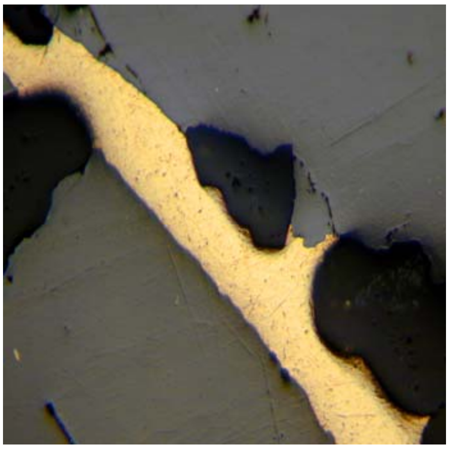
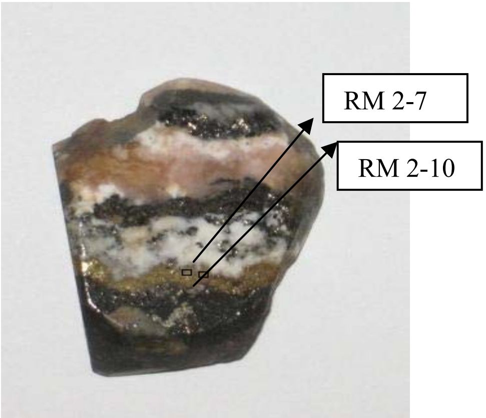


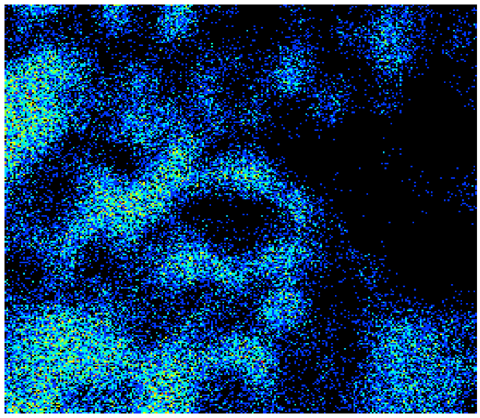
Figure 3. Native gold between quartz grains

Microscopic images, NII, 40X (*Panphot Leitzer, Nikon Eclipse*)

PLATE III

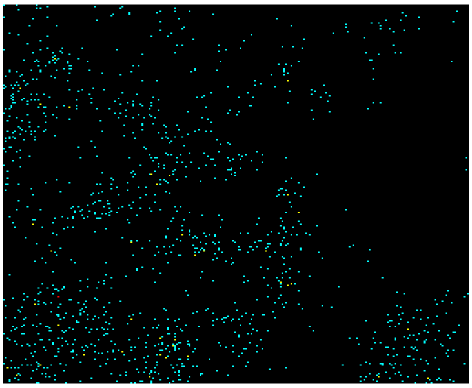
ROŞIA MONTANĂ (RM 2-10)



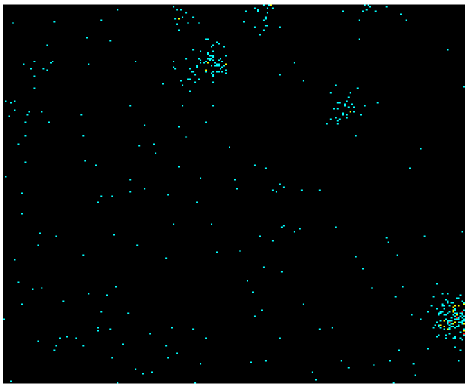


Au

Figure 1. Polished sample 1X, Roşia Montană ore deposit
There are the two areas where the Au, Ag, Cu contents were analyzed.



Ag



Cu

Figure 2. Au, Ag and Cu distribution in the RM 2-10 area (see Fig. 1, Plate III)

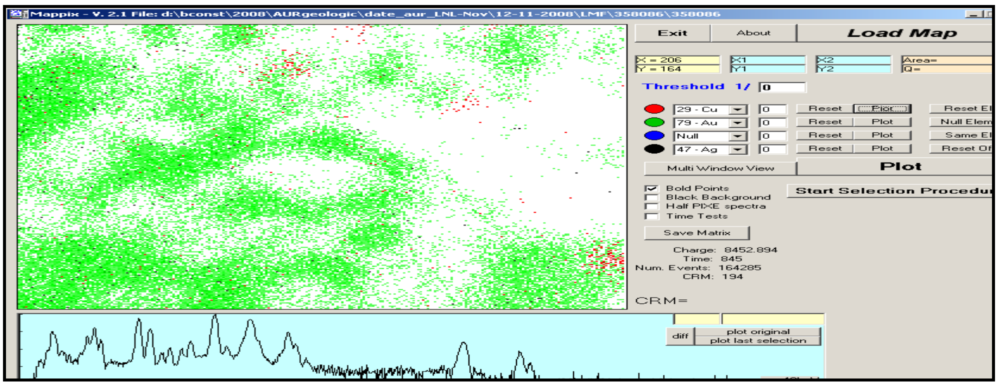
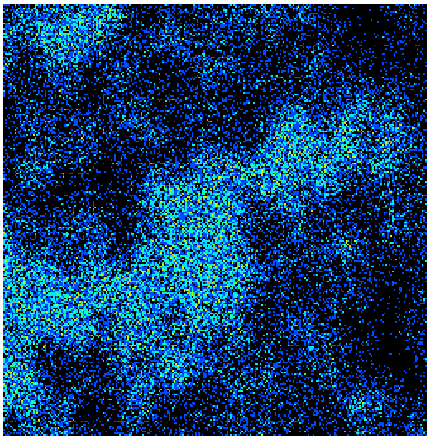
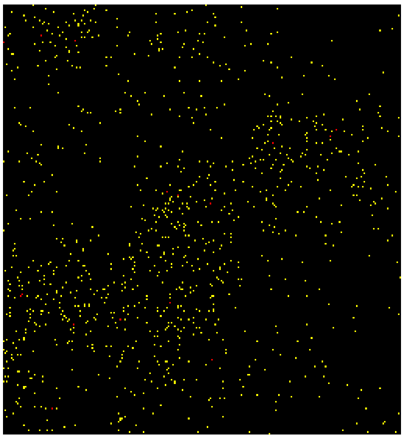


Figure 3. Integrated map of Au, Ag and Cu distribution from the Fig. 2, Plate III

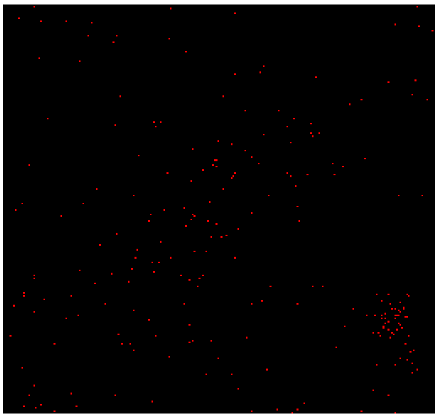
ROŞIA MONTANĂ (RM 2-7)



Au



Ag



Cu

Figure 1. Au, Ag and Cu distribution in the RM 2-7 area (see Fig. 1, Plate III)

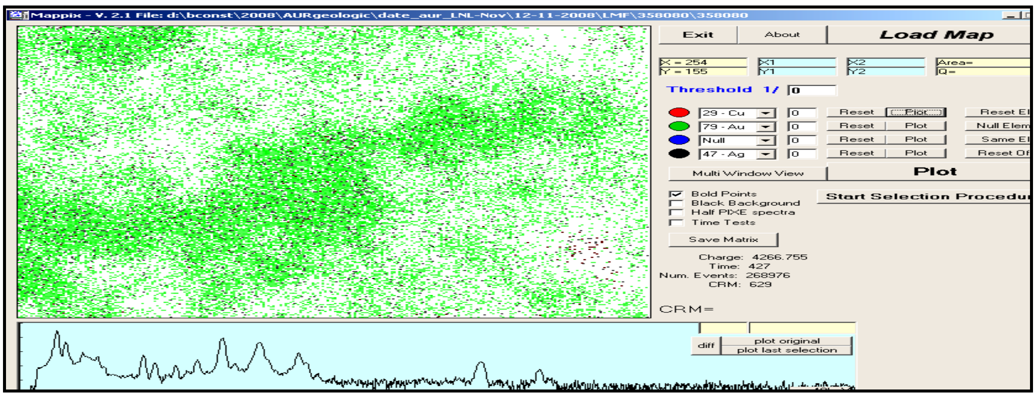
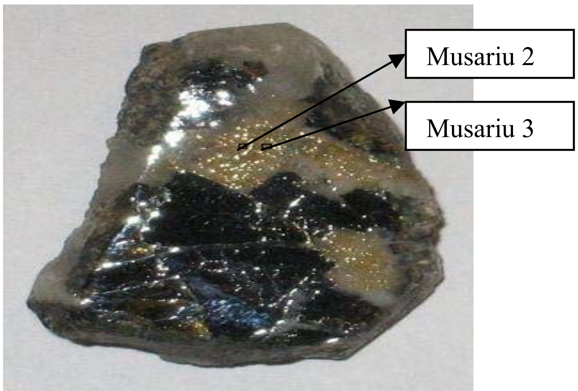
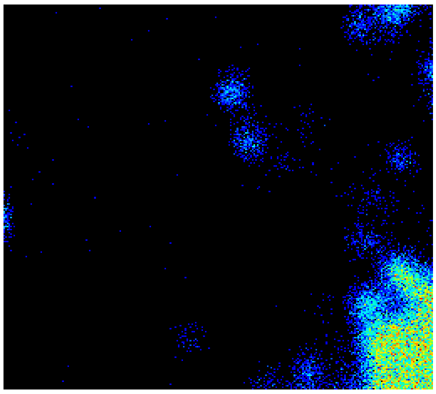


Figure 2. Integrated map of Au, Ag and Cu distribution from the Fig. 1, Plate IV

PLATE V

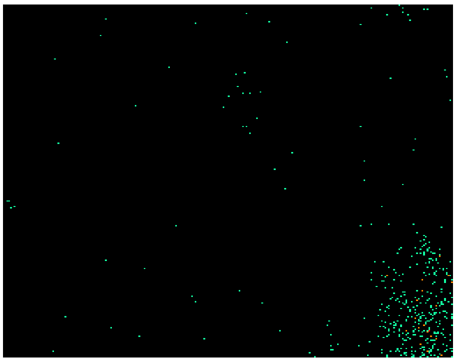
MUSARIU 2



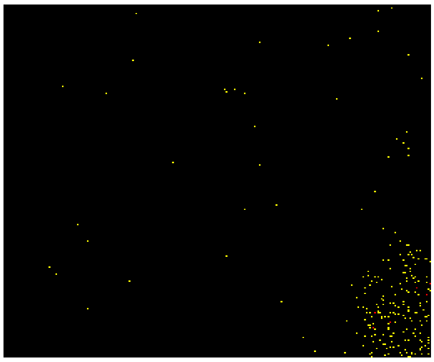


Au

Figure 1. Polished sample 1X, Musariu ore deposit
There are the two areas where the Au, Ag, Cu contents were analyzed.



Ag



Cu

Figure 2. Au, Ag and Cu distribution in the Musariu 2 area (see Fig. 1, Plate V)

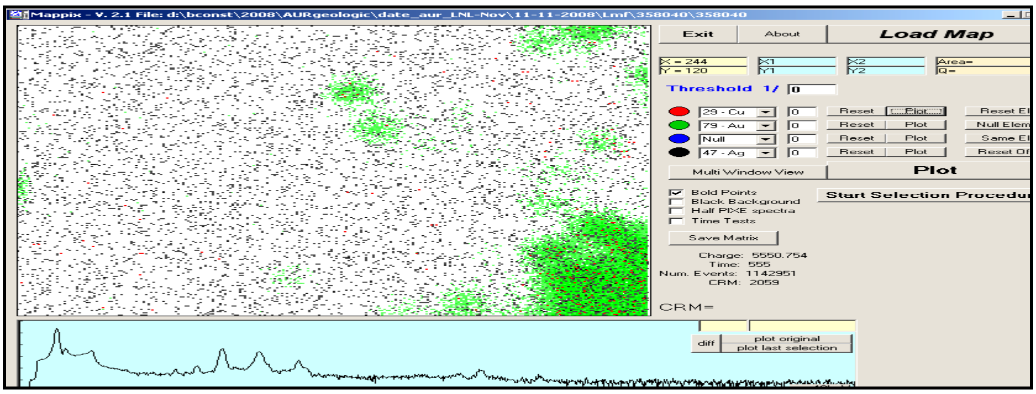
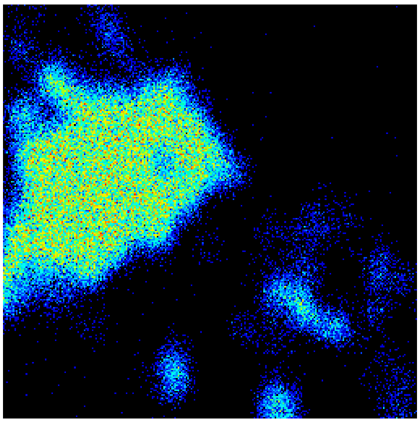


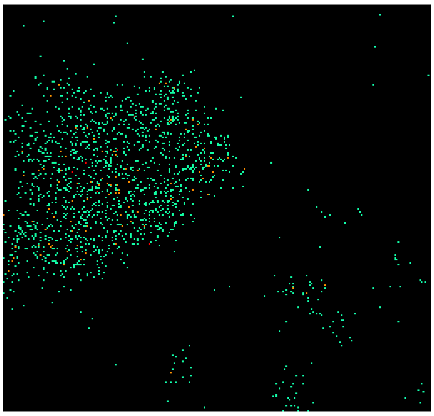
Figure 3. Integrated map of Au, Ag and Cu distribution from the Fig. 2, Plate V

PLATE VI

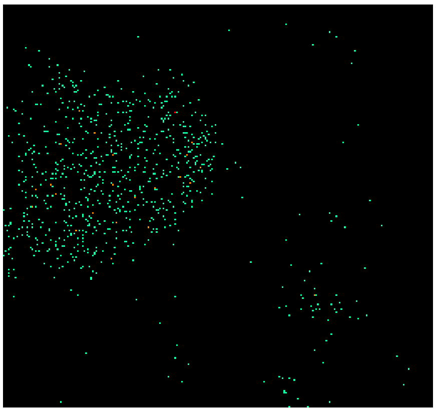
MUSARIU 3



Au



Ag



Cu

Figure 1. Au, Ag and Cu distribution in the Musariu 3 area (see Fig. 1, Plate V)

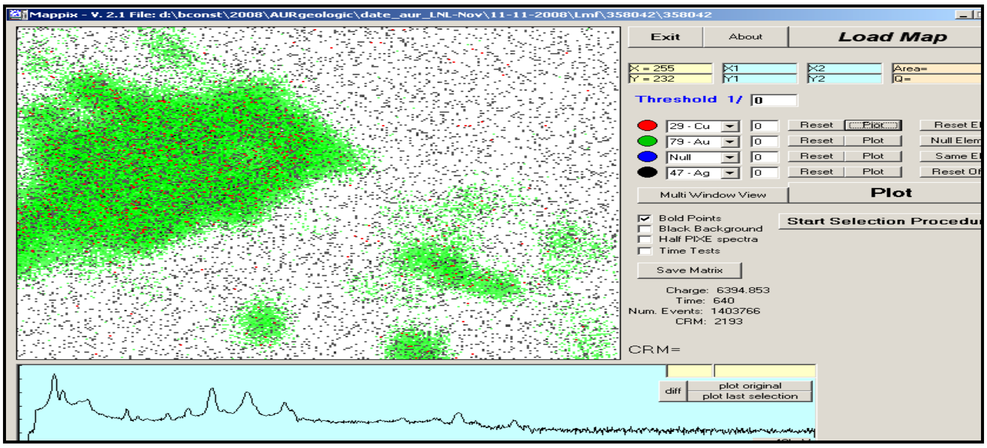


Figure 2. Integrated map of Au, Ag and Cu distribution from the Fig. 1, Plate VI

4. RESULTS

Roşia Montană

Polished samples were obtained from a sample from Roşia Montană ore deposit, where a native gold band could be macroscopically seen (Fig 1, Plate III). Gold occurs also like native gold in carbonate minerals (Fig. 1, Plate I), or associated with galena, sphalerite, chalcopyrite and quartz (Fig. 2, 3, Plate I).

The Au/Ag ratio obtained by micro-PIXE experiment is very different from a point to another: 53.58/16.30 on maps RM 2-10 (Fig. 3, Plate III); 34.60/10.78 on maps RM 2-7 (Fig. 2, Plate IV); 13.83/3.75 on maps 7RM-4; 34.60/10.53 on maps 9RM-6. On the maps a weak presence of copper in the gold region in comparison with silver may be observed (Fig. 2, Plate III and Fig. 1, Plate IV). Gold and silver are strongly mixed. On the outlying gold grains there are Sb, Te, Zn and also Ag-rich areas.

Musariu

In the Musariu ore deposit (Fig. 1, Plate V) the reflected-light microscopy shows native gold distributed at the border of sphalerite (Fig. 1, Plate II), native gold enclosed and along the margins of sphalerite (Fig. 2, Plate II) and native gold between quartz grains (Fig. 3, Plate II).

The Au/Ag/Cu ratio is strong variable: 3.24/0.42/0.0027 on maps Musariu 3; 6.05/1.32/0.0217 on maps Musariu 2 (Fig. 3, Plate V), 19.13/4.19/0.0078 on maps Musariu 3 (Fig. 2, Plate VI). In the case of the Musariu ore deposit gold, silver and copper are evidently mixed; a strong presence of copper is observed (Fig. 2, Plate V, Fig. 1, Plate VI). A significant amount of Si (quartz) was observed surrounding the gold grains. On the distribution map, Zn-rich areas are observed, beside Au, Sb, and less Ag. There are some metallic Cu-points, Fe-points (pyrite), Pb-points (galena), Mn-points (alabandine) and native As-rich points.

5. CONCLUSIONS AND DISCUSSIONS

One of the main features observed is the strong variation of the Au-Ag ratio both in Roşia Montană and Musariu ore deposits. Secondly, a significant amount of copper in Musariu was observed, in comparison with Roşia Montană. Thirdly, the silver concentration is larger in Roşia Montană than in Musariu ore deposit, most probably in connection with the deeper and older mineralization in Roşia Montană.

As for the possibility to use these data in archaeology the Au/Ag ratio alone or even the Au/Cu ratios cannot clarify the origin of gold; other microanalytical data concerning other elements, i.e. Sb, Bi, Te, Pt and PGE are necessary.

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