BEAM REQUEST at Bucharest 3 MV TANDEM

Experiment title:

Determination of the elemental composition of pigments used on Chalcolithic (*c*. 4900-4000 BC) and Late Bronze Age (*c*. 1550-1350 BC) ceramics from Southern Romania through the PIXE/PIGE method

Experiment responsible

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Short presentation of the scientific project (maximum four pages): see below

Beam time request (unit=days)*: 20 days organized as 4 sets x 5 days each at intervals of 1-2 months; Desired Period*: March 1–December 15, 2018

Desired beam properties

Type*: protons; Energy (MeV)* 3; Intensity*(p/nA): ~ 5 nA

Vacuum Requests*: 10^{-6} torr

Special requirements for detectors, electronics, acquisition system:

Experimental set-up belonging to the PIXE-PIGE reaction chamber, including the external beam setup.

Minimal information needed for the radiological risk evaluation:

a) Source activity*: none

b) Use of open sources*: none

c) Estimate of the residual activity as a result of irradiation*: none

d) Means of storage/transportation for irradiated targets*: none.

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The aim of the current proposal is twofold:
1. To contribute to a more comprehensive study concerning the chemical characterization of Chalcolithic and Late Bronze Age ceramics from Southern Romania. This is a follow up of our previous experiment (see below) with the aim of extending the information and acquiring a statistically relevant set of data.
2. To contribute to the founding of E-RIHS RO, the Romanian hub of E-RIHS (European Research Infrastructure for Heritage Science), through experimental development and shared experience of archaeologists, physicists and chemists from different institutions.

Previous work
The project submitted previously (for the experiment carried out in 2016) was titled *Determination of elemental composition of prehistoric, antique and modern artefacts through the PIXE/PIGE method: A contribution to the study of technology and production as social process*
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We focused on prehistoric ceramics (the antique and modern artefacts were only a few). Our aim was to determine the elemental composition of pigments and in one case-study also of the paste and gain some insight into the origin of raw materials and the technological choices.

The number of detectable chemical elements was limited by the experimental conditions.
The IBA end station from the 3 MV Tandetron™ allows in vacuum and in air measurements.
Due to some technical difficulties the collected data concerning the low atomic number was limited. Two new SDD detectors for LE & HE X-rays were installed to facilitate detection of Al and Si.
The preparation of samples was limited to the slight scratching of the surface immediately before measurement to avoid measuring possible post-depositional layers.

Results:
Case study 1: *Early Chalcolithic clay objects from Nanov-'Vistireasa' (4800-4500 cal BC)*: we determined the basic composition of the white (Ca based with low Si based compounds), orange red (mainly iron oxides with Ca and quartz) and dark red pigments (iron oxides with quartz) as well as of the paste; one potsherd was identified as an import due to its different

chemical composition (abundant carbonate inclusions); paste analyses indicated that sources of clay were situated close to the settlement, but different sources were used for pottery and constructions (hearths and plaster).
Case study 2: Pottery and ritual objects from the so-called sanctuary at Căscioarele (early Chalcolithic in Southeastern Romania, c. 4800-4500 cal BC): we determined the basic composition of the white, yellowish white (mixtures of calcite and Ca based compounds, quartz, kaolinite and even monohydrated calcium oxalates) and red pigments (iron oxides, silicon oxides as well as traces of kaolinite, calcite and gypsum).
Case study 3: Middle and Late Bronze Age pottery from Southern Romania (c. 2000-1350 cal BC). The analysis of pigments – all white with no macro optically distinguishable differences in shade – lead to the identification of three types of composition – i.e., based mainly on gypsum, white bones and white bone plus gypsum, to which also calcite or sulphur based minerals were added; the variety of pigments was broader in the Middle Bronze Age than in the Late Bronze Age.

Conclusions of the previous experiment:

- Because the beam was focused on a minimal spot of 2x2 mm and many pigments inlays are narrower than the targeted spot, suitable samples have to be found;
- To obtain statistically relevant results in Case studies 2 and 3 more measurements are needed.

Current proposal
Determination of the elemental composition of pigments used on Chalcolithic (c. 4900-4000 BC) and Late Bronze Age (c. 1600-1300 cal BC) ceramics from Southern Romania through the PIXE method

Case study 1: Elemental composition of white and red pigments from the early Chalcolithic pottery (the Vidra phase of the Boian Culture, c. 4900-4700 cal BC) at four sites in Southeastern Romania continues Case study 1 from 2016. We aim at determining: pigment preparation; comparison with the pigments used in the preceding period (s. Case study 1 from 2016) in terms of continuity vs. innovation; possible sources of raw materials; possible exchange networks of raw materials and technologies (40 samples).
Case study 2: *Elemental composition of white and red pigments from two Chalcolithic sites in the Danube Valley: Căscioarele (Romania) and Atmageaua Tătărască (Bulgaria)* continues Case study 2 from 2016. Căscioarele and Atmageaua Tătărască are two multi-layered, contemporaneous settlements (attributed to the Boian and Gumelniţa Cultures, *c*. 4900-4000 cal BC). The aim of the study is to gain information on pigment preparation; compare pigments to the supposed lumps of raw materials found in the settlement; compare the pigments between the two contemporaneous habitations and among settlements and graves (40 samples).
Case study 3: *Elemental composition of white pigments from Late Bronze Age pottery in Southern Romania (c. 1550-1350 cal BC)* continues Case study 3 from 2016. Then all the samples characteristic of the Late Bronze Age in Southern Romania came from one settlement (Popeşti, near Bucharest) and, in contrast to the preceding period, they had mainly the same chemical composition: white bone with various percentages of calcite. In this new case study we aim at determining the chemical composition of the pigments from further four contemporaneous sites, with stylistically identical pottery, but situated hundreds of km afar (Cârcea, Govora, Copăcelu, Gătejeşti) to verify whether the stylistic the uniformity established by macro optic examination is also present at the level of the chemical composition of the pigments. This is part of the answer to a broader question: How did this stylistic uniformity came into being on such an unusually large area? (40 samples).

To facilitate adjustments to observations made during the experiment, it is better to have the beam time divided into 4 periods: 20 days as 4 sets of 5 days each at 1-2 months intervals.
After determining the elemental composition by PIXE/PIGE, further analyses (FT-Raman spectroscopy, FTIR and SEM/EDX) will be carried out to determine the chemical forms of those elements and the composition of mixtures for the pigments.

Experiment proposal:
Application of **PIXE and PIGE techniques (3 MeV protons)** to determine elemental contents of samples at the 3 MV Tandetron^{TM} of IFIN-HH.
Elements investigated by PIGE: F, Na, Mg, Al, Si, P, S, Cl, Cr, Mn, Fe, Cu.
Elements investigated by PIXE: Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Sr.

Experimental set-up:
- Ion Beam Analysis (IBA) reaction chamber.
- Detectors: For PIXE (X-ray detection): IGLET-X-06135-S High Purity Germanium (diameter 6 mm, depth 6 mm), with Be window of 0.0127 mm, placed inside the reaction chamber.
For PIGE (γ-ray detection): GEM10P4-70 High Purity Germanium (1.75 keV FWHM at 1.33 MeV of ^{60}Co) placed at 15 cm from the target support, outside of the reaction chamber.

References:
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