

SOME APPLICATIONS OF X-RAY BASED ELEMENTAL ANALYSIS METHODS FOR STUDIES ON ROMANIAN GOLD MINERALS

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Abstract. Geological characterization of native gold – primary and alluvial – is very important for gold archaeological objects authentication. The values of ratios between native gold alloy main components (Au-Ag-Cu) as well as some traces elements (Sn, Te, Sb, Hg, Pb, Platinum Group Elements – PGE) – “fingerprints” for Transylvanian mines and placers – are used to determine the provenance of ancient gold items found on Romanian territory. Two samples – polished sections – from Rosia Montana and Musariu ore deposits were investigated using complementary analytical techniques: X-Ray Fluorescence (XRF), micro – Proton Induced X-Ray Emission (micro-PIXE), micro-Synchrotron Radiation induced X-Ray Fluorescence (micro - SR-XRF). Results concerning Au-Ag-Cu native alloy composition, the presence of specific trace elements as Te, Sb, Sn, but also associated minerals – quartz and metallic sulfides – are presented.

Key words: XRF, micro-PIXE, micro-SR-XRF, gold, minerals, elemental composition.

1. INTRODUCTION

The elemental composition of gold, gold minerals and gold associated minerals gives important information from both scientific (geologic) and economic point of view, referring to metallogenesis, minerals content in gold and their exploitation activity [1].

We focused on two samples – polished sections – from Rosia Montana and Musariu ore deposits – see Figs. 1 and 2 – from the so-called “Transylvanian gold quadrilateral” of Metaliferi Mountains. The samples were studied, using reflected light microscopy, with a Panphot Microscope equipped with an automatic Nikon Eclipse camera E-400, 40 W. The polished section was placed on the stage of the microscope and preliminarily observed in plane-polarized light by interposing one

polarizer (nicol). The final examination was performed with inserting two nicols at 90^0 . In the Rosia Montana sample, beside the native gold band which could be seen macroscopically, gold also occurs like native gold in carbonate minerals, or associated with Galena, Sphalerite – ZnS, Chalcopyrite – Cu FeS₂, and Quartz – SiO₂ (Fig. 3) [2].

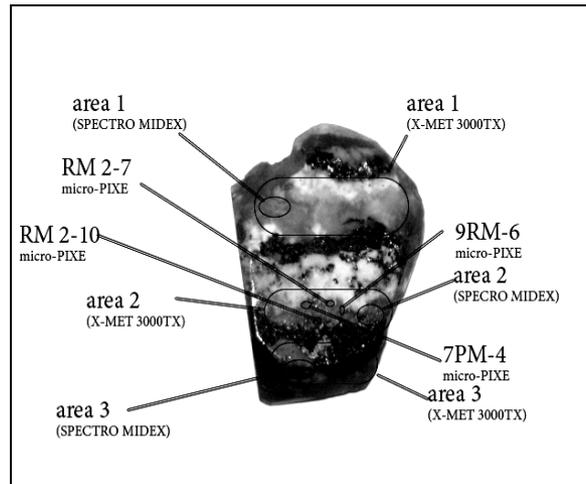


Fig. 1 – Rosia Montana sample – areas and points of measurements.

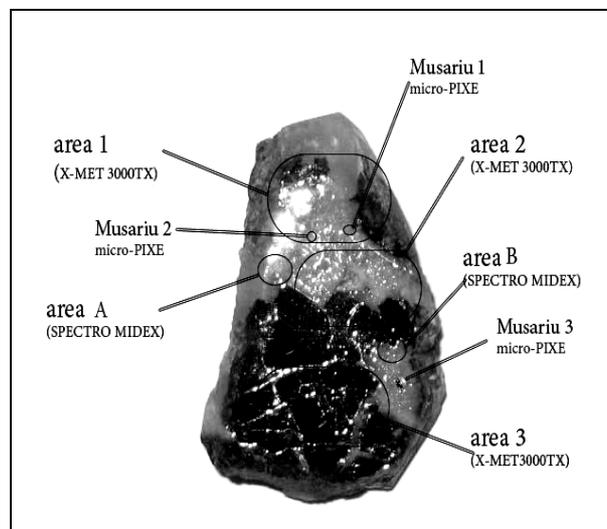


Fig. 2 – Musariu sample – areas and points of measurements.

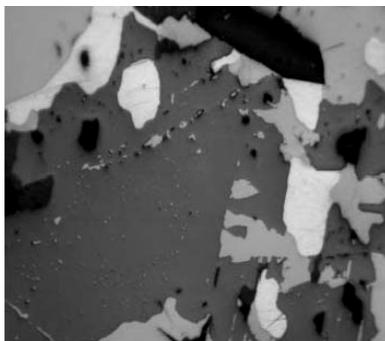


Fig. 3 – Native gold with Galena, Chalcopyrite and Quartz.

In the Musariu sample, native gold is distributed enclosed and along margins of Sphalerite or between Quartz grains (Fig. 4).

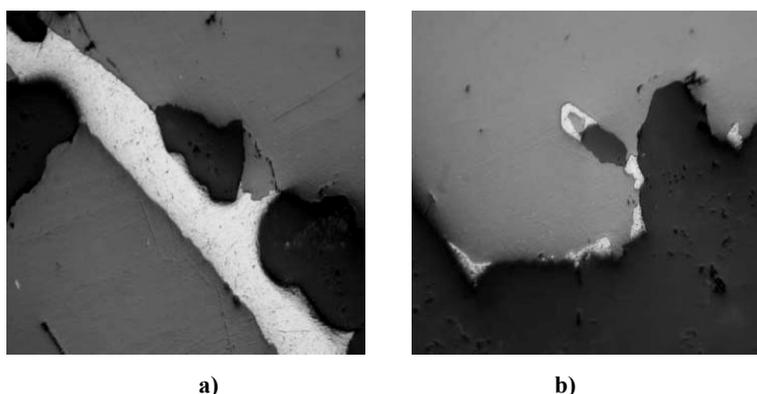


Fig. 4 – Native gold enclosed and bordered in Sphalerite (a) and at the border of Sphalerite (b).

The geological (primary-vein or placer-alluvial gold) provenance of gold artifacts recovered from archaeological sites can be examined using the ratios between the main components of the native gold alloy (Au-Ag-Cu) and the presence of some trace elements as Sn – especially for placers, Te, Sb, Hg, Pb, and Platinum Group Elements (PGE) – Ru, Rh, Pd, Os, Ir, Pt [3, 4]. We tried to investigate whether an elemental “signature” exists for Romanian gold, especially for the Transylvanian gold (Metaliferi Mountains), where the most significant Au-Ag ore deposits exist.

The “Transylvanian gold” is found both as a natural alloy (Au-Ag-Cu) and as gold tellurides. The natural gold alloy has an important content of silver (18 to 36 %) and it is usually called electrum or argentian gold [1]. In the last three years, gold and silver were analyzed by scanning electron microscope (SEM) and electron microprobe in two samples from Roşia Montană (Orlea gallery +755m and Racoşi

gallery, Cetate, open pit). Both samples were found as electrum, with $Au > Ag$ and $Ag > Au$, respectively [5]. Another feature of the “Transylvanian gold” is its small copper content.

The gold tellurides are uncommon. The main gold tellurides are: Sylanite – $(Au, Ag)Te_4$, Krennerite – $(Au, Ag)Te_2$, Petzite – (Ag_3AuTe_2) , Nagyagite – $Pb_5Au(Te, Sb)_4S_{5-8}$, Hessonite – Ag_2Te .

The associated minerals with “Transylvanian gold” are metallic sulphides as Sphalerite, Pyrite – FeS_2 , Galena – PbS , Alabandite – MnS , Arsenopyrite – $FeAsS$, Chalcopyrite – $Cu FeS_2$ and Quartz.

2. EXPERIMENTAL

Three characteristic X-ray based elemental analysis methods were used: X-Ray Fluorescence (XRF), micro-Synchrotron Radiation induced X-Ray Fluorescence (micro-SR-XRF) and micro-Proton induced X-Ray Emission (micro-PIXE).

All these methods require no sample preparation (the samples are measured practically in any shape delivered) – opposite to Scanning Electron Microscopy (SEM) which needs polished specimens – and provide non-destructive, accurate and relatively fast measurements. Sample areas from 1 cm^2 – XRF spectrometers – to a few micrometer diameter (“points”) – micro-PIXE and micro-SR-XRF – can be investigated.

The samples were cut with a circular diamond saw in a dedicated laboratory of the Faculty of Geology. Lubrication of the saw blade was made by water, to prevent specimens heating during cutting. After that, the specimens were cast in a mounting resin to facilitate the handling. Sample thickness is arbitrary but the total thickness of the polished section must not exceed 1 to 2 cm. Once a sample was cut to an appropriate size and cast in a mounting medium, it is ready for grinding and polishing. The purpose of grinding is to remove surface irregularities and casting resin that covers the sample, to reduce the thickness and to prepare a smooth surface by removing any zone of major deformation [6]. Grinding was performed using 600-mesh silicon carbide. Rough polishing, involving the use of a fabric loaded with 15 and 6 micron graded abrasives, removes the remaining zone of surface deformation and the deeper scratches. Final polishing, using less than 6 micron graded abrasives, removes only a very small amount on specimen surface, producing a relatively scratch-free surface. For final polishing, Al_2O_3 suspended in water on a napped cloth is also used.

We used two X-ray tube XRF spectrometers: a portable one – X-MET 3000TX and a stationary one – SPECTRO MIDEX.

For the portable spectrometer, the exciting X-ray beam is generated by a 40 kV tube with Rh-anode. The detection system is a PIN silicon diode detector with Peltier cooling. The resolution of the detector is 270 eV for the K_{α} line of Mn

(5.89 keV). The measurement spot size is about 30 mm². The X-MET XRF analyzer has a Hewlett-Packard (HP) iPAQ personal data assistant (PDA) for software management and data storage.

The stationary spectrometer has a 50 kV Mo-anode tube and a Peltier cooled Si drift chamber detector, with 170 eV resolution for the K_α line of Mn (5.89 keV). The typical diameter of the measurement spot is 0.7 mm, but it can be optimized for different tasks to 0.2 mm, 0.6 mm, 1 mm or 2 mm with four integrated – software controlled – collimators. A double video system with different magnifications is used to determine the exact measurement position in the large sample chamber.

The two gold samples were also analyzed by micro-PIXE at the AN2000 accelerator of Laboratori Nazionali di Legnaro (LNL), INFN, Italy. The experiment was carried out with a 2 MeV proton microbeam (6x6 μm² beam area), maximum beam current ~1000 pA. The characteristic X-rays were measured with a Canberra HPGe detector (180 eV FWHM at 5.9 keV). An Al funny filter (80 μm thick and 8% 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). 2 mm² maps and point spectra were acquired. The quantitative analysis was performed using the GUPIXWIN software. More details about the AN2000 micro-PIXE experimental facility are given in [7].

Complementary experiments on the samples – due the improved condition offered by the high-energy X-rays – focused on Sb, Sn, Te detection were performed at BESSY Synchrotron Radiation Facility, Berlin. During the experiment, point spectra were acquired at 35 keV excitation energy using a spatially resolved synchrotron radiation XRF set-up dedicated to analysis. The beam was focused to a size of 300x150 μm². The gold samples were mounted in air in a special frame for *passé-partouts* on a motorized xyz stage at an angle of 45° to the X-ray beam. Fluorescence signals were collected for 300 s each by an HPGe detector, with no filtering. A video system and a long distance microscope allowed monitoring and selection of samples analyzed points. Relative elemental concentration was determined using a procedure based on different metallic standards (Au, Ag, Cu, Sn). Data analysis was performed by means of the PyMCA software [8].

3. RESULTS AND DISCUSSIONS

As mentioned above, in order to establish the “fingerprint” of the Transylvanian gold, it is necessary to investigate the ratio Au-Ag-Cu and the presence of specific trace elements (e.g.: Te, Sb, Pb for Transylvanian gold; Sn – from Cassiterite – SnO₂, for alluvial gold).

The portable spectrometer was used for a preliminary investigation, providing only a rough sample characterization due to the large measurement spot size (6 mm × 5 mm). The results are summarized in Tables 1 and 3 (see also Fig. 1).

Table 1

Rosia Montana sample – elemental composition – X-MET 3000TX spectrometer

	Au(%)	Ag(%)	Pb(%)	Zn(%)	Cu(%)	Fe(%)	Mn(%)
Area 1	nd	nd	25.2	1.3	6	0.5	57.8
Area 2	14.2	4	1.9	6.8	2.9	5.8	64
Area 3	1.7	2.1	3.1	0.2	0.8	87.1	1.6

For Rosia Montana sample, the Au/Ag/Cu ratio is strongly variable from 14.2/4/2.9 in Area 2 to 1.7/2.1/0.8 in Area 3. As associated minerals, we found Sphalerite, Pyrite, Chalcopyrite, Galena and Alabandite in all three areas, but in different concentrations.

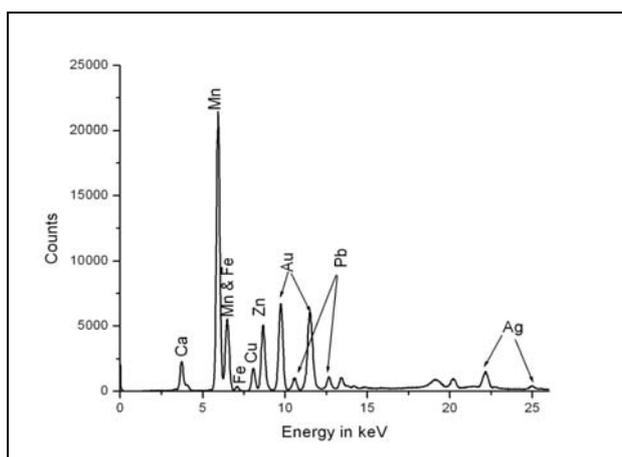


Fig. 5 – The XRF spectrum – Rosia Montana sample – area 2 (X-MET 3000TX spectrometer).

Using the stationary spectrometer, we performed measurements in smaller areas (about 1 mm²) from the same zones (upper – 1, middle – 2, lower – 3, see Fig. 1) as for X-MET analysis – see Table 2.

Table 2

Rosia Montana sample – elemental composition – SPECTRO MIDEX spectrometer (nd= not detected)

	Au(%)	Ag(%)	Cu(%)	Pb(%)	Fe(%)	Mn(%)	Si(%)	Tr
Area 1	nd	nd	nd	nd	3.35	0.15	82.45	Ti, Ca, P, S
Area 2	49.72	11.94	0.1	nd	nd	37.6	nd	Al, S,
Area 3	traces	traces	8.76	52.94	16.78	13.98	0.24	Sb, Ni, Te, S, P

From these measurements, we can estimate as associated minerals:

- in Area 1 – an important quantity of Mn (Alabandite, Rhodonite, Rhodochrosite), but also Si (Quartz) and Pb (Galena)
- in Area 2 – Au and Ag, Mn (Alabandite, Rhodonite, Rhodochrosite), Zn (Sphalerite) and Fe, Cu (Chalcopyrite)
- in Area 3 – Fe (Pyrite), Pb (Galena), Fe and Cu (Chalcopyrite) and Mn (Alabandite, Rhodonite, Rhodochrosite).

The same measurements were performed on the Musariu sample. The results are summarized in Tables 3 and 4 (see also Fig. 2).

Table 3

Musariu sample – elemental composition – X-MET 3000 spectrometer

Musariu	Au(%)	Ag(%)	Cu(%)	Zn(%)	Pb(%)	Fe(%)	Ti(%)
Area 1	10	1.2	nd	86.9	traces	1	nd
Area 2	33.00	23.00	2.40	20.00	0.80	15.00	4.70
Area 3	57.8	16.7	nd	22.7	0.7	1.2	nd

The Au/Ag/Cu ratio is strongly variable from 57.8/16.7/nd in Area 3 (Fig. 1) to 33.00/23.00/2.40 in Area 2. As associated minerals we found for area 1 Sphalerite, for area 2 Pyrite and Chalcopyrite, and for area 3 again Sphalerite.

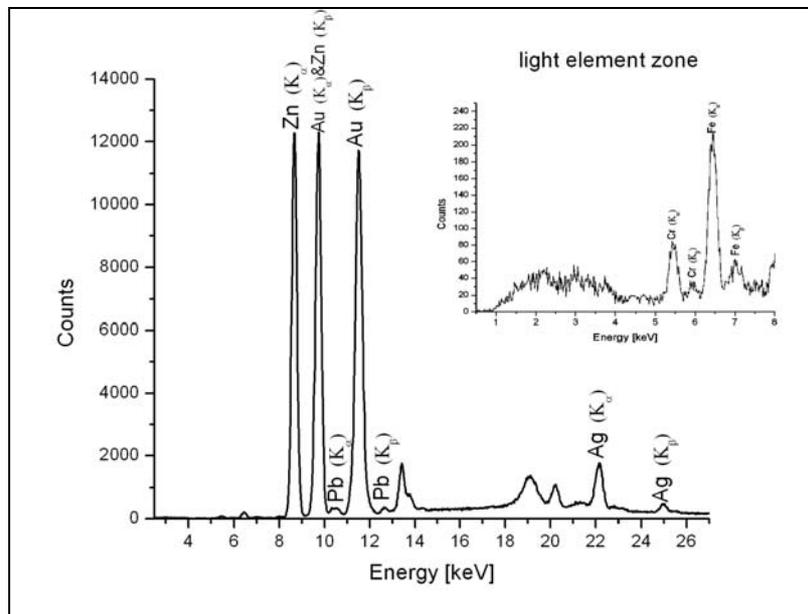


Fig. 6 – The XRF spectrum – Musariu sample – area 3 (X-MET 3000TX spectrometer).

Table 4

The elemental composition, Musariu – SPECTRO MIDEX spectrometer

	Al(%)	Si(%)	S(%)	Fe(%)	Zn(%)	Ag(%)	Au(%)	Traces
Area A	11.1	12.96	3.8	0.71	66.04	0.4	traces	Cd, Cu
Area B	0.77	91.76	0.2	traces	traces	1.88	6.05	K, Ca,

For Musariu sample, the minerals associated with gold (Table 4) are:

- Area A is very rich in Zn (Sphalerite), and also some quartz is present;
- Area B: an important amount of Si (Quartz) is detected.

The preliminary studies were followed by more sensitive investigations: micro-PIXE at Laboratori Nazionali di Legnaro and micro-SR-XRF at BESSY.

For the Rosia Montana sample (Fig. 1), 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; 34.60/10.78 on maps RM 2-7 (Fig. 7); 13.83/3.75 on maps 7RM-4 (Fig. 8); 34.60/10.53 on maps 9RM-6. A low presence of copper in the golden region in comparison with silver is observed. Gold and silver are strongly mixed. On the outlying gold grains Sb, Te, Zn and also Ag-rich areas are present.

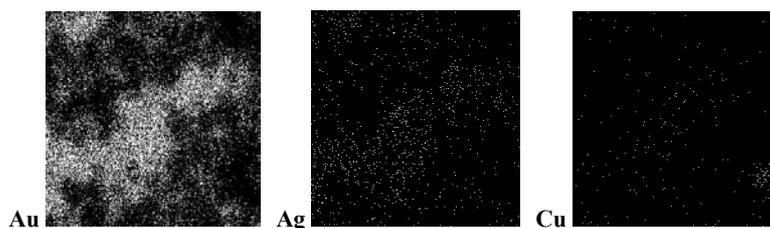


Fig. 7 – Au, Ag and Cu distributions in Rosia Montana RM 2-7 area.

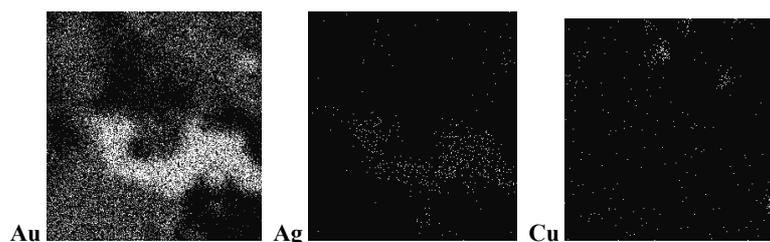


Fig. 8 – Au, Ag and Cu distributions in Rosia Montana 7RM4 area.

For the Musariu sample (Fig. 2), the Au/Ag/Cu ratio is strongly variable from 3.24/0.42/0.0027 (Musariu 1), 6.05/1.32/0.0217 (Musariu 2) to 19.13/4.19/0.0078 (Musariu 3 – see Fig. 9). Gold, silver and copper are evidently mixed; a relatively important presence of copper is observed. A significant amount of Si (Quartz) was

observed surrounding the gold grains. Zn-rich areas are also observed, beside Au, Sb, and – sometimes – Ag zones. There are some metallic Cu-points, Fe-points (Pyrite), Pb-points (Galena), Mn-points (Alabandite) and native As-rich points.

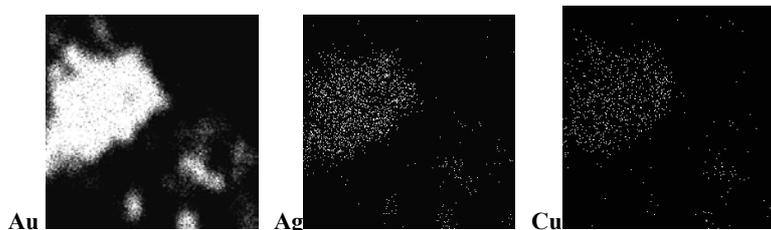


Fig. 9 – Au, Ag and Cu distributions in Musariu 3 area.

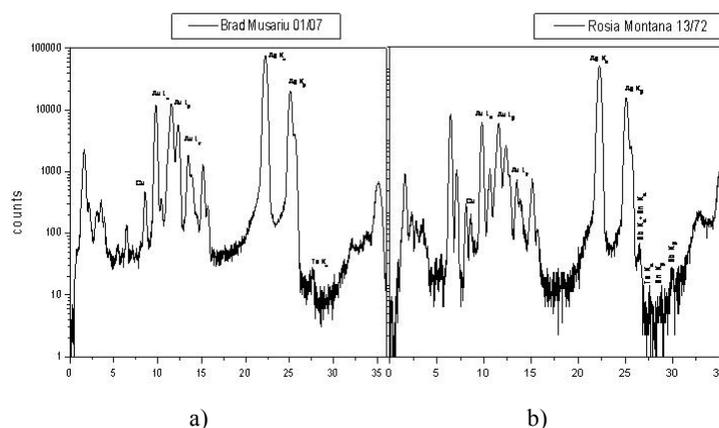


Fig. 10 – Micro-SR-XRF spectra: a) Musariu with Te; b) Rosia Montana with Te, Sn and Sb traces.

A spectrum on a Musariu gold sample obtained at BESSY is shown in Fig. 10a – Te presence clearly observed, while the spectrum from Fig. 10b illustrates the presence of Te, Sn and Sb in a Rosia Montana sample. More examinations are needed to determine the chemical composition of gold tellurides and of antimony (probably mainly associated with silver) compounds.

4. CONCLUSIONS

Together with classical geological investigations based on optical microscopy, the use of complementary X-Ray based analytical techniques – X-Ray Fluorescence (XRF), micro-Proton Induced X-Ray Emission (micro-PIXE), micro-Synchrotron Radiation X-Ray Fluorescence (micro-SR-XRF) – gives the opportunity to perform a complete characterization of gold geological samples. To

definitely solve the problem of identification of Rosia Montana and Musariu deposits as metal sources for manufacturing ancient gold objects more detailed studies are necessary, because the ratios Au-Ag-Cu are strongly variable in both samples. The identification of more trace elements for each gold deposit is also necessary.

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