# Archaeometry with PIXE at small accelerators


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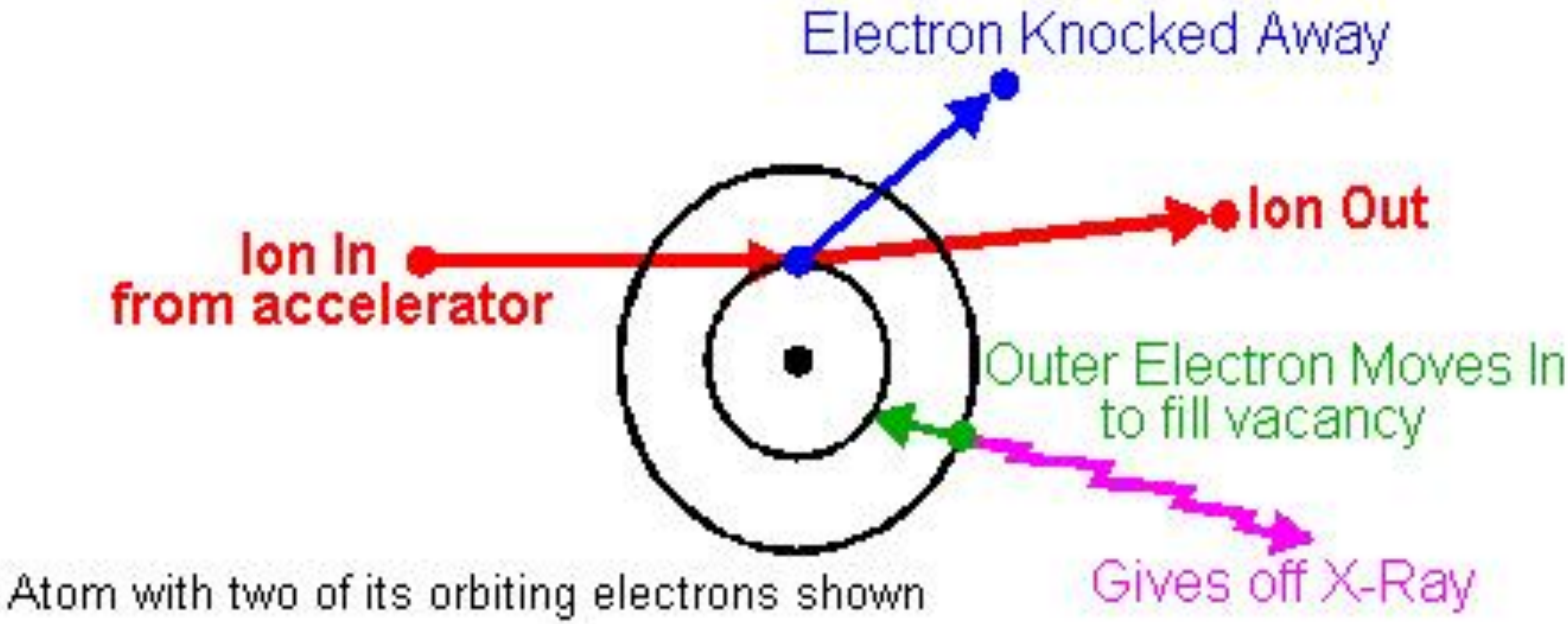
# PIXE Technique

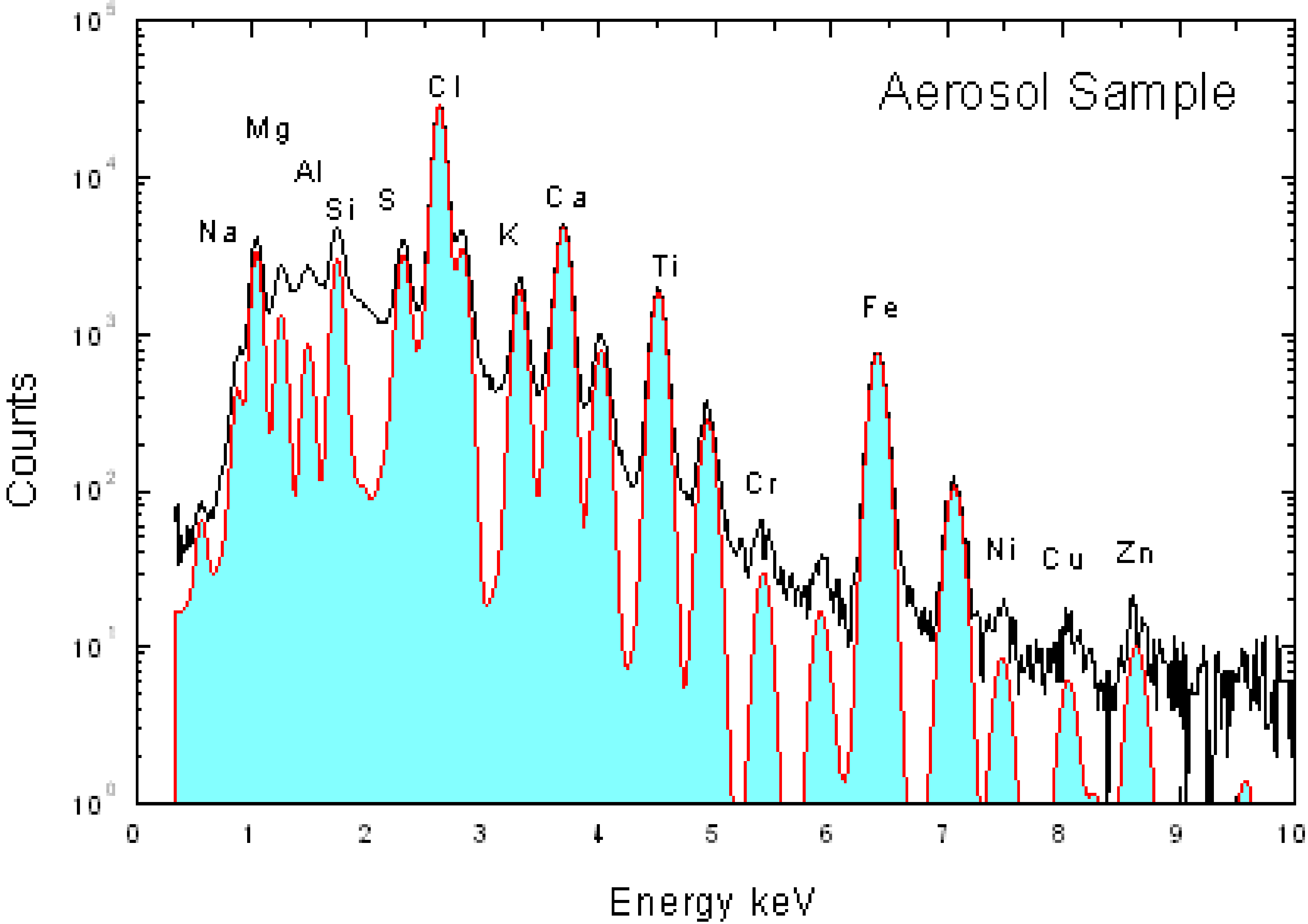
## Using Ion Beam from Accelerator




**PIXE - Particle Induced X-ray Emission**

**Catch and measure the X-ray.**

**Characteristic energy of the X-ray identifies the element.**



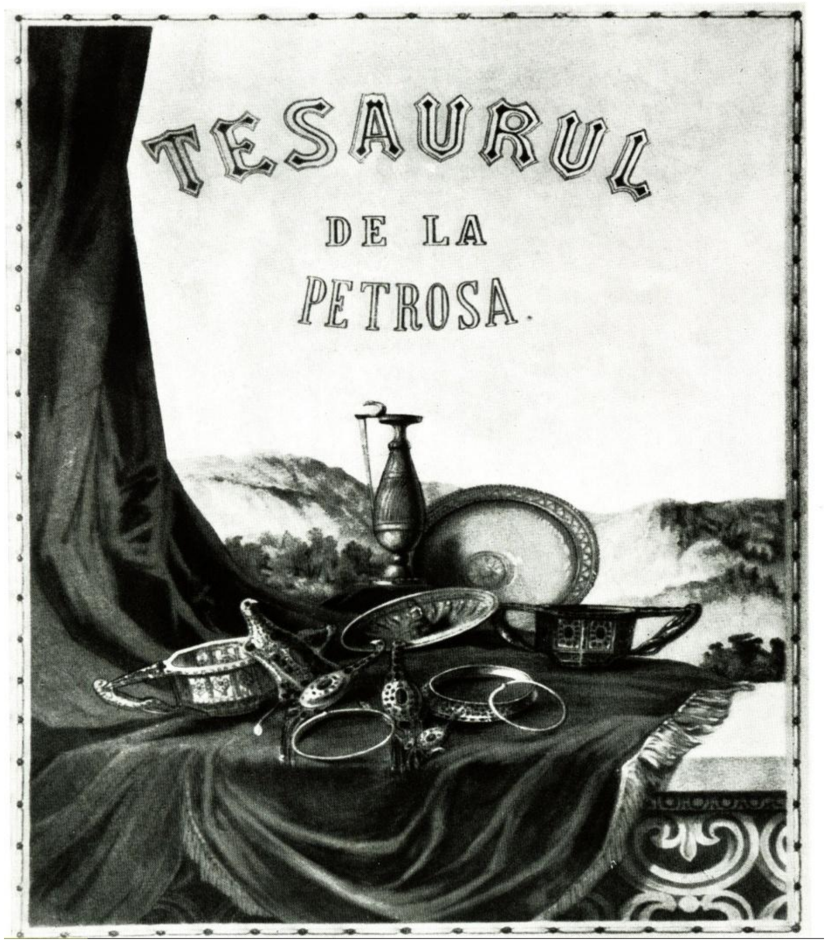
Aerosol Sample
Counts
Energy keV
Na
Mg
Al
Si
S
Cl
K
Ca
Ti
Cr
Fe
Ni
Cu
Zn

# Romanian ancient gold objects provenance studies using microbeam methods: the case of “Pietroasa” hoard

*The Pietroasa Hoard – “The Golden Brood Hen and its Chicken”*

# Romanian ancient gold objects provenance studies using microbeam methods: the case of "Pietroasa" hoard

- The hoard discovered in 1837 at Pietroasa, Buzau county, Romania by two peasants entered the historical literature and the history of arts as "Closca cu Puii de Aur" ("The Golden Brood Hen with its Chickens"). This hoard is one of the most famous collections of archaeological objects ever found in Romania, due to its fine artistic quality and to the myths created around it.
- This treasury belonged to the Germanic populations of Visigoths, living in the period of the IV$^{th}$-V$^{th}$ Century A.D. on the actual Romanian territory.



## Romanian ancient gold objects provenance studies using microbeam methods: the case of “Pietroasa” hoard

- The study of trace-elements in archaeological metallic objects can provide important clues about the metal provenance and the involved manufacturing procedures, leading to important conclusions regarding the commercial, cultural and religious exchanges between the antique populations.
- Ancient metallic materials are usually inhomogeneous on a scale of $10\ \mu m$ or less: they contain remains of imperfect smelting (segregated phases in alloys) and inclusions.
- Gold owes its significance to two important properties: its resistance to corrosion and its extraordinary malleability.
- Due to their exceptional chemical stability, gold artifacts remain almost unchanged during weathering and aging processes.
- Gold is usually alloyed with silver as electrum.
- The complicating factor for archaeological study of jewelry treasuries is the scarcity of such artifacts, since they are luxury products and precious metal deposits.

# Romanian ancient gold objects provenance studies using microbeam methods: the case of "Pietroasa" hoard

- The presence of PGE as inclusions in gold objects can constitute a fingerprint for the ore that the object was manufactured from.

- Gold alloys also contain low amounts of trace elements – Sn (cassiterite – alluvial gold), Cu, Sb, Te, Cr, Nb, Ta - potential fingerprints for geological metal deposits.

# Romanian ancient gold objects provenance studies using microbeam methods: the case of “Pietroasa” hoard

Five small pieces from five different objects belonging to Pietroasa hoard were analyzed:

- The large fibula
- The middle fibula
- The small fibula
- The dodecagonal basket
- The central figure representing the goddess Cybele sitting in the center of the patera

Due to the exceptional value of the artifacts and to the fact that in-vacuum micro-PIXE measurements can be carried out only on reduced dimension samples, fragments of the original objects were taken. All these samples were small in size (less than one millimeter area - magnitude order), being obtained by mechanically cutting the artifacts. Cautions were taken in order to obtain the samples from unimportant, but original zones of the objects, to avoid the deterioration of these precious museum artifacts.

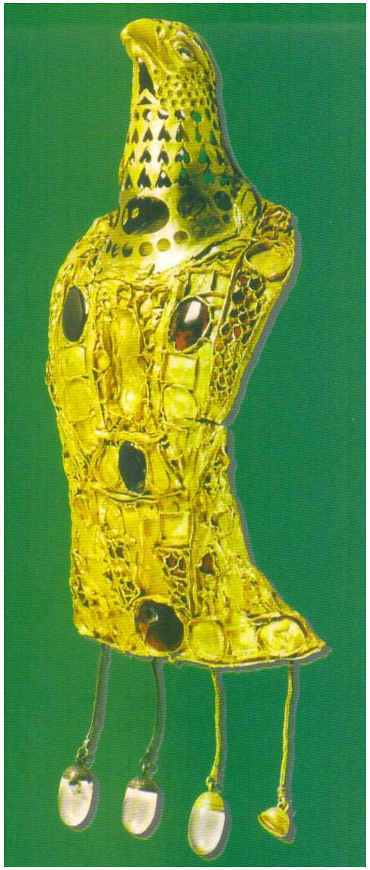
# Romanian ancient gold objects provenance studies using microbeam methods: the case of “Pietroasa” hoard

***Pietroasa hoard fibulae***

***Pietroasa hoard patera***

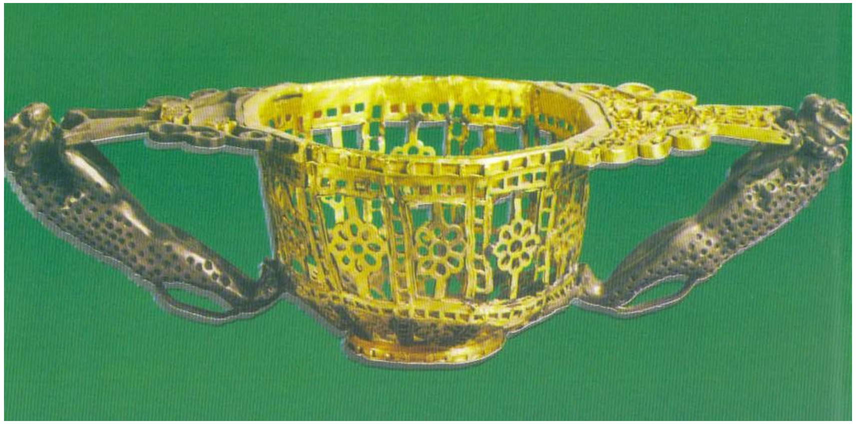
# Romanian ancient gold objects provenance studies using microbeam methods: the case of "Pietroasa" hoard

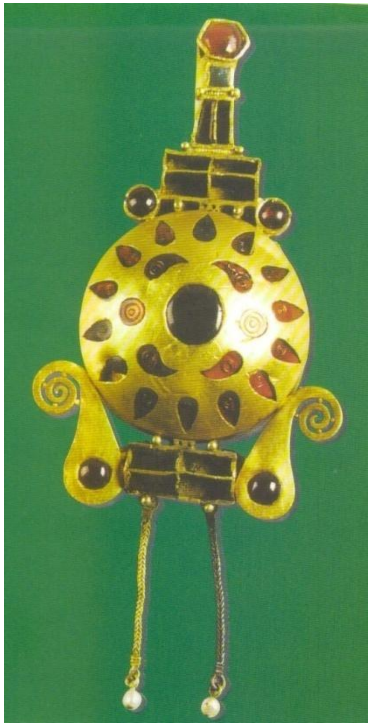
*Pietroasa hoard large fibula*



*Pietroasa hoard small fibula*

*Pietroasa hoard dodecagonal basket*





## Romanian ancient gold objects provenance studies using microbeam methods: the case of “Pietroasa” hoard

### Experimental

**micro-PIXE elemental mapping and point analyses performed at:**

1. **Nuclear Microprobe Facility at the Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, Germany, in the frame of an European Union Large Scale Facility Access (LSFA) action**

- **Rossendorf microprobe facility: based on a 3 MV Tandetron accelerator and a Danfysik magnetic quadrupole triplet for beam focusing**
- **3 MeV proton beam**
- **Beam current ~ 400 pA**
- **Beam - focused down to 6×6 μm$^2$**
- **Rastered area - 800×800 μm$^2$ (128×128 pixels elemental maps)**
- **Characteristic X-rays detection - Si(Li) detector positioned at 120° with respect to the incident beam**
- **Mylar absorbers of different thickness - employed to reduce the soft X-ray region of the spectra**
- **Total accumulated charge for the scanned areas ~3 μC**
- **PIXE spectral analysis - GUPIX code**

**Romanian ancient gold objects provenance studies using microbeam methods: the case of "Pietroasa" hoard**

## Experimental

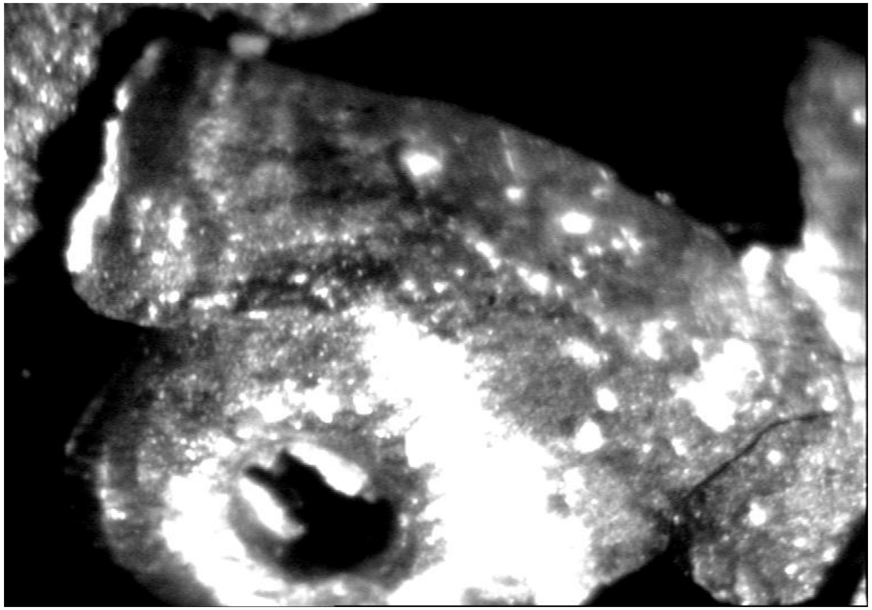
2. AN 2000 Van de Graaff accelerator of Laboratori Nazionali di Legnaro (LNL)

- 2 MeV proton microbeam
- Beam diameter - 5 μm
- The maximum beam current ~1 nA
- Mylar funny filter (171 μm thickness, 3.3% hole) - to reduce the intensity of the peaks in the low-energy spectral region (below 4 keV)
- Scanned areas - up to 6.25 $mm^2$
- Spectral analysis - GUPIX software
- The good Si(Li) detector efficiency gave access to (15-25) keV spectral region, allowing the detection of Nb, Ru, Rh, Pd, Ag K lines.

# Romanian ancient gold objects provenance studies using microbeam methods: the case of “Pietroasa” hoard

One of the samples was cracked ⇒ to subtract any spurious signals, a set of spectra for the sample holder and the carbon tape on which the samples were stuck were also acquired.

7 p



Romanian ancient gold objects provenance studies using microbeam methods: the case of "Pietroasa" hoard

# Results

There is no Sb, Te or Sn in the investigated Pietroasa hoard samples.

⇒ According to the previous measurements performed by Pernicka on Transylvanian gold, the conclusion is that there is no chance that Carpathian gold from Transylvania was used to manufacture the Pietroasa hoard artifacts.

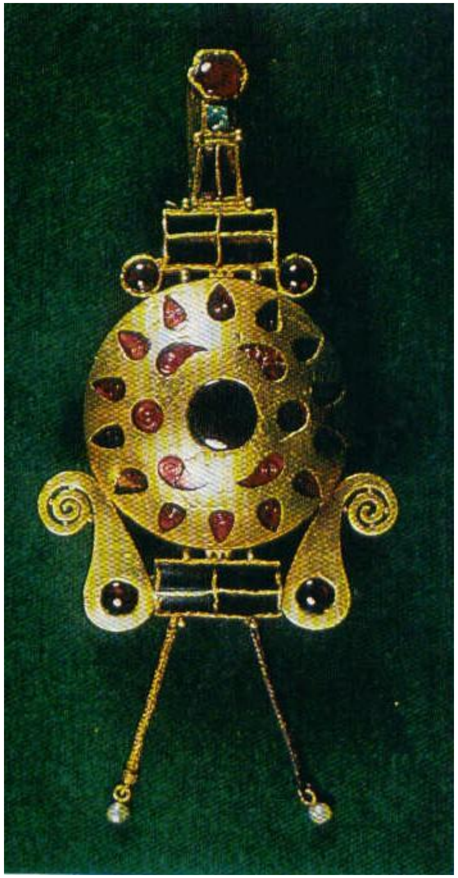
## Romanian ancient gold objects provenance studies using microbeam methods: the case of "Pietroasa" hoard

### Results

Inclusions of Ta and Cr were clearly found analyzing the elemental maps for the large and small fibulae.

- Ta and Cr have high melting points, and they resist the gold processing techniques.
- The Legnaro micro-PIXE measurements confirmed the presence of Ta and Cr inclusions on the Germanic style small fibula and revealed Nb content.

*The small fibula*



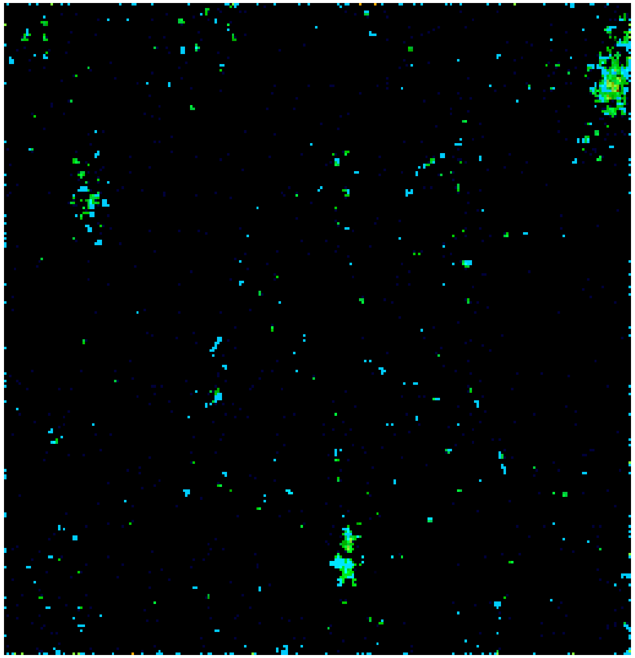
# Romanian ancient gold objects provenance studies using microbeam methods: the case of “Pietroasa” hoard

## Results

- The combination Ta and Nb is found in “samarskite”, a mineral of columbite type which is characteristic to the Ural Mountains (Southern region from Perm to Tchelyabinsk).

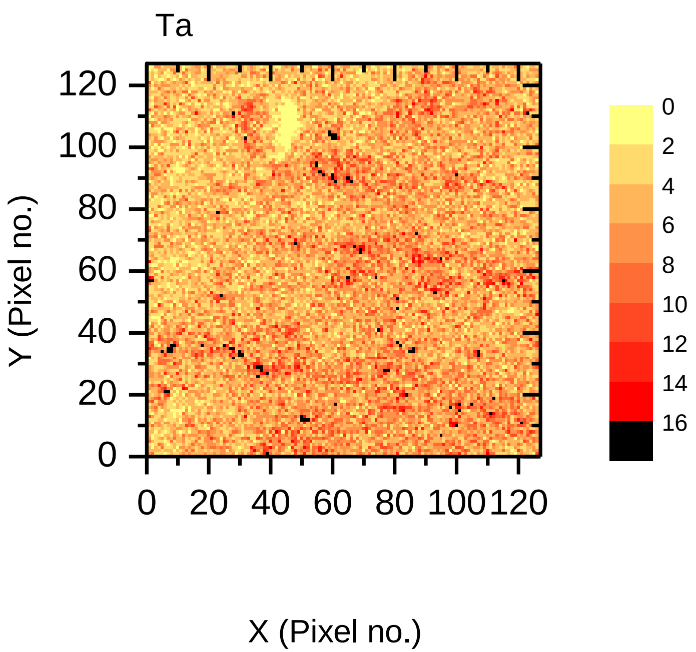
⇒ The Germanic ‘owners’ of the treasuries were coming from the region between Caucasus and Ural Mountains in the second half of the III$^{rd}$ Century A.D., bringing along their precious jewelry (Ammianus Marcellinus).

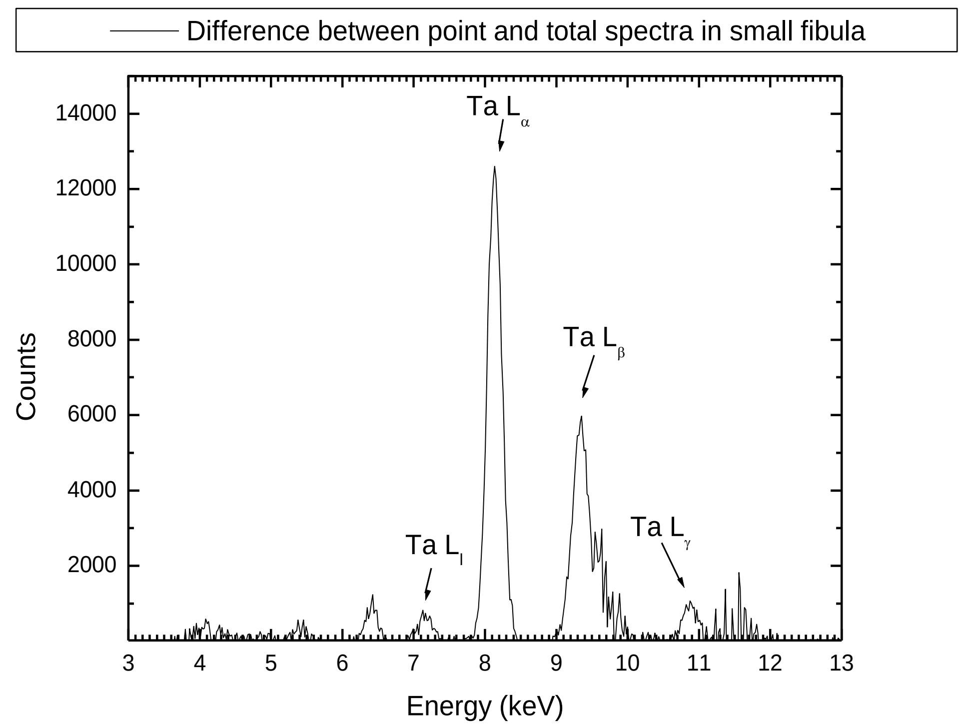
*Ta map on small fibula fragment*



# Romanian ancient gold objects provenance studies using microbeam methods: the case of "Pietroasa" hoard

**7P**
3 MeV p



# Romanian ancient gold objects provenance studies using microbeam methods: the case of "Pietroasa" hoard

## Results

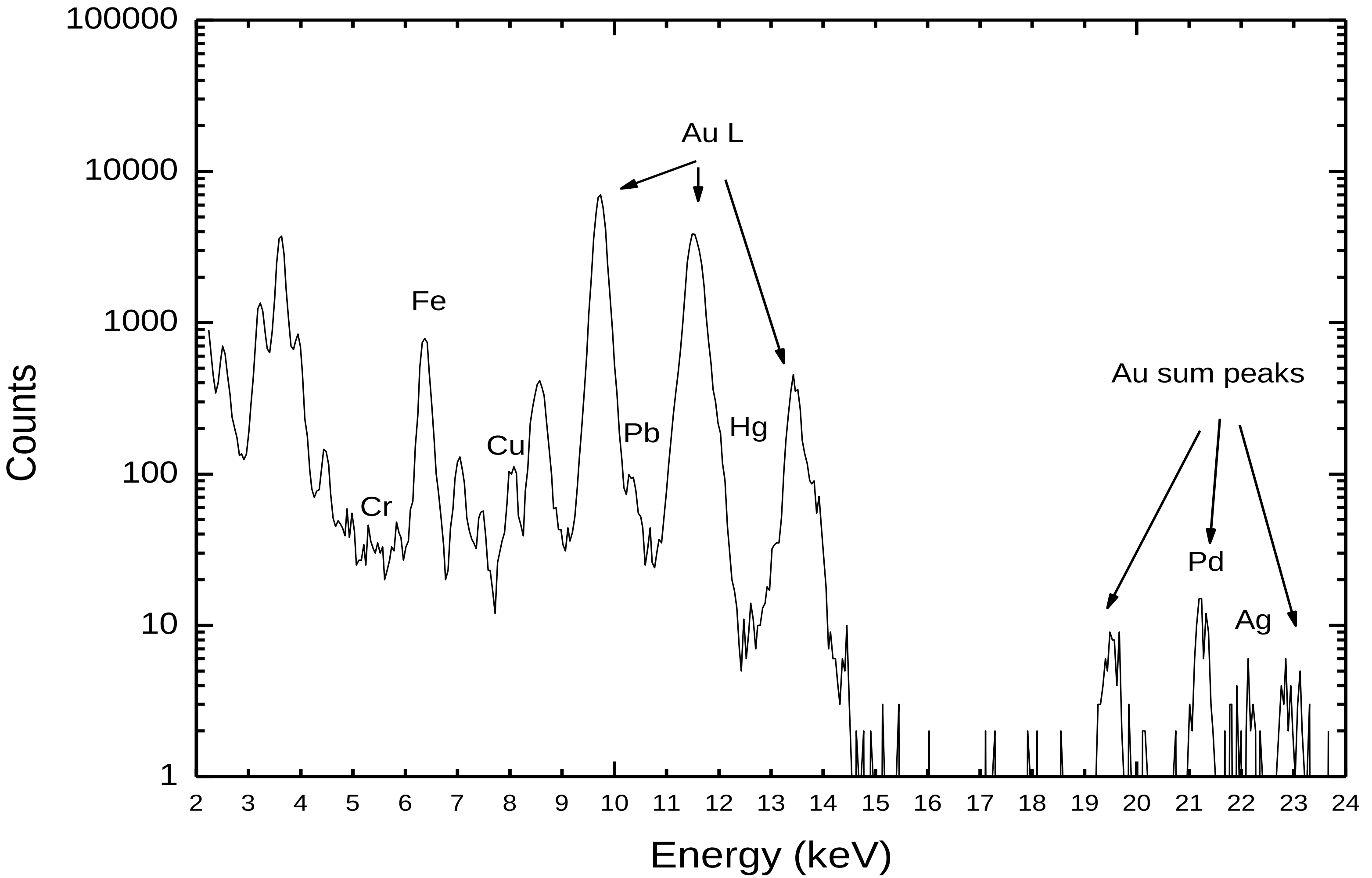
*The dodecagonal basket*

Small Pd inclusions in the dodecagonal basket were revealed.

- The two accessible gold sources with Pd in the IV$^{th}$ Century A.D. were Nubia (Sudan) and Anatolia (Turkey) deposits, intensively used in Egypt (Alexandria) and Syria (Antiochia) workshops (see previous works of Guerra, who determined Pd in Alexander the Great coins, minted after the Persian Empire conquest and in early Alexandria Byzantine coins).
- The main composition (Au = 98.3%, Ag = 1%, Cu = 0.5%) suggests a remelting procedure using Roman imperial coins struck in Oriental provinces.

# Romanian ancient gold objects provenance studies using microbeam methods: the case of “Pietroasa” hoard

***Point spectrum on the dodecagonal basket, exhibiting a high concentration of Pd***



# Romanian ancient gold objects provenance studies using microbeam methods: the case of "Pietroasa" hoard

The composition of the middle fibula is mainly characterized by the very high quality of gold (Au = 99.6%, Cu = 0.3%), the absence of silver and the lack of metallic inclusions ⇒ gold is likely to be obtained by remelting Roman imperial coins circulating and treasured in the IV$^{th}$ Century A. D. - e.g. aurei emissions of Probus, Diocletianus, Constantinus I, Constantius II.

*The middle fibula*

## Romanian ancient gold objects provenance studies using microbeam methods: the case of "Pietroasa" hoard

### Conclusions

- The results obtained by micro-PIXE experiments on gold ancient artifacts, especially the inclusions findings, provided some useful hints regarding the possible provenance of the manufacturing metal.
- The Pietroasa hoard artifacts were again proved to be of different origins, confirming the stylistic arguments by the three possible gold sources identified: Southern region of Ural Mountains, Nubia (Sudan) deposits and Roman imperial coins emissions.
- Further analyses on other artifacts belonging to the same hoard are necessary.
- A correct answer to the question of the native metal provenance used for each artifact is still a difficult task as long as a comprehensive data bank for the composition of Euro-Asian native gold is not available.

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# Romanian ancient gold objects provenance studies using micro-beam methods: the case of "Pietroasa" hoard

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Available online 17 March 2005

## Abstract

Five fragments of ancient gold objects belonging to Pietroasa "Cloşca cu Puii de Aur" ("The Golden Brood Hen with Its Chickens") Romanian hoard were analysed using the micro-PIXE (particle induced X-ray emission) technique. The purpose of the study was to gain some more knowledge regarding the metal provenance by determining the presence of PGE (Platinum Group Elements) and other high-temperature melting point trace elements (Ta, Nb, Cr) at a micrometric scale. Ta and Nb inclusions (micrometric areas of composition different from the surroundings) on three samples and Pd inclusions on one sample were found. The measurements led to some conclusions for the possible gold ore sources of Pietroasa treasury: the South-Ural Mountains, Nubia (Sudan) and/or Anatolian deposits and Roman imperial coins.



*PACS:* 29.30.Kv; 82.80.Ej; 07.79.−v; 68.37.Yz

*Keywords:* Micro-PIXE; Archaeometry; Gold; PGE; Inclusions; Provenance

# The case of Spiraled Dacian Bracelets

**Several hoards containing at least twenty four gold spiral bracelets and few thousands of gold coins (staters) of pseudo-Lysimachus and Koson types (Koson with and without monogram) have been unearthed in the time frame between 1999 and 2001, by organized gangs of illegal treasure hunters, in five different spots in the area of Sarmizegetusa Regia, in the Orastie Mountains, Romania.**

B. Constantinescu, E. Oberlander-Tarnoveanu, R. Bugoi, V. Cojocaru, M. Radtke,
*The Sarmizegetusa Bracelets*, Antiquity Journal (London) 84 Issue 326 (2010)1028-1042.

**Sarmizegetusa Regia - The Sacred Zone**


**Pseudo-Lysimachus stater**


**Dacian Koson with monogram**

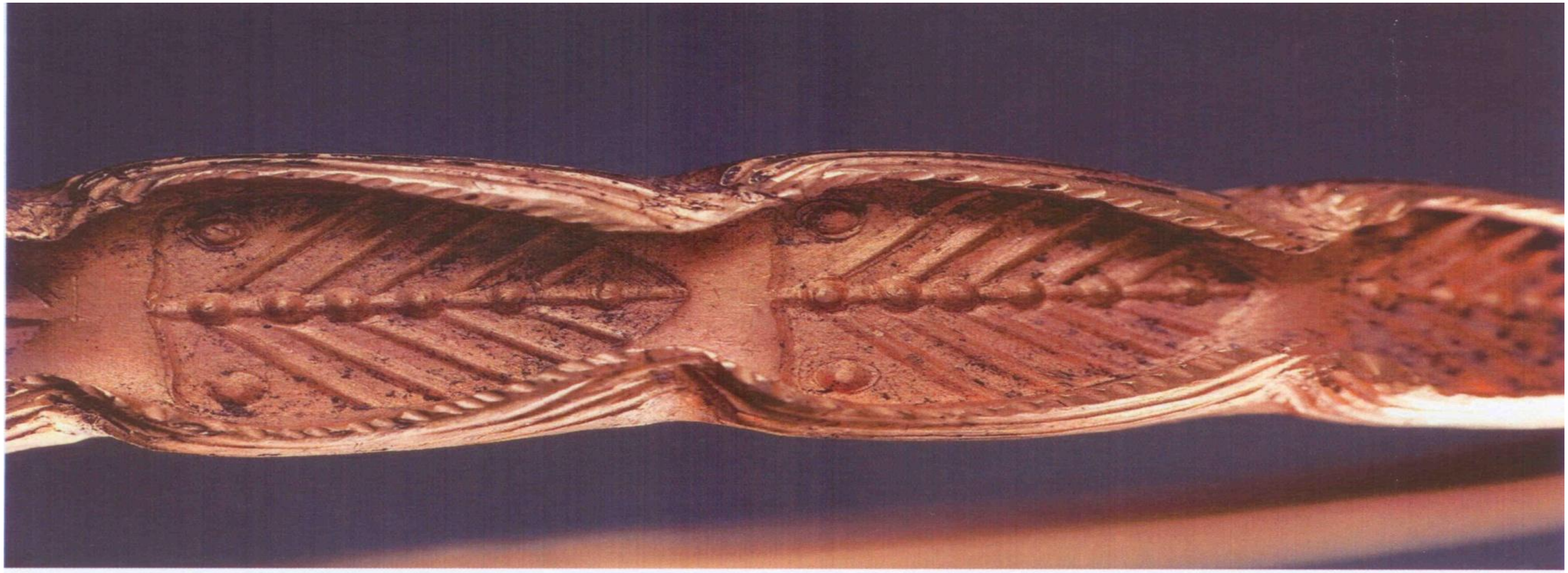

**Dacian Koson without monogram**

**The composition of the twelve Dacian bracelets recovered up to March 2010 (the numbering of the bracelets is related to the succession in which they were recovered)**

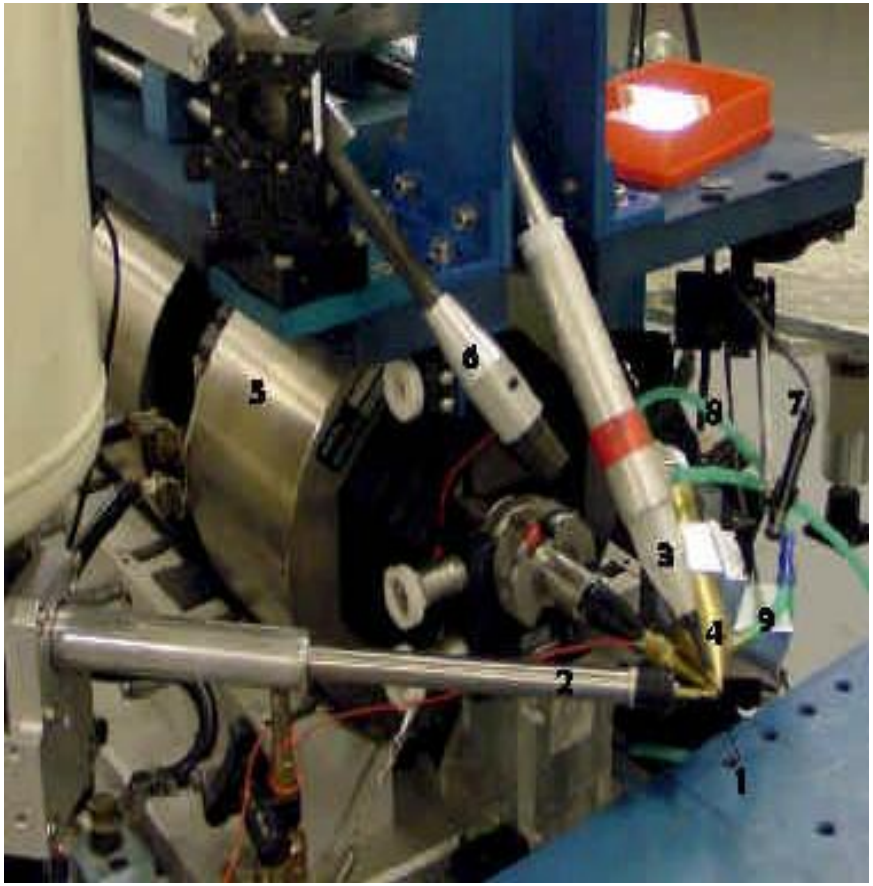
| Bracelet no. | Weight (g) | Au (wt%) | Ag (wt%) | Cu (wt%) | Sn ($mg \cdot kg^{-1}$) |
|---|---|---|---|---|---|
| 1 | 982.2 | 89.8 | 9.5 | 0.6 | 200 |
| 2 | 1076.72 | 78.2 | 20.3 | 1.5 | 60 |
| 3 | 1115.31 | 82.4 | 16.2 | 1.4 | 360 |
| 4 | 927.98 | 91.5 | 8.1 | 0.4 | 125 |
| 5 | 764.95 | 92.8 | 6.9 | 0.3 | <MDL* |
| 6 | 1062.55 | 92 | 7.1 | 0.9 | 230 |
| 7 | 1196.03 | 92.9 | 6.3 | 0.7 | <MDL * |
| 8 | 1136.06 | 85 | 12.8 | 2.1 | 1500 |
| 9 | 682.3 | 87.1 | 12.2 | 0.6 | 120 |
| 10 | 1047 | 88.7 | 10.3 | 0.9 | 425 |
| 11 | 825 | 86.1 | 12.6 | 0.7 | 400 |
| 12 | 884.37 | 83.5 | 14.3 | 1 | 500 |

*MDL – Minimum Detection Limits

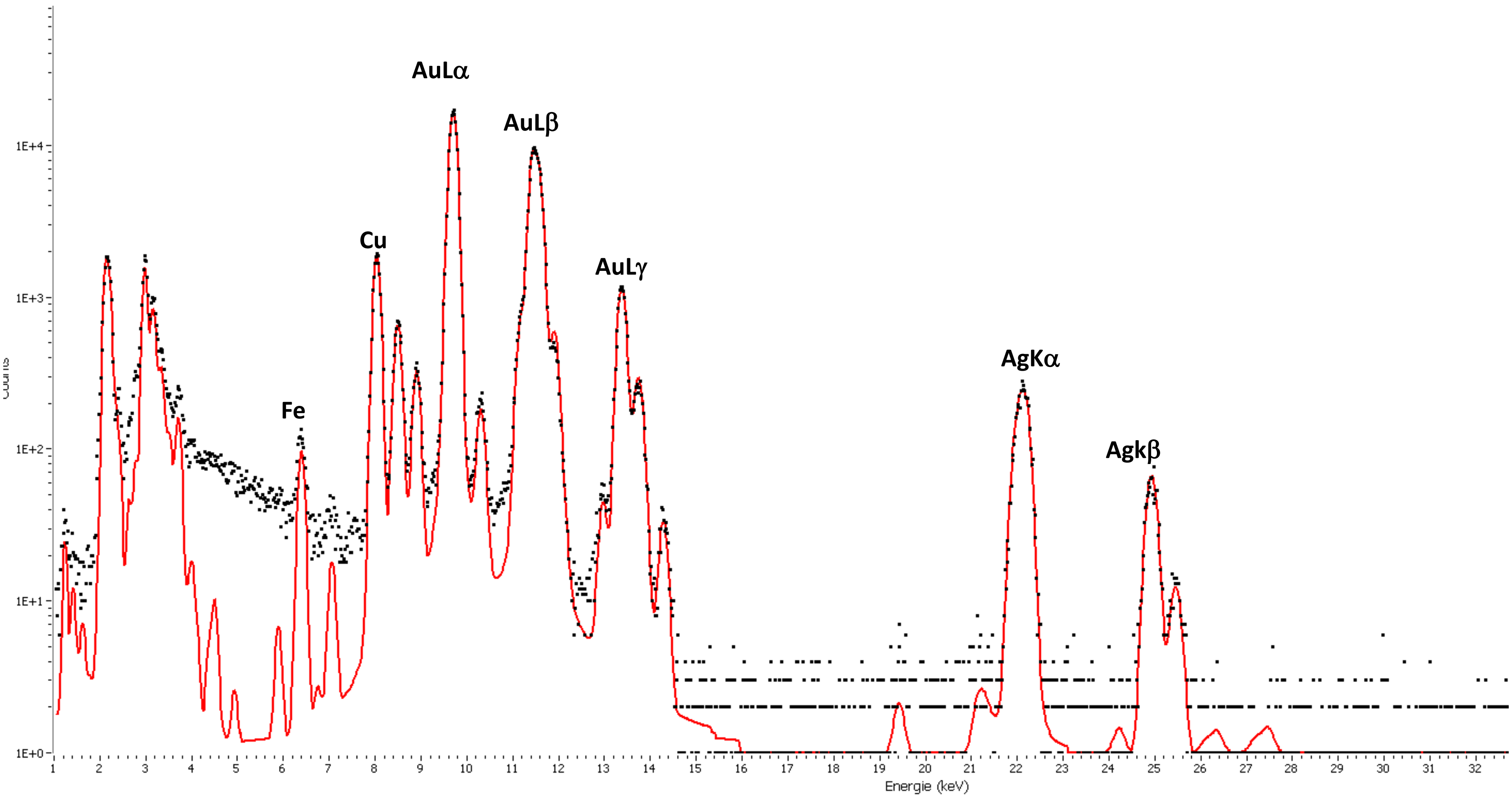
In early 2011, we obtained the permission of the Romanian authorities to take two sets of very small (1-2 mg) samples from the extremities of the bracelets to separately analyze them by micro-PIXE at AGLAE Paris and by micro-SR-XRF at BESSY.



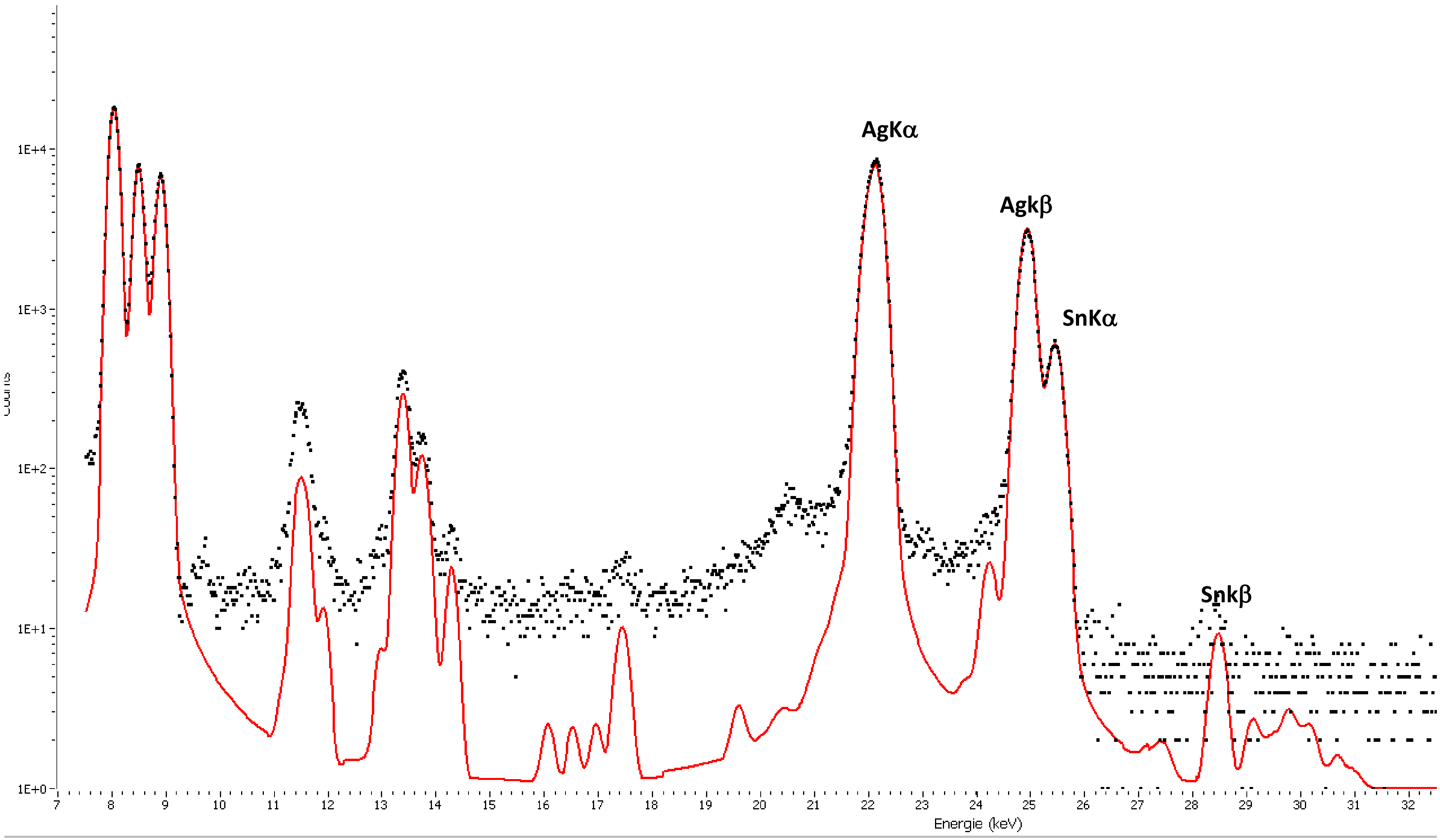
# Micro-PIXE at AGLAE accelerator of CNRS-Musee du Louvre, Paris, France



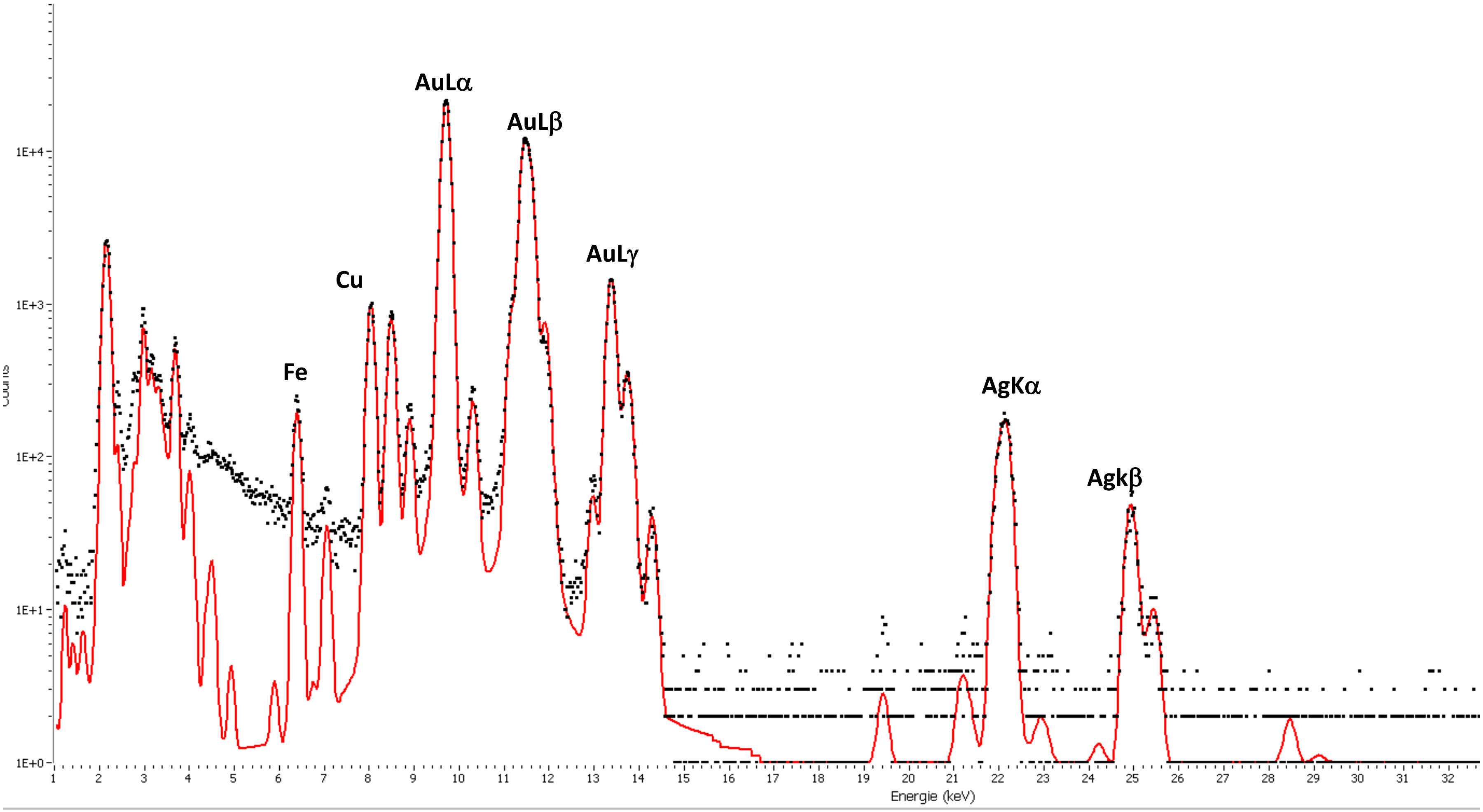

- 3 MeV proton micro-beam (roughly 50 μm diameter) extracted into air
- irradiation with a 10 nA beam current for about 15 minutes
- two Si(Li) detectors: low-energy (1-10 keV) - for the determination of matrix elements (Au, Ag, Cu) and high-energy (5-40 keV) – for trace-elements (Sn, Sb, Te)
- to reduce 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



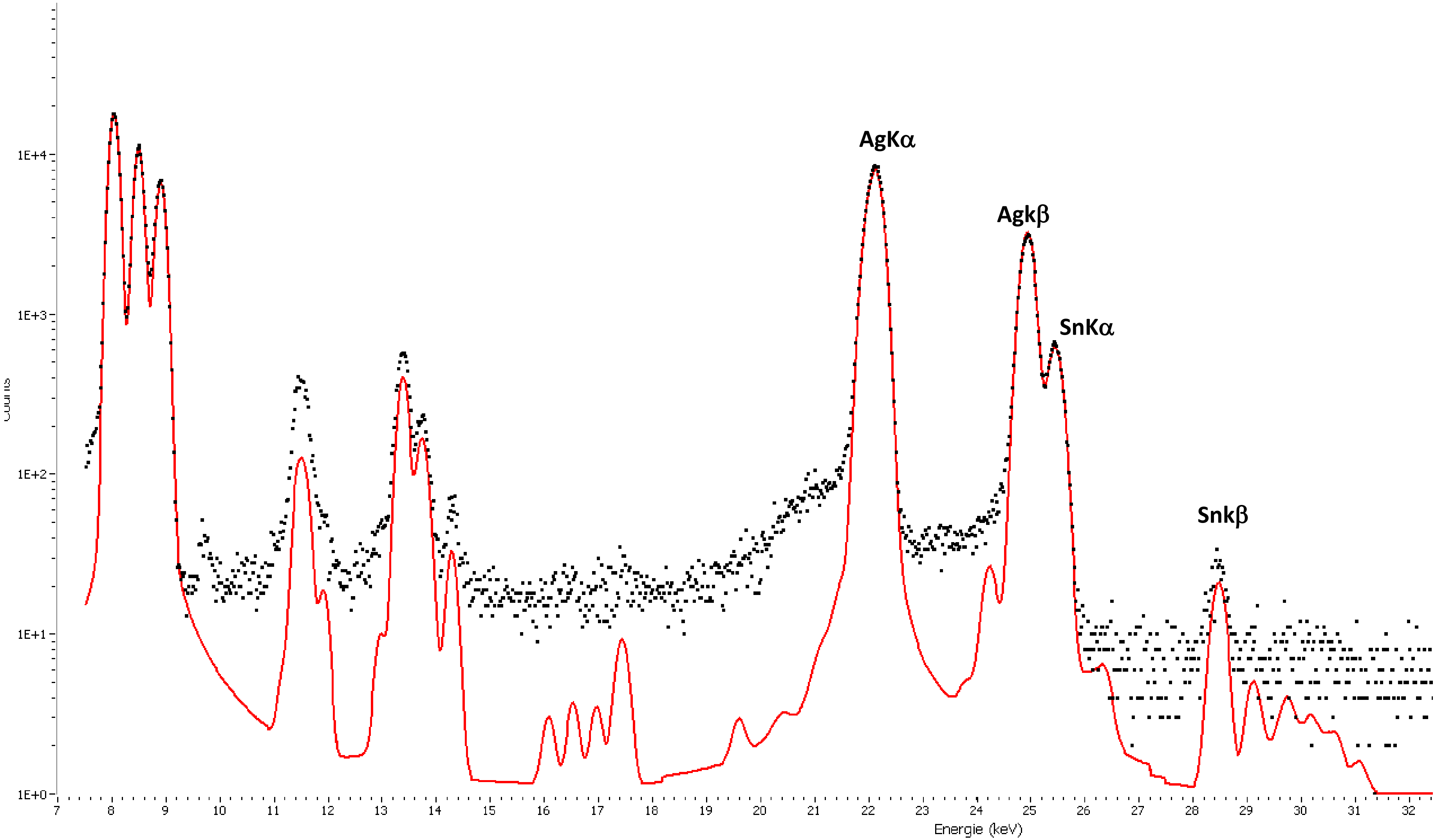

**Bracelet no.11 head A - Micro-PIXE spectrum without filter**




**Bracelet no.11 head A - Micro-PIXE spectrum with 70 microni Cu filter**




**Bracelet no.11 head B - Micro-PIXE spectrum without filter**




**Bracelet no.11 head B - Micro-PIXE spectrum with 70 microni Cu filter**

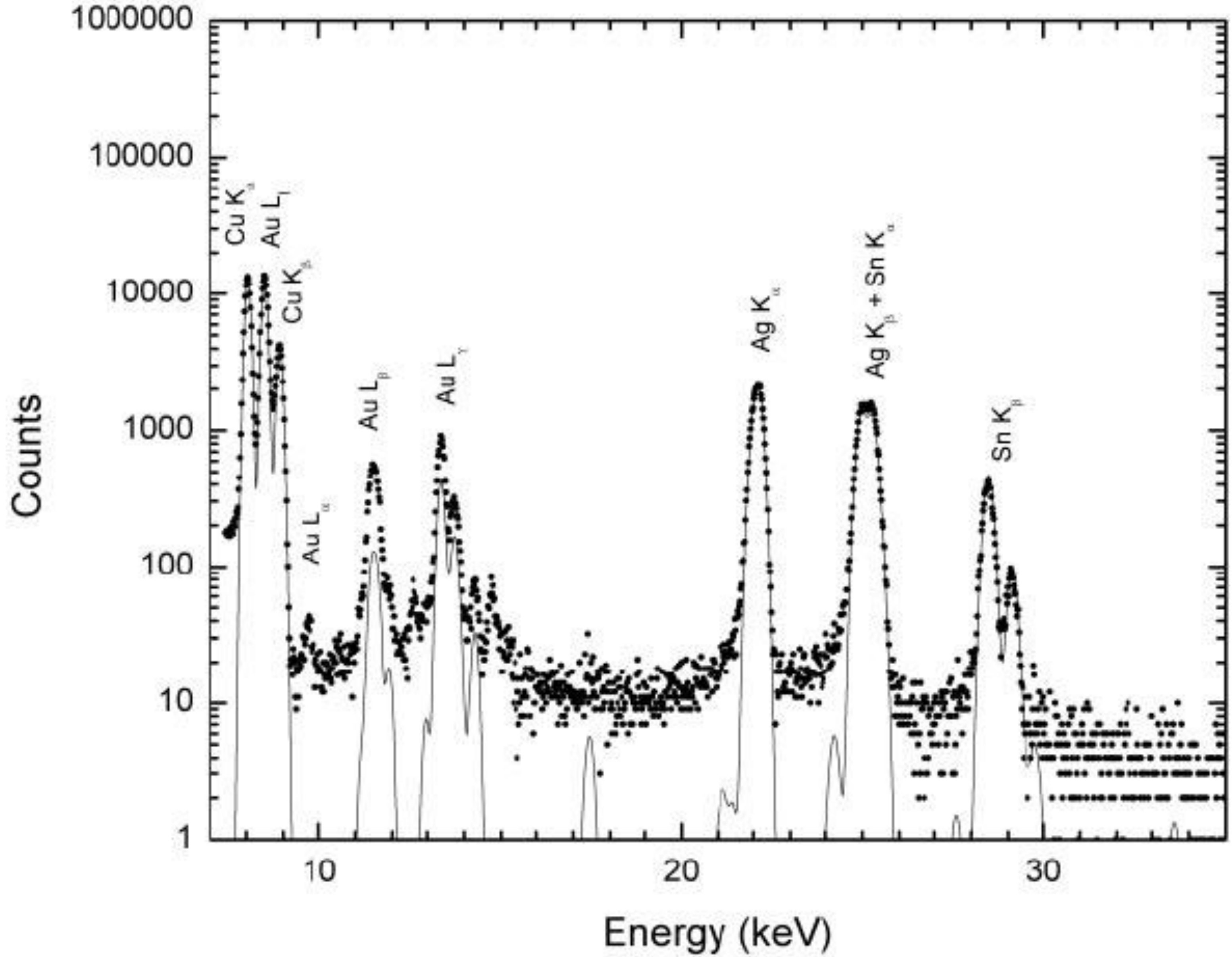
| AGLAE micro-PIXE results: | Au % | Ag % | Cu% | Fe% | Sn ppm | Sb ppm | Te ppm |
|---|---|---|---|---|---|---|---|
| Bracelet 1 "Head" A Measurement 1 | 87.46 | 8.85 | 2.16 | 0.209 | 84 | n.d. | 33 |
| Bracelet 1 "Head" A Measurement 2 | 87.82 | 8.68 | 2.14 | 0.138 | 143 | 38 | n.d. |
| Bracelet 1 "Head" B Measurement 1 | 86.07 | 10.33 | 2.84 | 0.026 | 146 | 22 | n.d. |
| Bracelet 1 "Head" B Measurement 2 | 89.7 | 6.99 | 2.43 | 0.051 | 162 | 14 | n.d. |
| Bracelet 2 "Head" A Measurement 1 | 81.5 | 15.18 | 1.5 | 0.45 | 143 | 43 | 18 |
| Bracelet 2 "Head" B Measurement 1 | 84.8 | 11.69 | 2.48 | 0.188 | 84 | n.d. | n.d. |
| Bracelet 3 "Head" A Measurement 1 | 82.77 | 11.34 | 1.88 | 2.732 | 161 | n.d. | n.d. |
| Bracelet 3 "Head" A Measurement 2 | 82.88 | 13.25 | 2.7 | 0.144 | 207 | n.d. | n.d. |
| Bracelet 3 "Head" B Measurement 1 | 86.54 | 11.66 | 0.93 | 0.069 | 97 | 16 | n.d. |
| Bracelet 4 "Head" A Measurement 1 | 93.14 | 4.95 | 0.24 | 0.21 | n.d. | 105 | n.d. |
| Bracelet 4 "Head" B Measurement 1 | 89.52 | 7.94 | 1.63 | 0.037 | 117 | n.d. | 36 |
| Bracelet 5 "Head" A Measurement 1 | 91.36 | 6.78 | 0.66 | 0.032 | 52 | 29 | n.d. |
| Bracelet 5 "Head" B Measurement 1 | 90.91 | 6.19 | 0.66 | 0.48 | 65 | n.d. | n.d. |
| Bracelet 5 "Head" B Measurement 2 | 90.33 | 7.66 | 0.75 | 0.033 | 80 | 48 | n.d. |

| AGLAE micro-PIXE results: | Au % | Ag % | Cu% | Fe% | Sn ppm | Sb ppm | Te ppm |
|---|---|---|---|---|---|---|---|
| Bracelet 6 "Head" A Measurement 1 | 89.82 | 6.94 | 1.38 | 0.064 | 146 | 32 | n.d. |
| Bracelet 6 "Head" B Measurement 1 | 91.16 | 6.16 | 1.46 | 0.172 | 120 | n.d. | 19 |
| Bracelet 7 "Head" A Measurement 1 | 91.18 | 6.49 | 1.44 | 0.057 | 217 | 24 | n.d. |
| Bracelet 7 "Head" B Measurement 1 | 88.76 | 6.48 | 0.65 | 0.09 | 94 | 0 | n.d. |
| Bracelet 8 "Head" A Measurement 1 | 82.15 | 14.79 | 1.51 | 0.188 | 592 | 31 | n.d. |
| Bracelet 8 "Head" B Measurement 1 | 84.59 | 12.31 | 1.7 | 0.241 | 619 | n.d. | 77 |
| Bracelet 9 "Head" A Measurement 1 | 87.68 | 10.84 | 0.42 | 0.054 | n.d. | 40 | n.d. |
| Bracelet 9 "Head" B Measurement 1 | 79.63 | 14.76 | 0.74 | 3.678 | 215 | 93 | n.d. |
| Bracelet 10 "Head" A Measurement 1 | 84.54 | 10.89 | 1.1 | 2.084 | 541 | n.d. | n.d. |
| Bracelet 10 "Head" B Measurement 1 | 88.95 | 8.67 | 0.4 | 0.214 | 215 | 80 | n.d. |
| Bracelet 11 "Head" A Measurement 1 | 84.85 | 12.15 | 1.94 | 0.084 | 396 | n.d. | 17 |
| Bracelet 11 "Head" B Measurement 1 | 90.84 | 7.28 | 0.86 | 0.153 | 540 | 43 | n.d. |
| Bracelet 12 "Head" A Measurement 1 | 84.6 | 12.19 | 2.03 | 0.039 | 250 | 30 | 21 |
| Bracelet 12 "Head" B Measurement 1 | 86.3 | 10.42 | 1.87 | 0.099 | 330 | n.d. | 29 |

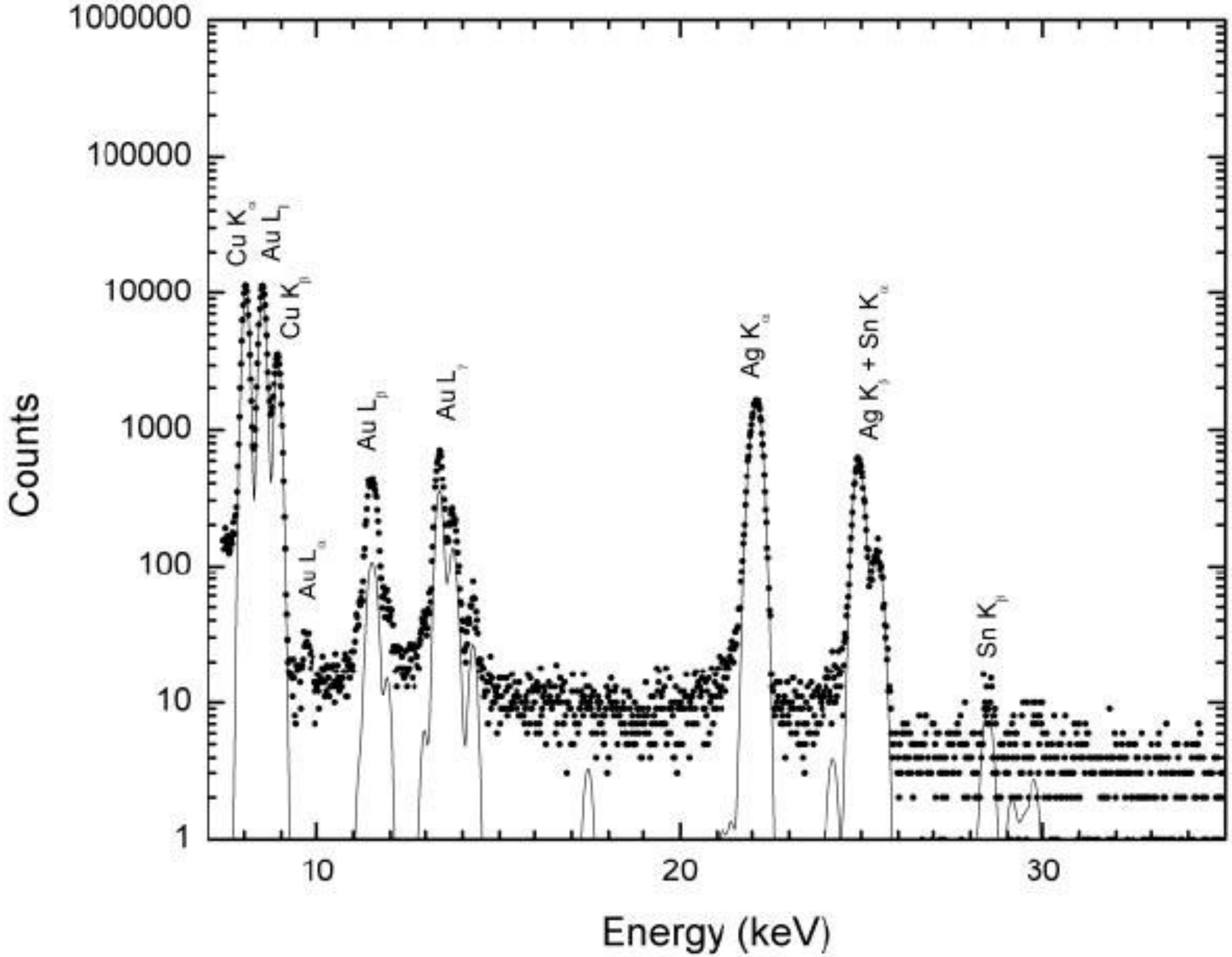
The differences are significant not only between the two “heads”(ends) of the bracelets (a “huge” item for gold jewelry: weight 1076.72 g, length 2.69 m, external diameter 112 mm, 8 spires), but also for the same fragment in the case of “head” A, indicating the use of small grains (“gold sand”) of alluvial gold melted partly or at all.

Comparing the title obtained in XRF measurements with the microscopic investigation results we see that on average the concentration of major elements is roughly the same.

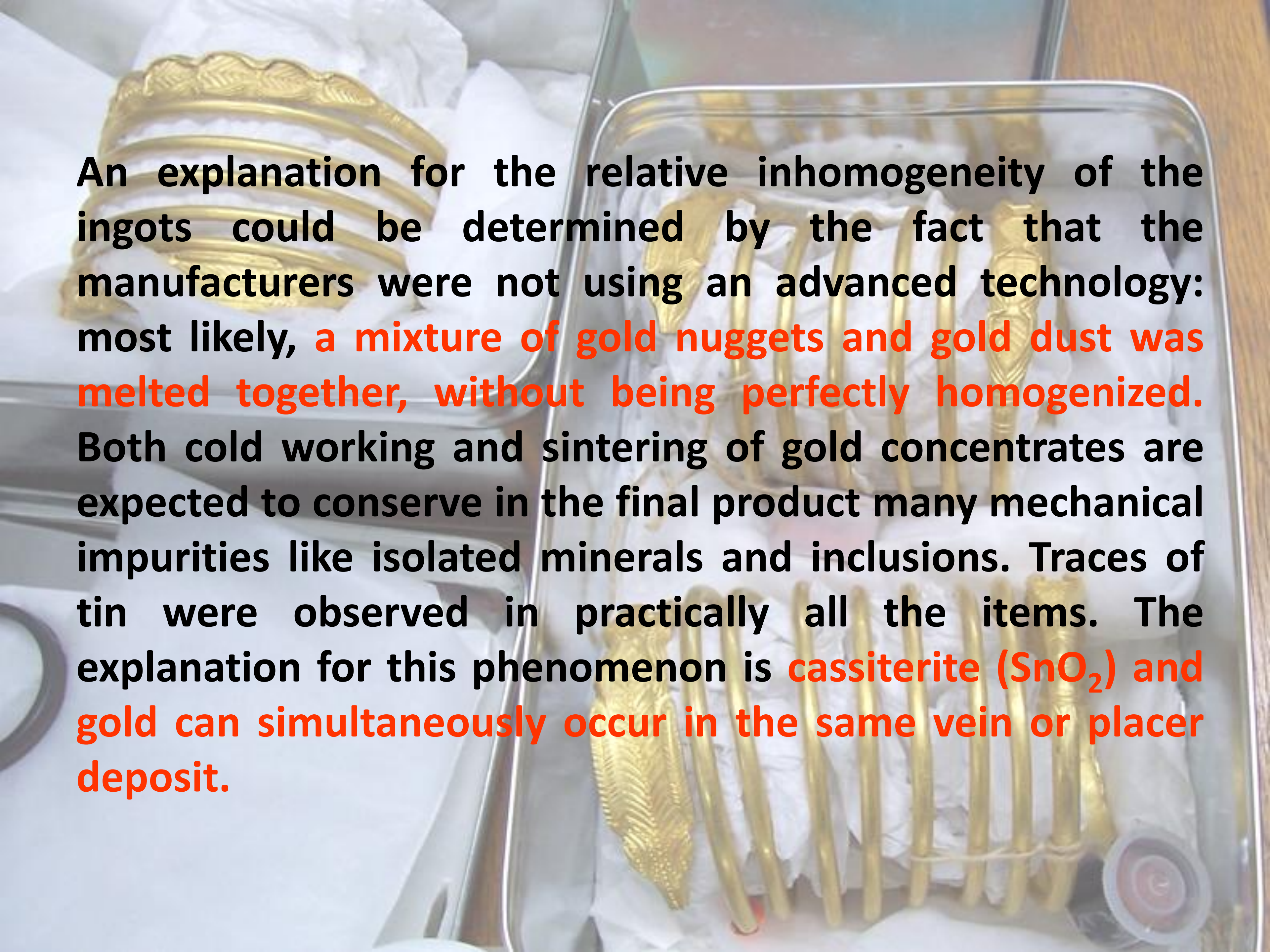

**Dacian Koson without monogram**




**Micro-PIXE spectrum of a minute fragment of a koson without monogram (first analyzed area) – the high tin signal is to be noted.**




**Micro-PIXE spectrum of the same fragment of a koson without monogram, but measured in a different spot (the second analyzed area) – a strong decrease in the tin signal (as compared with the previous spectrum) can be observed.**



An explanation for the relative inhomogeneity of the ingots could be determined by the fact that the manufacturers were not using an advanced technology: most likely, a mixture of gold nuggets and gold dust was melted together, without being perfectly homogenized. Both cold working and sintering of gold concentrates are expected to conserve in the final product many mechanical impurities like isolated minerals and inclusions. Traces of tin were observed in practically all the items. The explanation for this phenomenon is cassiterite ($SnO_2$) and gold can simultaneously occur in the same vein or placer deposit.

The copper concentration found in the artifacts is higher than the one in Transylvanian native gold, related to the presence of accompanying gold minerals in gold dust and nuggets - e.g. chalcopyrite ($CuFeS_2$) - “fool’s gold” and pyrite ($FeS$) – due to the probable confusion made by Dacian “miners” and to the primitive processing of the raw material.

Our micro-structural investigations reveals details about the “fingerprints” of gold geological deposits and for main characteristics of ancient gold metallurgy as relatively low temperature (lower than Au melting point) and hammering during heating to obtain an ingot through “sintering”. The “sintering” procedure was proved in the case of analyzed Dacian items – spiraled bracelets and Koson without monogram coins - as a tradition starting from Bronze Age for Transylvanian gold processing.

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**PAPER**

Angela Vasilescu *et al.*

Studies on archaeological gold items found in Romanian territory using X-Ray-based analytical spectrometry

# Neolithic obsidian from Transylvania

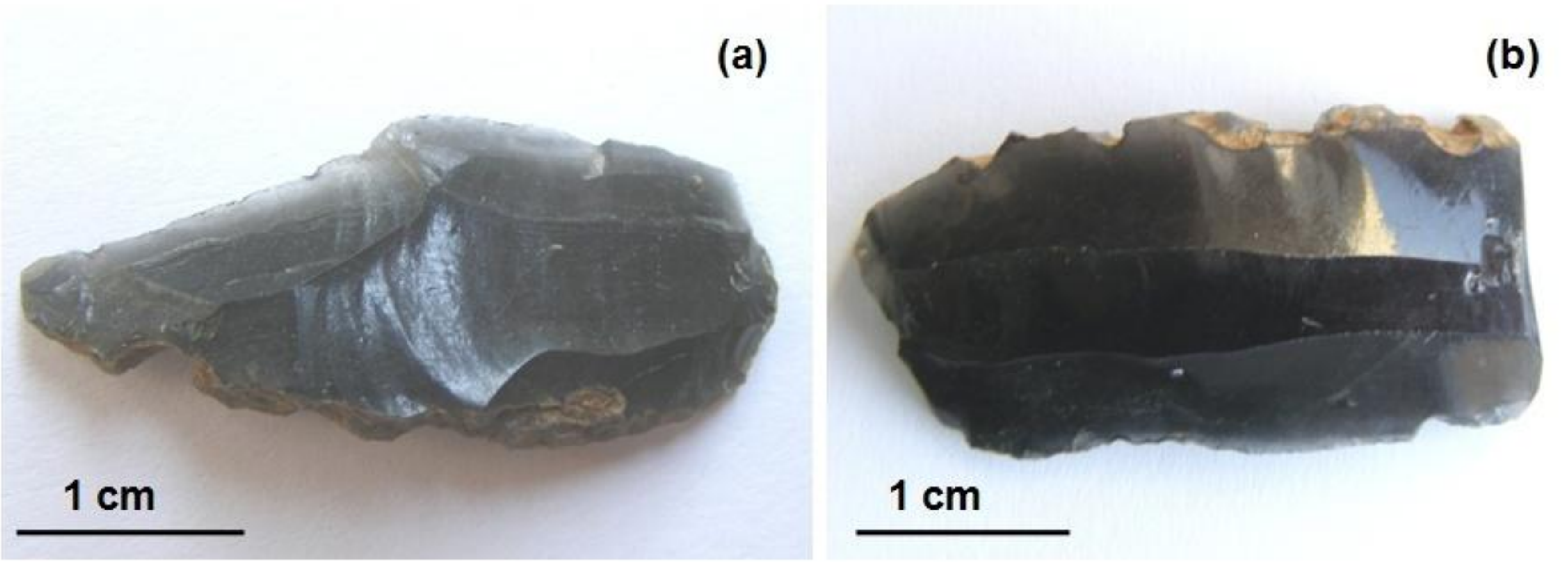
**Obsidian is a natural volcanic glass widely used for prehistoric stone tools and traded over long distances.**

**Obsidian is almost the ideal material for source characterization using elemental analysis. Moreover, it permits analysis, on a methodological level, of factors which could have influenced the choice of deposit by prehistoric people. The chemical composition of obsidian is not altered in the hands of the artisan, therefore, elemental analytical techniques are suitable for identification of the obsidian geological pattern.**

**In Romania, obsidian archaeological items were found in Transylvania, Banat - near Danube border with Serbia, and Southern Muntenia. Archaeological samples i.e. Neolithic obsidian tools were obtained from "Țara Crişurilor" Museum, Oradea, Transylvania's History National Museum, Cluj-Napoca and from Institute of Archaeology ''Vasile Pârvan", Bucharest.**

**The studied samples are from archaeological sites within Oradea region (Seleuş, Bucin, Taşad), Cluj area (Iclod, Țaga, Turda, Silagiu), Iron Gates on Danube area (Cuina Turcului) and Teleorman area near Danube (Măgura).**

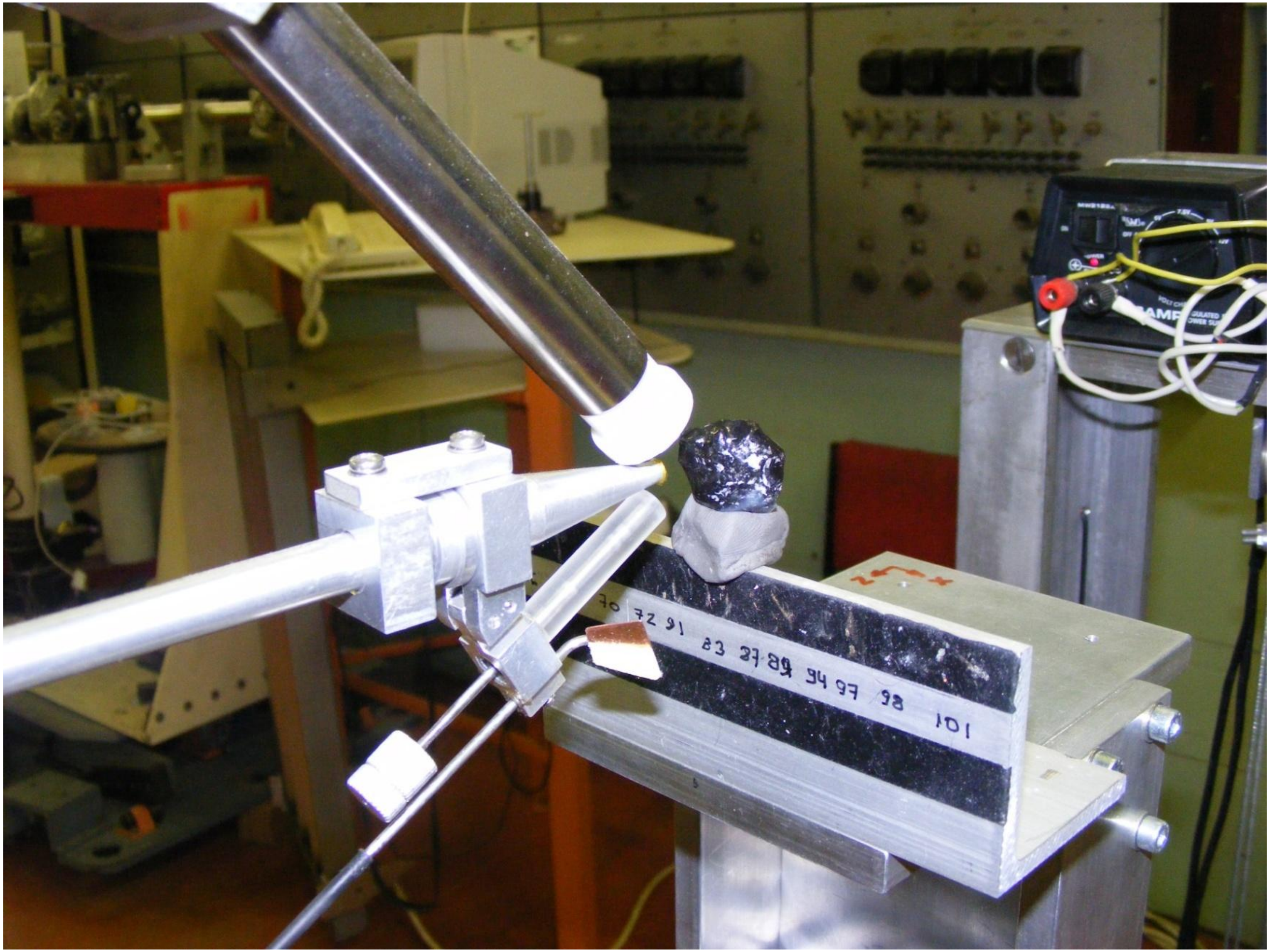
**Archaeological obsidian samples from Melos (a) and Carpathian I type (b).**



Geological obsidian samples from Vinicki or Carpathian I (a) and Lipari (b).

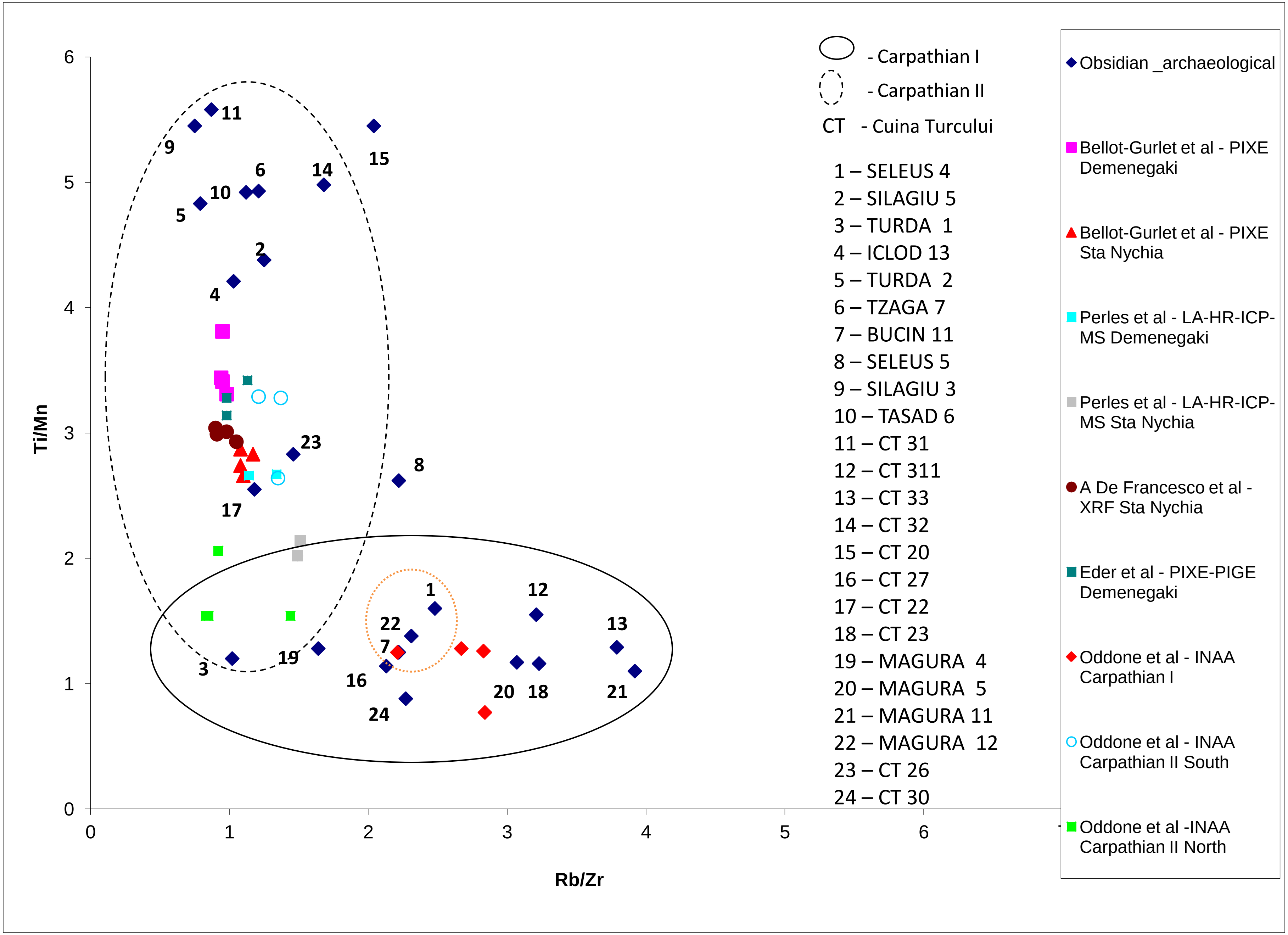
# Geographical locations of archaeological sites and geological obsidian sources

# Milli-PIXE method at the 5 MeV Van de Graaff accelerator of the Institute of Particle and Nuclear Physics, Wigner Research Centre of the Hungarian Academy of Sciences.



Milli-PIXE measurements were performed at the 5 MeV Van de Graaff accelerator of the Institute of Particle and Nuclear Physics, Wigner Research Centre of the Hungarian Academy of Sciences. The properly collimated proton beam of 3 MeV energy was extracted from the evacuated beam line to air through a 7.5 μm thick Kapton foil. A target-window distance of 10 mm was chosen where the beam diameter was found to be about 1 mm. For the analyses the external beam intensity was varied from 1 to 10 nA depending on the actual total X-ray count rate. The obsidians were fixed to a micro-manipulator allowing for an accurate three-dimensional positioning. The final target positioning was achieved using a mechanical “aiming” pin pointer.

X-ray spectra were collected by using a computer controlled Amptek X-123 spectrometer with an SDD type detector of 25 $mm^2$ x 500 μm active volume and 8 μm thick Be window. The detector with an energy resolution of 130 eV for the Mn Ka line was positioned at $135^o$ with respect to the beam direction. The target-detector distance was 25 mm. The net X-ray peak intensities and concentrations were calculated subsequently with the GUPIX program package. In order to arrive at the final conclusions our PIXE results were compared to data from the literature obtained on samples from the same geological sources using different analytical techniques.




**Scatter plot of Ti/Mn versus Rb/Zr ratios**

# Legend

- **Archaeological obsidian samples**

  Cluj (centre of Transylvania) - Iclod, Tzaga, Turda, Silagiu
  Oradea (North-West of Transylvania) - Seleus, Bucin,Tasad
  Iron Gates (on Danube border, between Romania and Serbia) - Cuina Turcului
  Teleorman, near Danube - Magura

- **Geological obsidian sources**

  Carpathian I – Slovakian Tokaj Mountains
  Carpathian II – Hungarian Tokaj Mountains
  Carpathian III – Ukraine
  Melos - Aegean Sea Island
  Yali - Aegean Sea Island
  Lipari - near Sicily Island
  Sardinia - Tyrrhenian Sea Island
  Armenia
  Eastern Anatolia

# Conclusion

The majority of Transylvanian Neolithic samples fit the Carpathian II pattern (Hungarian Tokaj Mountains). The Carpathian I pattern (Slovakian Tokaj Mountains) can be attributed to the Neolithization period samples both for Cuina Turcului (Southern Banat – Iron Gates) and Măgura (Southern Muntenia – Teleorman County). For Cuina Turcului Mesolithic samples the situation is special, they could fit Carpathian II pattern but two of them are close to Melos values, so, more samples from this category must be analyzed and an archaeological discussion is necessary.

Our study demonstrates that minor and trace elements as Rb, Sr, Y, Zr, Ti, Mn, can be successfully used to determine the provenance of archaeological obsidian, i. e. to identify the geological obsidian deposits.

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# Provenance studies of Central European Neolithic obsidians using external beam milli-PIXE spectroscopy

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ABSTRACT

External beam milli-PIXE technique was used for the determination of the elemental concentration ratios in some Prehistoric obsidian tools found in Transylvania, in the Iron Gates region near Danube, as well as on a few relevant geological obsidian samples from Slovak Tokaj Mountains, Lipari, Armenia. As provenance "fingerprints" the Ti to Mn and Rb to Zr ratios were used. The results confirm that the Transylvanian Neolithic samples have a Slovak Tokaj Mountains provenance. For Iron Gates samples, there are at least two different geological sources: for Late Neolithic tools, the origin is also the Slovak Tokaj Mountains but for Late Mesolithic–Early Neolithic samples, the sources are clearly different, possibly of the Hungarian Tokaj Mountains or the Balkan–Aegean origin.

# Mineral pigments of glazed Iznik (Turkey) ceramics

**Following the establishment of the Ottoman Empire, the name of Iznik became famous throughout the world due to the development of a ceramics industry in the 16$^{th}$ and 17$^{th}$ centuries. Combining the Ottoman style with external influences from China, Asia, the Balkans and even Europe, Iznik vessels and tiles reached the peak of Ottoman ceramic art. Iznik fritware was the result of a search by the Ottoman court in Istanbul for a recipe to make porcelain with the goal of imitating the much-admired and pricely Chinese Yuan and Ming Dynasty blue-and-white porcelain.**

The initial copies of the Chinese designs gradually gave way to a uniquely Turkish style which included a broader color palette. The mineral pigments used for the famous Turkish Iznik ceramics are very important for the understanding of commercial routes of late Middle-Age period. The most interesting problem related to the Iznik mineral pigments is the use of Cobalt to obtain the blue color, because Cobalt minerals deposits in Europe and Middle-East are only in Saxony ("Erzgebirge") and in Persia (Kashan region), both deposits involving special trade, political and military relations.

# Examples of analyzed Iznik shards


**LEGEND**

**Cobalt mineral deposits:**

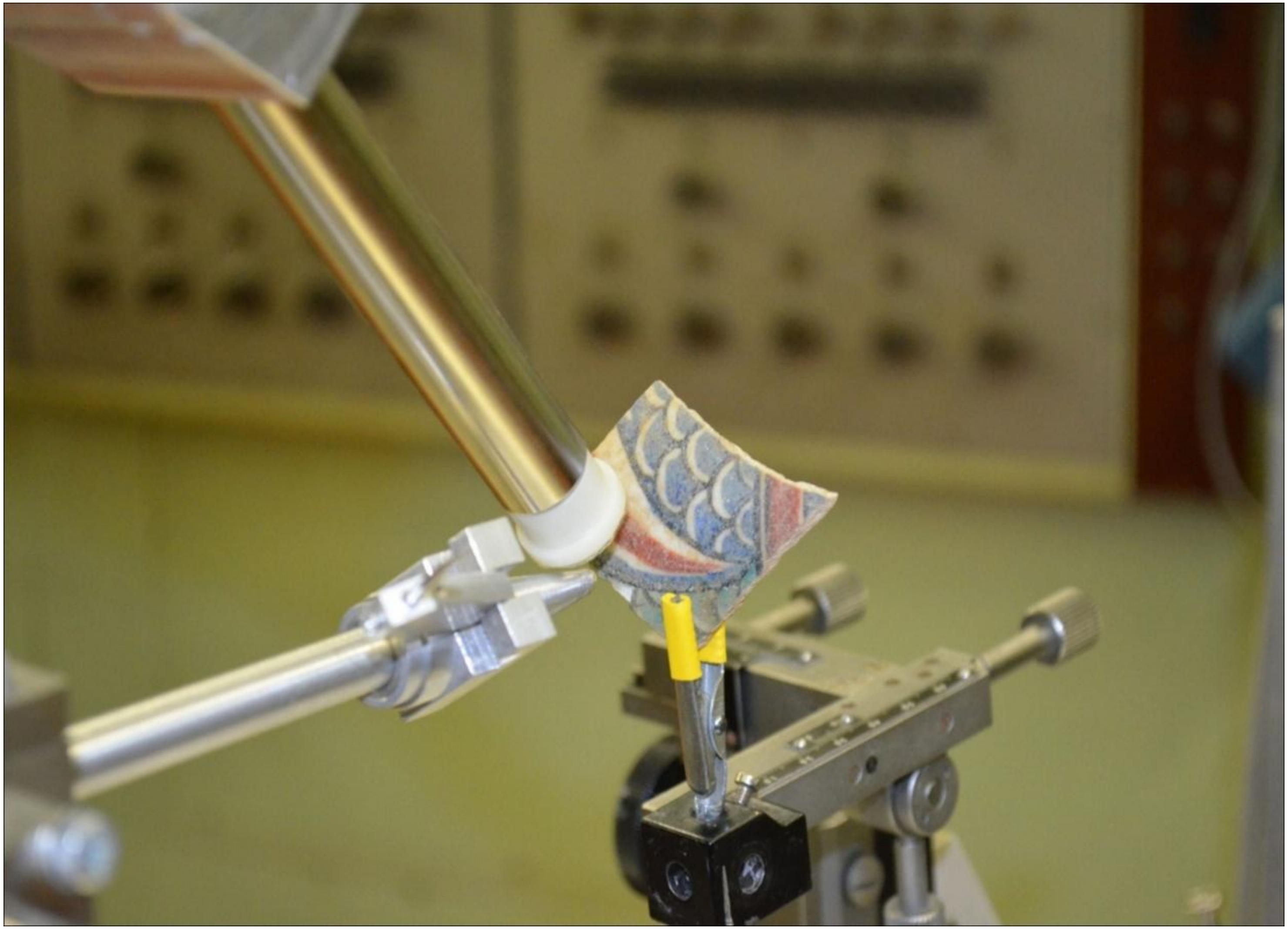
- **Saxony**
- **Kashan**

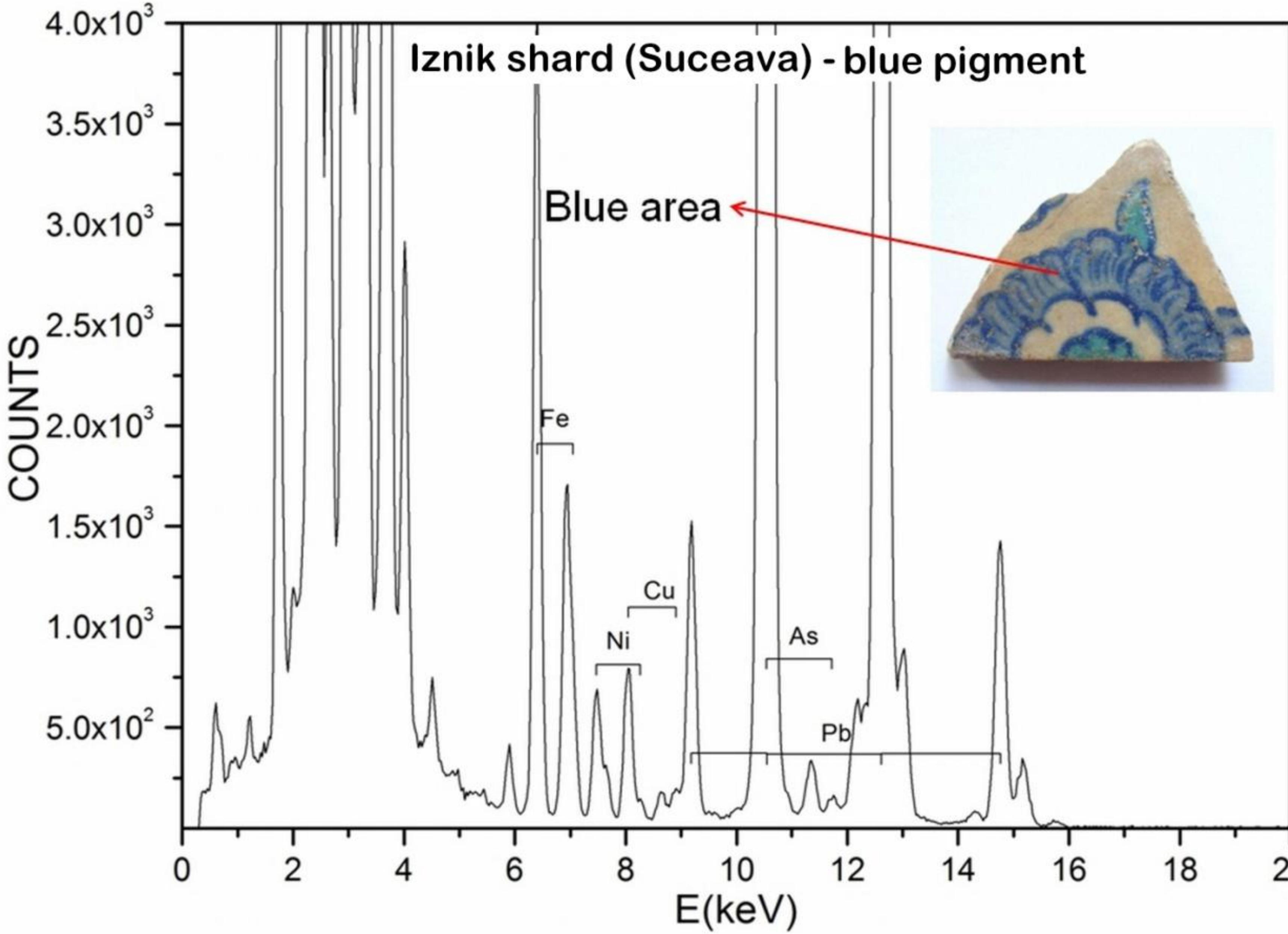
- **Iznik - pottery production centre**

**Sites:**

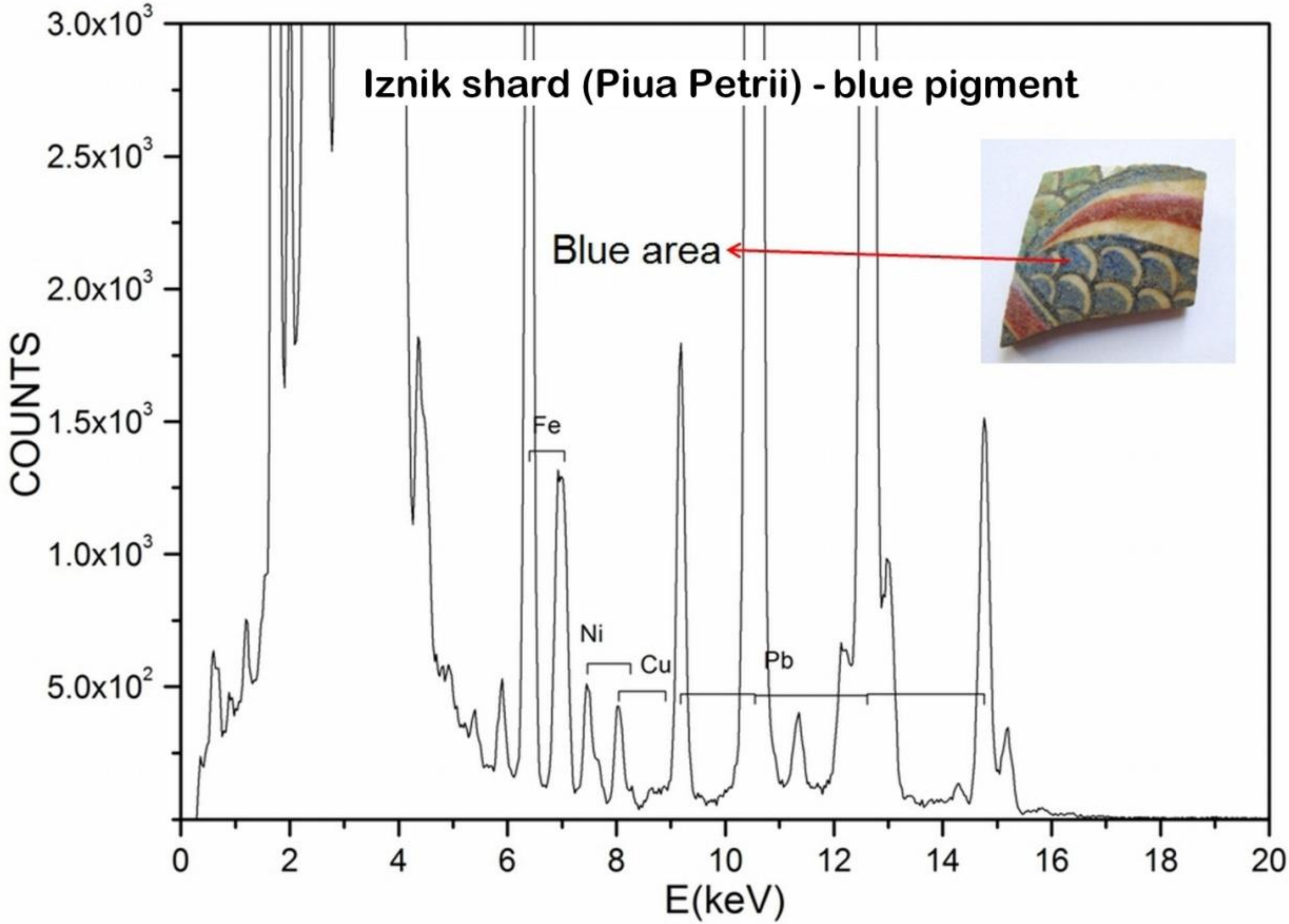
- **Piua Petrii - Commercial settlement**
- **Suceava - Historical Capital of Moldavia**

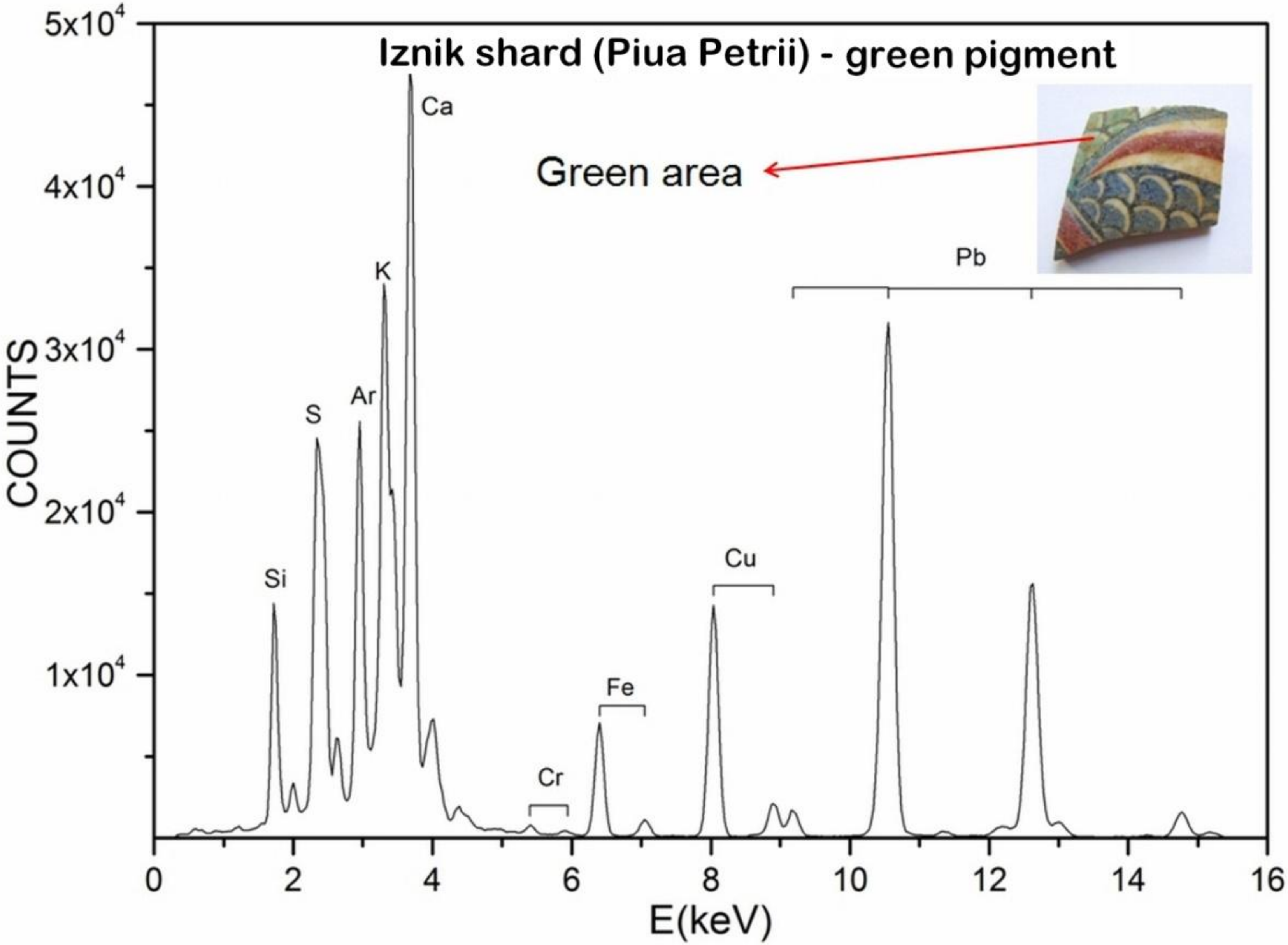
**Milli-PIXE method at the 5 MeV Van de Graaff accelerator of the Institute of Particle and Nuclear Physics, Wigner Research Centre of the Hungarian Academy of Sciences.**





Iznik shard (Suceava) - blue pigment
Blue area
COUNTS
E(keV)
Fe
Ni
Cu
As
Pb
4.0x10^3
3.5x10^3
3.0x10^3
2.5x10^3
2.0x10^3
1.5x10^3
1.0x10^3
5.0x10^2
0
2
4
6
8
10
12
14
16
18
20


Iznik shard (Piua Petrii) - blue pigment
Blue area
Fe
Ni
Cu
Pb
COUNTS
E(keV)
3.0x10^3
2.5x10^3
2.0x10^3
1.5x10^3
1.0x10^3
5.0x10^2
0
2
4
6
8
10
12
14
16
18
20



Iznik shard (Piua Petrii) - green pigment
Green area
COUNTS
E(keV)
Si
S
Ar
K
Ca
Cr
Fe
Cu
Pb
5x10^4
4x10^4
3x10^4
2x10^4
1x10^4
0
2
4
6
8
10
12
14
16

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and applied topics on *Environment*, *Archeometry* and *Cultural Heritage*

# External milli-beam PIXE analysis of the mineral pigments of glazed Iznik (Turkey) ceramics

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## Abstract

25 Iznik glazed ceramics fragments - shards of vessels, plates for wall decorations found in Moldova's capital Suceava, in Prince Vasile Lupu (1600-1640) palace and shards excavated from a Danube ford - Piua Pietrii, a renowned commercial centre during 17$^{th}$ Century were studied. We used external milli-beam PIXE (Particle Induced X-ray Emission) spectroscopy to investigate the capabilities of this method to identify the metals from ceramics mineral pigments. Cobalt, Lead-Antimony, Copper, Chromium, Iron and Manganese minerals used to obtain blue, yellow, green, red and brown colours were identified. Our PIXE results were compared with data from literature obtained on Iznik tiles samples using Raman spectroscopy proving a good compatibility.

*Key words:* external milli-beam PIXE; Iznik ceramics; pigments; Cobalt sources.

# New information on monetary arrowheads found in Dobroudja based on X-rays analysis of their alloy composition

**Bogdan Constantinescu[1], Gabriel Talmatchi[2], Daniela Cristea-Stan[1]**

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[2]*National History and Archaeology Museum, Constanta, Romania*

# Early Scythian types of arrowheads – VIII – VII – VI Centuries B.C.

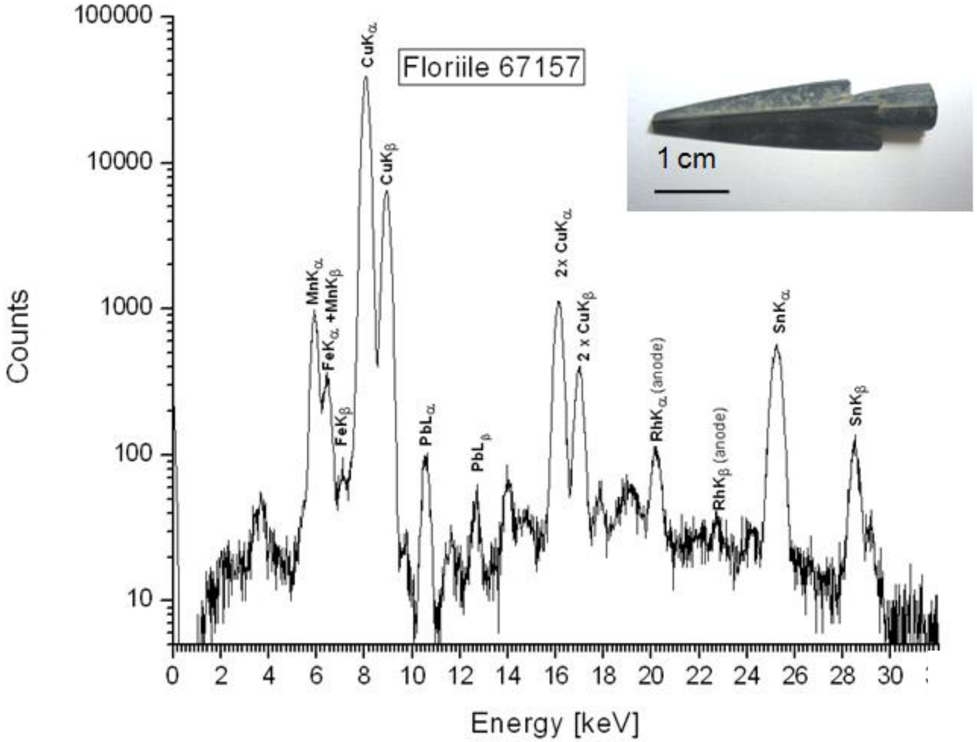
# Histria monetary signs

# "Whell" coins
# V$^{th}$ –IV$^{th}$ Century BC - first issue of coins by Histria after the use of monetary signs


OLBIA
ISTROS
APOLLONIA
MILETUS
CAUCASUS
EASTERN ANATOLIA
Germany
Czech Republic
Ukraine
Slovakia
Austria
Hungary
Switzer-land
Liecht
Alps
Mol-dova
Carpathians
Romania
Slove-nia
Croatia
Bosnia and Herzego-vina
Serbia
San Marino
Italy
Apennines
Vatican City
Monte-negro
Balkan Mountains
Bulgaria
Rhodopes
Mace-donia
Al-ba-nia
Pindus
Greece
Black Sea
Caspian Se
Caucasus Mountains
Georgia
Azerbaijan
Armenia
Pontic Mountains
Turkey
Taurus Mountains
Syria
Iraq
Leba-non
300 Kilometers
300 Miles

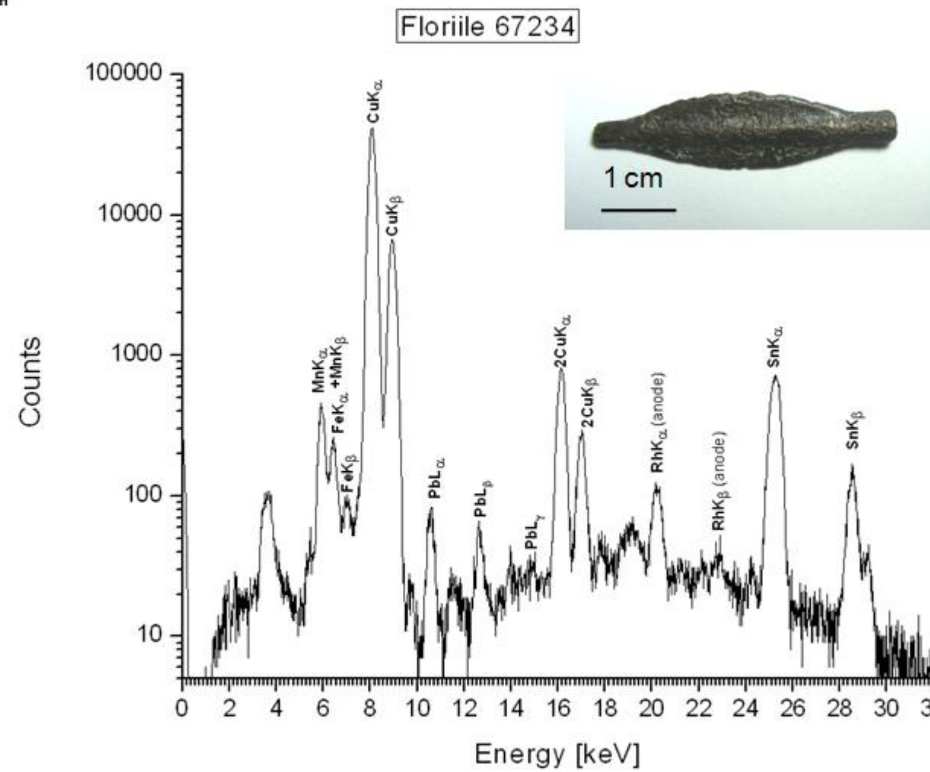

Galați
Ізмаїл
Izmail
Buzău
Brăila
Tulcea
Rezervația
Delta Dună
Ploiești
București
E81
Constanța
Pyce
Ruse
Варна
•Golovita
•Sinoe
•Histria
•Tariverde
•Cogealac
•Tomis
•Floriile

An interdisciplinary program to study the alloy composition of warfare and pre-monetary Scythian design “arrowheads” (trilobates or dilobates, sometimes with thorn) found together in same deposits in Dobroudja was started using XRF (X-Ray Fluorescence) and micro-PIXE (Proton Induced X-ray Emission) methods. Besides the “classical” Copper-Tin-(Lead) bronze type, with various proportion of tin (to increase hardness) or lead (to facilitate the casting process), two unusual types of bronze - used both for warfare (including pieces with cut pointed-end impossible to use as weapon) and for pre-monetary arrowheads - were identified: Cu-Sn-Mn-Pb for Golovita, Cogealac and Floriile items and Cu-Sn-Sb-Pb for Tariverde, Sinoe-Zmeica and many Istros items. We also identified some pre-monetary “arrowheads” with a mixed alloy containing both Mn and Sb, more probably from re-melting of warfare arrowheads.

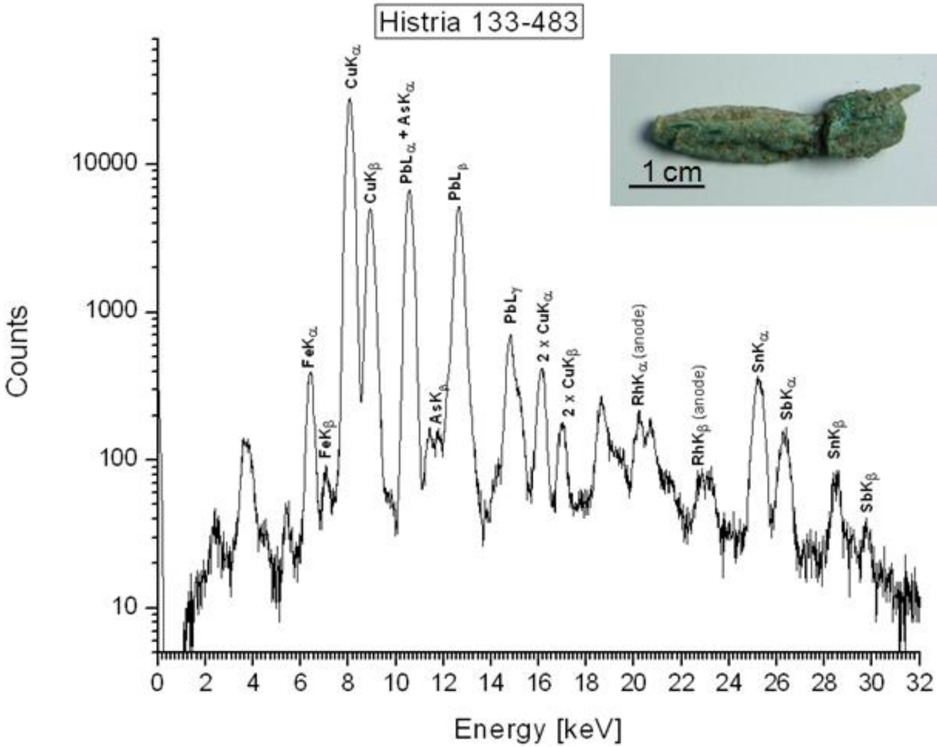


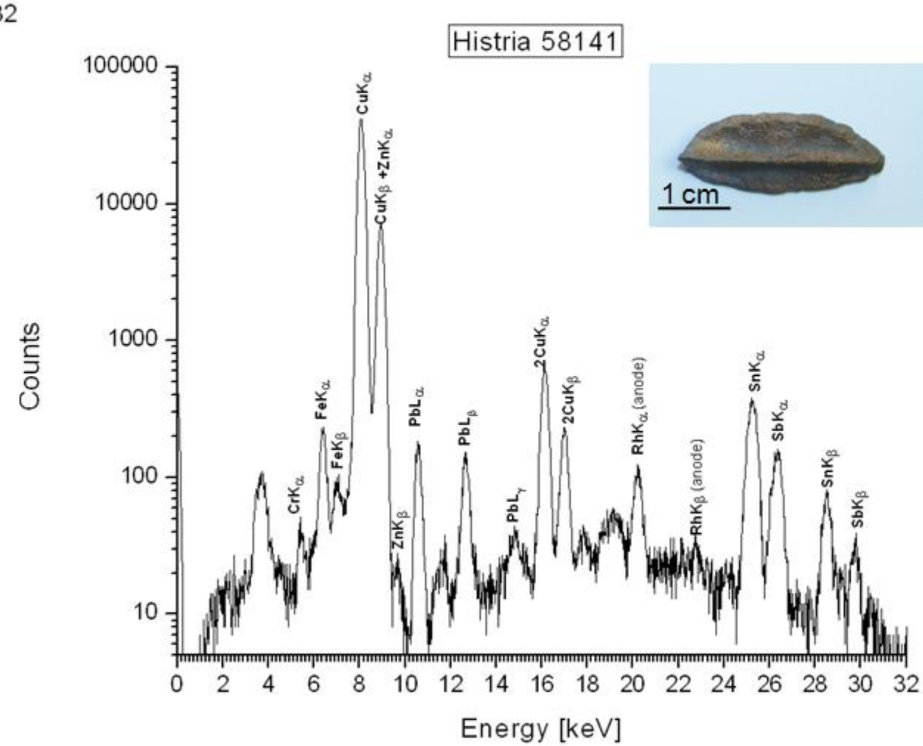

**Floriile arrowhead (left) and pre-monetary sign (right) - photos and XRF spectra.**

**The most relevant for numismatists result is that for each finding place the same type of alloy was used both for fighting arrowheads and for pre-monetary signs.**

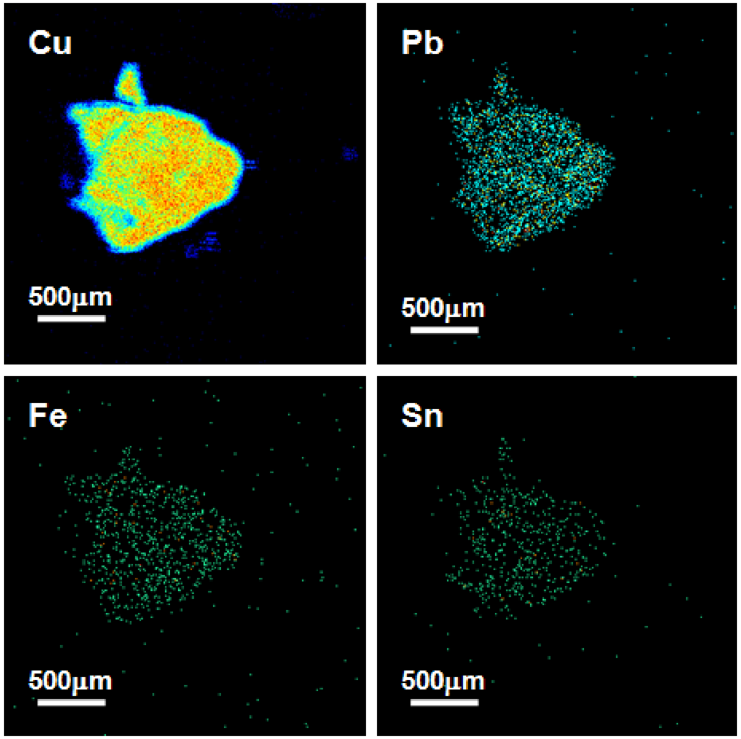


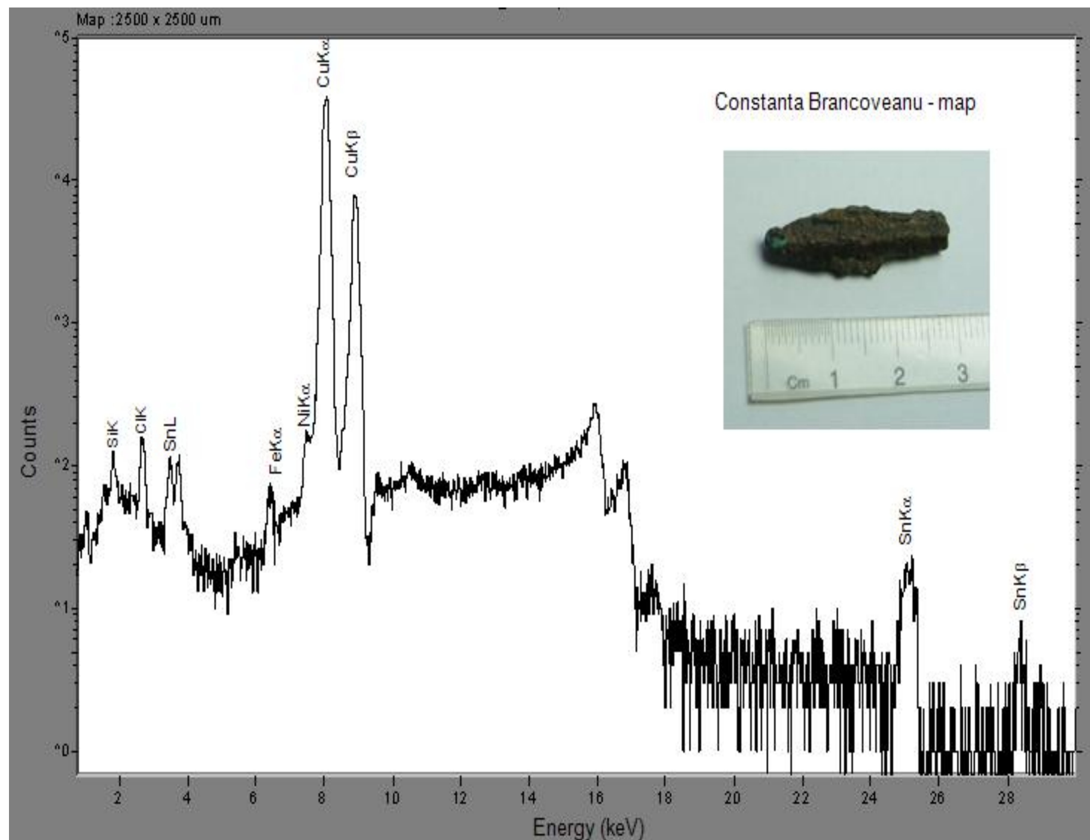
# Histria (Istros) arrowhead (left) and pre-monetary sign (right) - photos and XRF spectra.

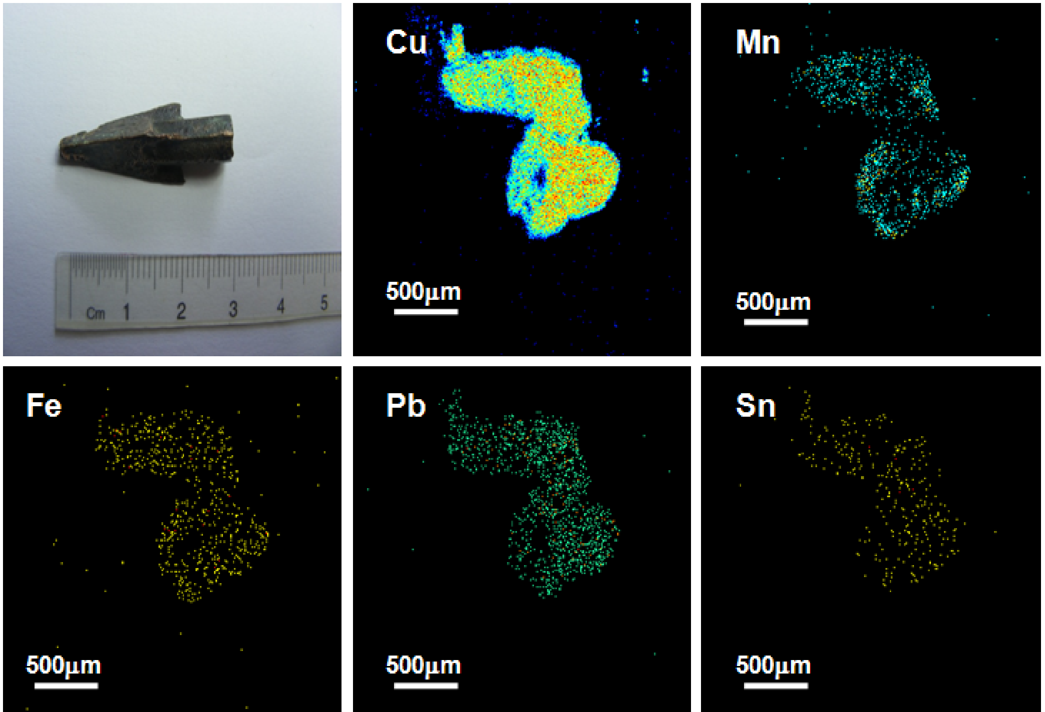


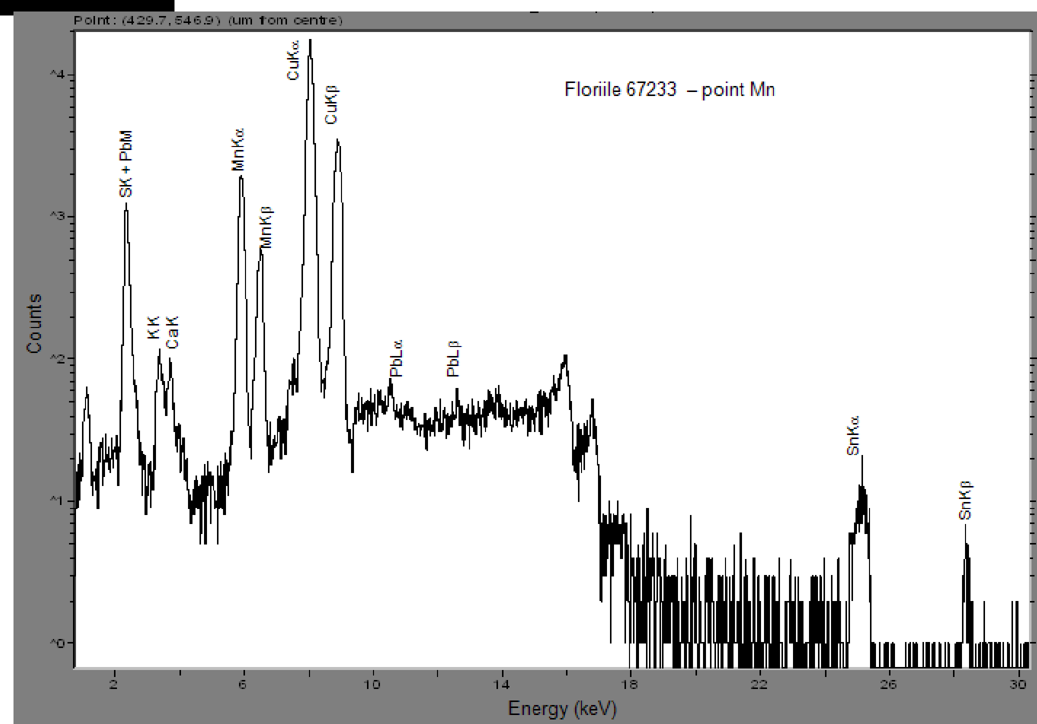
**Histria "Constantin Brancoveanu" pre-monetary sign micro-PIXE elemental maps (left) and point spectrum (right); Pb segregation – non-homogeneous composition.**






**Floriile 67233 arrowhead photo, micro-PIXE elemental maps (left); and point spectrum (right) - small areas with Mn concentrations**



The big problem to be solved is how antimony and manganese can be components of a copper alloy. As mentioned in J. Curtis and M. Kruszynski, *Ancient Caucasian and Related Material in The British Museum*, Occasional Paper Number 121, 2002, antimony is a component of poly-metallic geological deposits, its presence being an indicator for the use of secondary enriched sulfide ores (grey ores or fahlerz) in bronze metallurgy, ores including copper, arsenic, antimony, but also, in small quantities, silver, nickel and bismuth. Chernykh suggests arsenical and antimonal bronze in Southern Russia are associated with pyritic copper mines from Southern Caucasus.

The analysis performed on bronze items belonging to British Museum collections suggested antimonal bronze is found mainly in Kuban area (North-East to Black Sea), a region with a strong Scythian presence. Unless a relatively pure Cu-Sb mineral was widely available, the two most likely explanations for the compositions seen are the co-smelting of copper minerals with a relatively pure antimony mineral (e.g. stibnite, $Sb_2S_3$), or the addition of metallic antimony to copper. So, the most credible hypothesis concerning the use of antimonal bronze for some “arrowheads” pre-monetary signs found both in Olbia and in Histria is its Scythian provenance.

The problem of ancient bronze containing manganese is more complicated. An explanation could be the use of manganese oxides as flux necessary to smelt oxidized ores. It is the case of Timna in the Sinai ores occurring in a highly siliceous gangue which must be fluxed with an iron mineral such as hematite or limonite (both often impurified with manganese oxides). Our hypothesis is a similar type of copper ores smelting in Ukraine – in the region of Nikolaev, very rich in manganese minerals – an area also known with a significant Scythian presence, but to definitely accept this hypothesis more studies will be necessary. Both antimony and manganese presence in Scythian bronze is facilitated by the use of primitive metallurgical procedures.

We must outline that copper minerals from North Bulgaria and Serbia don't contain manganese or antimony.

*9th International Physics Conference of the Balkan Physical Union (BPU-9)*
AIP Conf. Proc. 1722, 140005-1–140005-4; doi: 10.1063/1.4944195



# Studies on Bronze Pre-monetary Signs found in Dobroudja using XRF and micro-PIXE

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**Abstract.** We performed compositional analyses on 180 Scythian-type arrowheads and pre-monetary signs using XRF method and on 60 small fragments of such items (approx. 100 microns diameter), sampling being performed on previously corrosion-cleaned areas on their surface, using micro-PIXE. The items are found in Dobroudja, Istros-Histria region. The most relevant for numismatists result is that for each finding place the same type of alloy was used both for fighting arrowheads and for pre-monetary signs. Our analyses revealed three types of alloys: Cu-Sn-Pb ("normal" bronze), Cu-Sn-Mn-Pb and Cu-Sn-Sb-Pb. The presence of antimony suggests the use of fahlore-type poly-metals deposits, most probably from Caucasus Mountains. The problem of ancient bronze containing manganese is more complicated; an explanation could be the use of manganese oxides as flux necessary to smelt oxidized ores.


Thank You very much for Your attention!