

MICRO-PIXE AND XRF STUDIES ON NATIVE GOLD
FROM CAVNIC ORE DEPOSIT (BAIA MARE DISTRICT)*

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Micro-PIXE (2 MeV protons at AN2000 accelerator of Legnaro and 3 MeV protons at AGLAE accelerator of CNRS-Louvre) and XRF were used for geochemical characterization of native gold from Cavnica-Roata mine (Baia-Mare district). Elemental composition, Ag/(Au+Ag) ratios, trace elements (Te, Sb) suggesting gold minerals (tellurides) and associated minerals were determined.

Key words: XRF, micro-PIXE, gold, scanning-maps spectra.

1. INTRODUCTION

Cavnica deposit [1] belongs to Baia-Mare metallogenetic district, which is located in the eastern part of the Carpathian belt, one of Europe's major metallogenetic provinces, extending from Slovakia, Hungary and Ukraine to Romania and including important epithermal gold-polymetallic ore deposits. The Baia-Mare district, with about 15 mines, provides most of Romania's lead and zinc and some gold, silver, copper and antimony [2]. The Cavnica deposit – see Figure 1 - is a polymetallic deposit with local Au–Ag enrichments (generally in the upper part of the system) which were selectively mined out in the past. The Cavnica deposit has a long history of mining, probably beginning in Roman times, but the most intense exploitation has occurred during the last 50 years. The deposit has current reserves of 20 million tons of ore with grades of 1 g/t Au, 30 g/t Ag, 1–2% Pb, 1–3% Zn, and 1% Cu [2].

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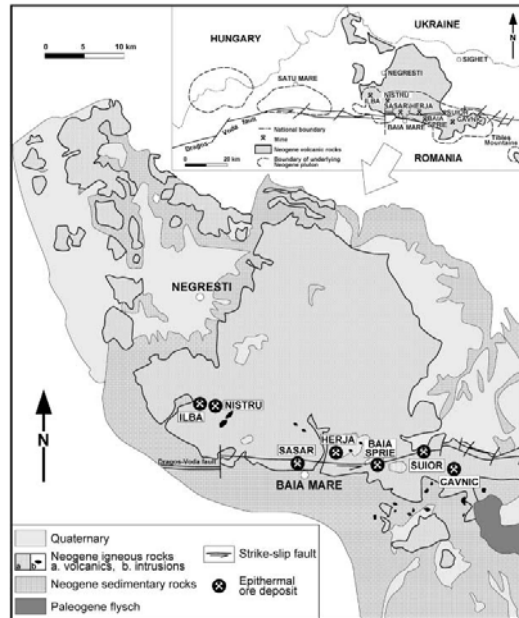


Fig. 1 – Simplified geological map of the Baia Mare district, with the location of the major epithermal deposits [3].



Fig. 2 – Gold samples from Cavnic deposit, Roata mine.

In the frame of our gold archaeometallurgy project – Dacian gold artifacts provenance – PN 91-029, we studied some geological native gold samples from Cavnic deposit - Roata mine – see Figure 2 - which, together with Boldut mine, are

the most important mining units of Cavnic deposit. The purpose of this study is to chemically characterize the Cavnic gold and to compare it with the archaeological gold of Prehistoric and Dacian objects found in Northern Transylvania.

This study was conducted on a total of five samples of native gold (electrum) using two methods based on X-ray elemental analysis:

- XRF (X-Ray Fluorescence) excited by an X-ray tube - using the X-MET TX3000 portable spectrometer at IFIN-HH

- micro-PIXE (micro Proton Induced X-ray Emission) at AN2000 accelerator of Laboratori Nazionali di Legnaro (LNL), INFN, Italy and at AGLAE accelerator of CNRS-Musee du Louvre, Paris, France

to obtain information on:

- electrum structure - values of ratio $Ag/(Au + Ag)$
- presence of gold and silver minerals (tellurides, antimony compounds) – mainly as inclusions
- presence of gold associated minerals – gangue (pyrite, arsenopyrite, sphalerite, galena, quartz, etc.)

2. EXPERIMENTAL

The XRF and micro-PIXE methods require no sample preparation (the samples can be measured practically in any shape delivered), which is their major advantage in such studies. For the X-MET TX3000 portable spectrometer, the exciting X-ray beam is generated by a 40 kV – Rh anode tube. 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 spectrometer has a Hewlett-Packard (HP) iPAQ personal data assistant (PDA) for software management and data storage [4].

For micro-PIXE at AN2000 accelerator of Laboratori Nazionali di Legnaro (LNL), INFN, Italy, a 2 MeV proton microbeam (6 μm x 6 μm beam area), maximum beam current ~1000 pA was used [5]. 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 mm x 2 mm maps and point spectra were acquired. The quantitative analysis was performed using the GUPIXWIN software [6].

At AGLAE accelerator of CNRS-Musee du Louvre, Paris, France, the experiment was carried out with a 3 MeV proton microbeam, roughly 50 μm diameter, extracted into air. Only point measurements (no scanning) were made. The X-ray spectra were acquired for a fixed dose, corresponding to an irradiation with a 10 nA beam current for about 15 minutes. For the characteristic X-rays acquisition, two Si(Li) detectors were used: low-energy (1-10 keV) - for the determination of matrix elements (Au, Ag, Cu) and high-energy (5-40 keV) - for trace-elements (Sn, Sb, Te) determination. To reduce the high contribution of Au L

X-ray lines in the X-ray spectra and the sum peaks interfering with the signals of elements neighboring Ag K X-ray lines, the measurements were performed using a 75 μm Cu filter in front of the high-energy Si(Li) detector. The elemental concentrations were obtained by processing the spectra with GUPIXWIN code. Specifically, the quantification was performed in two steps, using a link to a so-called pivot element (Ag) appearing both in low- and high-energy spectra. In the first step, the major constituents of the samples were derived from the low-energy spectrum; their concentrations were constrained to sum up to 100%. In the second step, the high-energy spectrum was processed with Ag as an internal standard and using the matrix determined in the first step. This very reliable procedure, totally independent of geometrical factors and the accumulated beam charge, was checked by analyzing two gold standards from Comptoir Lyon Allemand Louyot & Co., namely standard 6917 (76% Au, 17% Ag and 6% Cu) and standard 6905 (75% Au, 6% Ag, 19% Cu) [7].

3. RESULTS AND DISCUSSIONS

A preliminary investigation on the samples was performed by XRF using X-MET TX3000 portable spectrometer - in the laboratory of archaeometry at IFIN-HH, measuring in different areas (about 30 mm²) for each sample to observe differences in composition from one area to another - see Table 1.

The most important results are:

- the ratio Ag/(Au/Ag) varies from 0.31 to 0.50, which means a high-silver electrum, practically similar to Rosia Montana and Musariu gold from Metaliferi Mts. [8].
- the presence of arsenopyrite (FeSAs) in all the samples – see Figure 3.
- the strong presence of wurtzite (Zn,Fe)S and sphalerite (ZnS) in sample 4
- the appearance of traces of Sb and Te in samples *Cavnic-Roata 1* and *2* – see Figure 3.

Table 1

Elemental composition of gold samples obtained by XRF

Sample Name	Cavnic-Roata 1		Cavnic-Roata 2		Cavnic-Roata 3	
Area No.	1.1	1.2	2.1	2.2	3.1	3.2
Au%	36.5	40.3	62.3	55.2	48.3	62.3
Ag%	18.7	18.2	31	28.3	24.6	32
Fe%	41.8	37	5.7	14.7	22.7	4.8
Mn%	1.4	1.7	0.1	0.7	3.8	0.3
As%	1.2	2	0.7	0.7	0	0.6
Pb%	> 0.05	0.1	0	0	0.5	0
Cu%	> 0.05	> 0.05	0.1	0.05	> 0.05	> 0.05

Table 1 (continued)

Cr%	0.1	0.1	0.1	0.1	0.05	0.2
Sb%	0.05	0.05	0.1	0.1	0	0.1
Te%	0.05	0.05	0.1	0.1	0	0.1
Zn%	0	0	0	0	0	0
Sample Name	Cavnic-Roata 4				Cavnic-Roata 5	
Area No.	4.1	4.2	4.3	4.4	5.1	5.2
Au%	8.6	13.9	46.5	38.8	65	35.9
Ag%	2.3	12.4	24.5	39.5	27.3	54.7
Fe%	7.9	19.2	12.3	8.4	3.1	9.4
Mn%	0.9	4.1	2.9	0.2	0.6	0
As%	0.6	0	0.4	5.2	0.3	0
Pb%	0.7	1.9	1.9	1	> 0.05	> 0.05
Cu%	0	0.05	0.05	0.05	0.1	0.1
Cr%	0.1	0.3	0.4	0.1	0.1	0.1
Sb%	0	0	0	0	0	0
Te%	0	0	0.05	0	0	0
Zn%	78.8	41.1	9.6	8.2	3.7	0.1

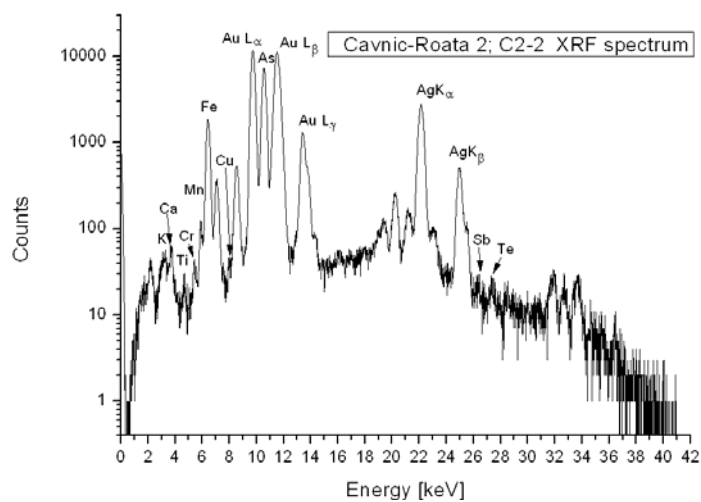
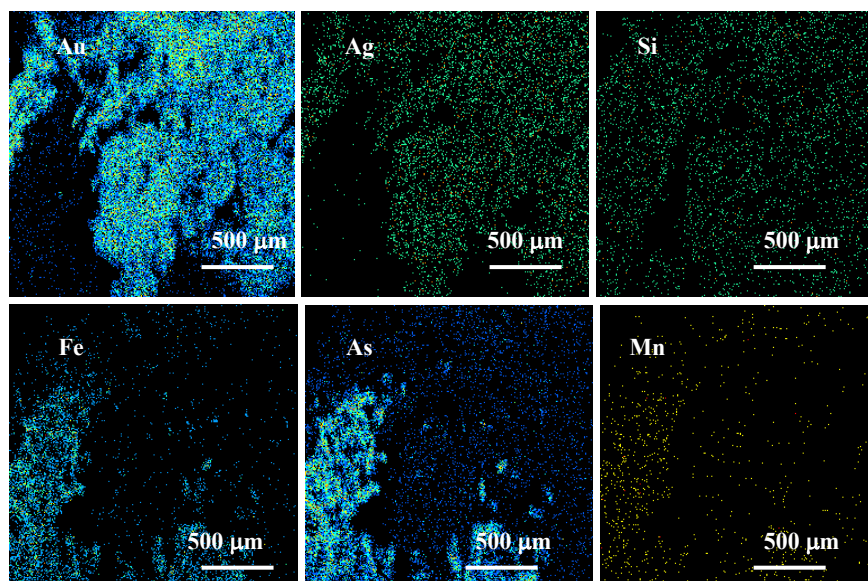
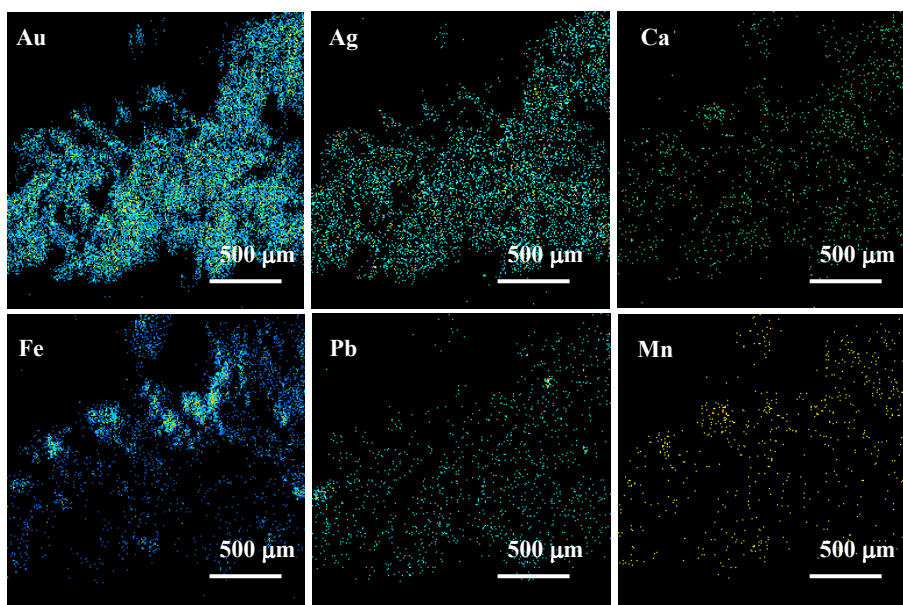


Fig. 3 – Cavnic-Roata 2; C2-2 XRF spectrum.

Using micro-PIXE at LNL AN2000 accelerator we concentrated on gold associated minerals (gangue) identification (the energy of 2 MeV for protons it is not enough to detect trace elements in $Z=50$ region). The most relevant are the maps spectra (2 mm x 2 mm) – see below.

Fig. 4 – *Cavnic-Roata 2* maps.

For sample *Cavnic-Roata 2*, we observed the complementary presence of electrum (Au+Ag) and arsenopyrite (FeSAs), a relatively homogeneous background of quartz (SiO₂) and a contribution from a manganese compound.

Fig. 5 – *Cavnic-Roata 3* maps.

For sample *Cavnic-Roata 3* we observed, besides the normal presence of electrum (Au+Ag), areas with pyrite (FeS₂), small grains of galena (PbS) and a contribution from manganocalcite (Ca,Mn)CO₃.

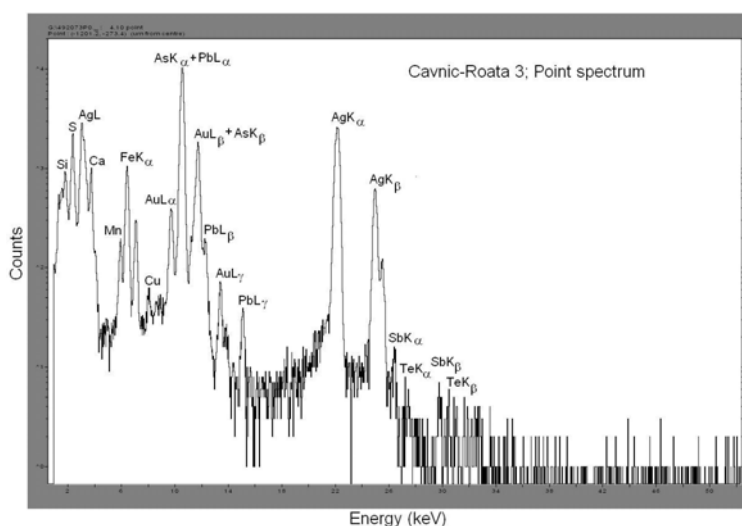


Fig. 6 – *Cavnic-Roata 3*, Point spectrum.

For sample *Cavnic-Roata 3* we performed a point spectrum (6 μm × 6 μm) (see Figure 6) where, besides arsenopyrite, manganocalcite, traces of galena, we detected the presence of Sb and Te.

To investigate gold and silver minerals - tellurides and antimony compounds, the most interesting samples - no. 2, 3, 4 – were also analyzed by micro-PIXE using a 3 MeV proton beam at AGLAE accelerator (3 MeV it is an adequate energy to have a good sensitivity for Sb and Te detection).

Table 2

Samples analyzed by micro-PIXE using AGLAE accelerator

Cavnic-Roata	2-11	2-12	3-11	3-13
S %	4.735	1.2089	0.3832	0.734
K %	1.4682	0	0.6409	0
Ca %	3.2728	0.2136	11.4673	2.3856
Mn %	0.8086	0.0738	1.3508	0.1274
Fe %	1.7359	0.9574	3.8343	0.823
Zn %	0.0344	0	0	0

Table 2 (continued)

As %	2.9145	0.0332	0.0239	0
Au %	50.0562	69.0568	57.1013	66.4814
Ag %	32.7513	28.1396	25.1133	29.3415
Sb ppm	2861	325	101	102
Te ppm	16657	1695	74	227
Ratio Ag/(Au+Ag)	0.395	0.289	0.240	0.333
Cavnic-Roata	4-A1	4-A3	4-B1	4-B2
S %	1.6782	0.8897	1.8967	0.9693
K %	0.3403	1.138	4.201	0
Ca %	1.911	21.3406	11.9185	0.2801
Mn %	0.1309	2.461	1.853	0.0205
Fe %	0.9059	7.0992	4.3189	0.0681
Zn %	0.1566	1.3942	0.6048	0.0378
As %	0.8057	0.2086	0.1956	0
Au %	60.7409	49.0031	49.1642	76.5956
Ag %	29.8797	15.7948	16.1104	21.811
Sb ppm	1830	228	0	49
Te ppm	54131	1682	219	0
Ratio Ag/(Au+Ag)	0.329	0.242	0.246	0.221

We analyzed “points” (areas of approx. 50 microns diameter) located in various regions of the samples. The study was focused on Sb and Te presence and on the variation of Ag/(Au+Ag) ratio values which characterize electrum’s metallogeny (geological provenance) [9].

The point 2-11 from the sample *Cavnic-Roata 2* (see Figures 7 a, b) revealed an important presence of tellurium (Te=16657 ppm of the area’s total composition), a significant presence of antimony (Sb=2861 ppm) and an increase of silver content (Ag=32.75% versus Au =50.05%), indicating the presence of a silver telluride containing also antimony. The high arsenic content (As=6.64%) could indicate benleonardite - $Ag_8(Sb,As)Te_2S_3$ highlighted in Kremnica, Slovakia [10] – also in Northern Carpathians Mts. We can not exclude the presence of a krennerite - $(Au, Ag)Te_2$ enriched in antimony, as revealed in Sacaramb, Metaliferi Mts. [11].

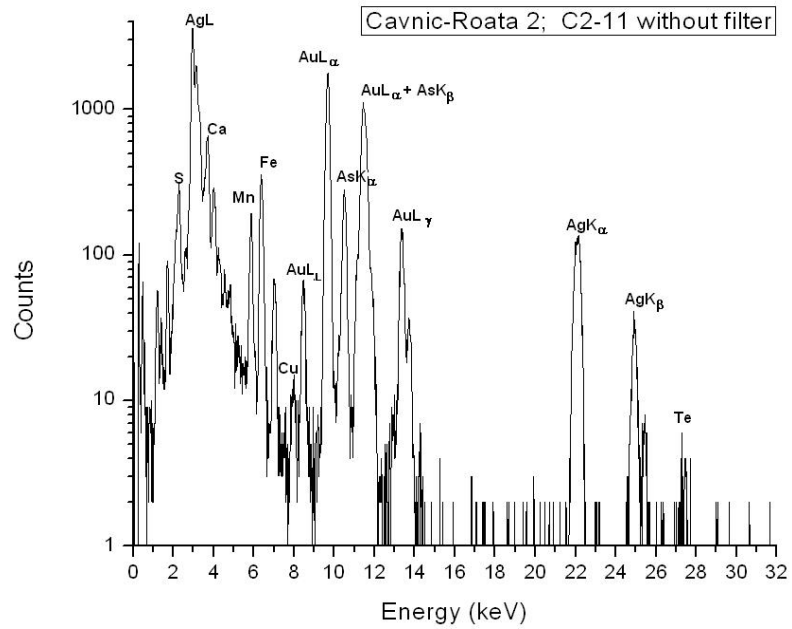


Fig. 7 a – Cavnic-Roata 2, spectrum C2-11 - without filter.

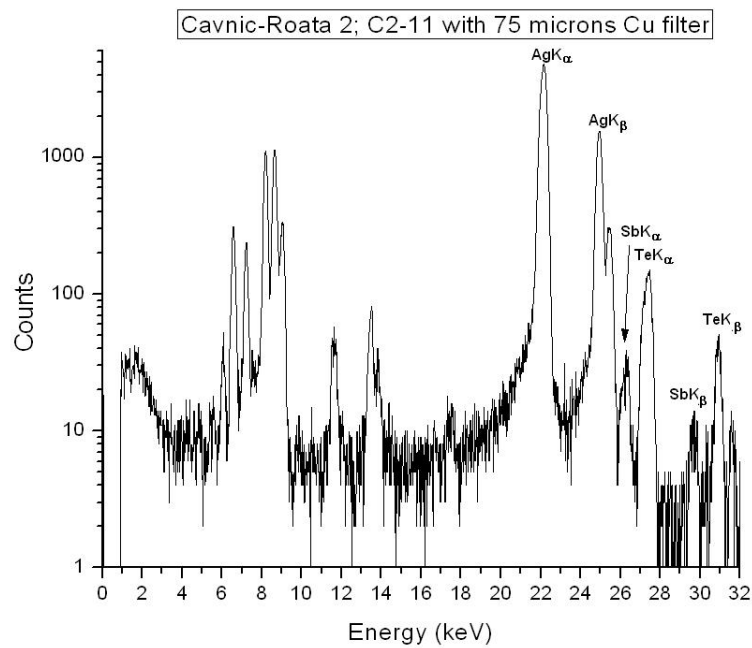


Fig. 7 b – Cavnic-Roata 2, spectrum C2-11- Cu filter.

The point C4-A1 from the sample *Cavnic-Roata 4* (see Figures 8 a, b) also contains a important quantity of silver telluride (Te=54131 ppm) and a significant presence of antimony (Sb=1830 ppm).

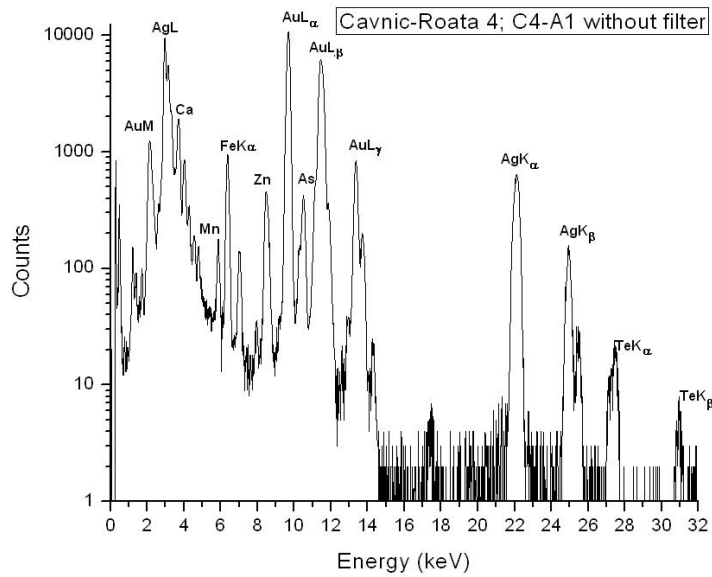


Fig. 8 a - *Cavnic-Roata 4*, spectrum C4-A1- without filter.

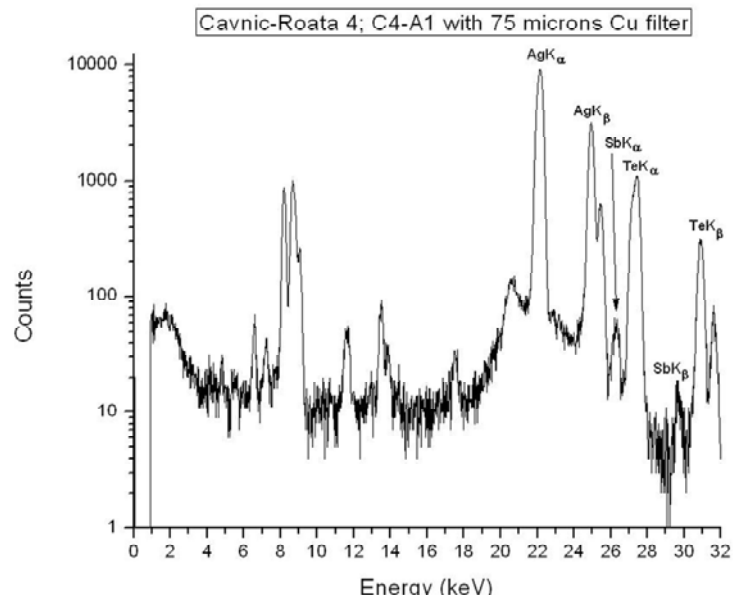


Fig. 8 b – *Cavnic-Roata 4*, spectrum C4-A1 Cu filter.

The existence of benleonardite and of a krennerite enriched in antimony, as discussed above for sample *Cavnic-Roata 2*, must be considered. The same structure, at a lower scale is repeated also for point C4-A3.

In table 2 we also observe the strong presence of calcium in points C4-A3, C4-B1, which correlated with the presence of Mn and Fe suggests the existence of rhodonite (Mn,Fe,Ca)SiO₃. A relevant presence of sphalerite (ZnS) is observed for point 4-A3.

So far, for Baia Mare geological district, tellurides are mentioned only in [12,13,14]. In [12] Butucescu et al mention traces of hessite (Ag₂Te), sylvanite (Au, Ag)₂Te₄ and petzite (Ag₃AuTe₂) at Nistru (North – West of Baia Mare – see Figure 1). In [13] Istvan et al note the presence of petzite and calaverite (AuTe₂) in Suior (North-West of Cavnic) and of an unspecified gold and silver telluride at Cavnic-Roata, observed only by optical microscopy, which is not sufficient for a real identification of a mineral. In [14] Plotinskaya et al highlighted by electronic microprobe altaite (PbTe) in a Cavnic-Boldut ore; we have not detected Pb in our samples, so, our telluride certainly is not altaite. To definitely identify the telluride(s) in our samples we intend to perform a micro-mineralogical study together with our colleagues from the Faculty of Geology - Bucharest University.

As concerning the Ag/(Au+Ag) ratio, it varies from 0.221 to 0.395 - see Table 2. For point C2-11 and C4-A1 the values are overestimated, because the X-rays detected from silver do not come only from electrum, but also from the telluride(s). We can consider an average value of 0.27 for all our samples, but big differences remain strong from point to point illustrating electrum's inhomogeneities. Ratio values are significantly lower than those given in [9] for Cavnic-Boldut - between 0.47 and 0.53, but approaching over Nistru data - 0.25 or rather Herja - 0.36. For Rosia Montana polished sample in [8] the range of ratio values is between 0.21 and 0.23. An interpretation in terms of electrum metallogeny will be performed together with the geologists.

As concerning the provenance of gold from Bronze Age and Dacian archaeological objects found in Northern Transylvania there is only one compositional analysis for Malaia Kopanya (North of Sighet, in Ukraine) Dacian treasure [15]: Au=92%, Ag=7%, traces of Cu, traces of Fe. This pattern is specific for alluvial gold and very different from Cavnic native gold (electrum with high silver content). With the help of our colleagues archaeologists, we intend to measure the Bronze Age gold items found in Oarta de Sus, Seini, Lapus (South-West of Baia-Mare) to verify if native gold from Cavnic was used to produce them.

4. CONCLUSIONS

Analytical techniques based on quantitative characteristic X-rays measurements – such as X-Ray Fluorescence and micro-PIXE, together with classical geological investigations based on optical and electronic microscopy -

give the opportunity to perform a complete geochemical characterization of geological gold samples. They can be successfully applied especially to provide answers regarding the identification of specific trace elements (Sb, Te, Sn, Pb, etc.) for each gold deposit.

The most important mineralogical results using our X-Ray based methods obtained on the Cavnic-Roata mine samples are:

– the identification of a silver telluride rich in antimony: benleonardite - $\text{Ag}_8(\text{Sb,As})\text{Te}_2\text{S}_3$ or krennerite - $(\text{Au, Ag})\text{Te}_2$; to definitely identify the telluride(s) in our samples we intend to perform a micro-mineralogical study together with our colleagues from the Faculty of Geology - Bucharest University.

– the $\text{Ag}/(\text{Au}+\text{Ag})$ ratio varies from 0.221 to 0.395, values significantly lower than those for Cavnic-Boldut - between 0.47 and 0.53, but approaching over Nistru data - 0.25 or rather Herja - 0.36 (for Rosia Montana polished sample the range of ratio values is between 0.21 and 0.23); an interpretation in terms of electrum metallogeny will be performed together with the geologists.

Our results demonstrate the important role of X-ray Fluorescence and micro-PIXE elemental analysis in interdisciplinary studies for mineralogical characterization of Romanian native gold in relation with provenance research on archaeological gold items from our museums.

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