PIXE Analyses of Byzantine Pottery from Romania

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An assemblage of 92 Byzantine ceramic shards discovered at Pâcuilul lui Soare and Castrul 22, and 5 samples originating from a shipwreck sunk in the Sinoie Lake, Constanţa County, Romania were investigated using Particle Induced X-ray Emission (PIXE) technique at LNL, INFN. Castrul 22 was a defensive fortification belonging to a stone wave, while Sinoie was a Black Sea gulf from Antiquity until the medieval period [1]. All analyzed ceramic fragments were dated to the 10th-12th centuries AD.

PIXE data were acquired at AN2000 accelerator using a 2 MeV proton beam. The experiment aimed to determine the chemical composition of the ceramic paste (milli-beam measurements of pelletized powders) and to study the decorations (micro-beam measurements of the interfaces between the glazed surfaces and underlying ceramic bodies).

Based on visual grounds, the ceramic fragments chosen for this study were divided by the archaeologist into several categories: fine or coarse fabric, with applied (glaze, paint, engobe) or incised decoration, fired in an oxidizing or reducing atmosphere. The fine ceramic samples, rare occurrences and thought to be import wares, consisted of 14 fragments decorated with a green-olive glaze or green and yellow stripes, while 4 shards feature a golden engobe. The analytical data were used to check if there is any connection between the stylistic classification and the one based exclusively on compositional data.

The results of this study were used to enlarge the analytical database of Byzantine ceramic from Romania, as in the previous stages of this on-going project, 170 ceramic shards excavated in other sites from the Lower Danube, such as Hârşova, Oltina, Valu lui Traian and Pantelimonu de Sus - see figure 1, were also analyzed using PIXE method at LNL [2 - 3].

The statistical analysis of the PIXE data conducted with either Hierarchical Cluster Analysis (HCA) or Principal Component Analysis (PCA) methods showed that for all analyzed potteries originating from any of the above listed archaeological sites, two main compositional groups can be distinguished: one including the fragments made of kaolinitic clays (i.e. containing high amounts of alumina) and another containing the rest of the samples, regardless if decorated or not and with no connection to their fineness or firing atmosphere. In some cases, several outliers were evidenced; archaeological explanations for these peculiar samples were sought, too.

This division indicates that either different raw materials (kaolinitic clays) or different working procedures (e.g. firing conditions, temper, decorations) were used to manufacture the analyzed potteries. A relatively close source of kaolinitic clays was localized in the Carasu river valley, source that was exploited starting from the Roman period.

These analytical results evidenced that the medieval potters selected distinct raw materials to produce vessels with different properties, such as mechanical or thermal resistance, reduced porosity, etc.

Micro-PIXE scans of the interfaces between the green glazes and the underlying bodies, particularly the Pb Lα maps, were used to estimate the thickness of the decorations and to get some information about the manufacturing procedures and raw materials. Similarly to the previously analyzed glazed ceramics, the thickness of the green glaze for Pâcuilul lui Soare and Castrul 22 shards turned out to be from ~50 μm up ~300 μm thick, the outer layer exhibiting a composition rich in lead oxide (PbO mean value: ~ 64 wt% for Pâcuilul lui Soare glazed potteries and ~ 57 wt% for Castrul 22). A peculiar feature of Castrul 22 glaze composition is its content of antimony (~ 5000 ppm of Sb2O3), suggesting that a lead-antimony compound might have been used to obtain the yellow hues of the glaze. In any case, for shards coming from both sites, the glaze decoration was obtained through the application of a lead mineral onto a non-calcareous ceramic body.

Fig. 1. Map indicating the location of all the archaeological sites where the Byzantine ceramic shards analyzed in this project were excavated
A particular attention was paid to the PIXE results on amphorae: 5 samples from Sinoie Lake, 3 from Pâcuil lui Soare and 3 from Castrul 22. All Sinoie Lake samples turned out to have very similar compositions. On the other hand, two of Pâcuil lui Soare amphorae have almost identical composition, while one of the them is completely distinct, with a composition specific for a kaolinitic clay pottery, as indicated by its high Al$_2$O$_3$ content (~ 23 wt%). The vegetal remains observed by the archaeologist during the visual analysis of this shard (PA14) suggest a possible local (i.e. at the Lower Danube) manufacturing of this particular recipient. According to the plot shown in figure 2, three clusters can be identified for the amphorae analyzed in this experimental campaign: one containing all the samples from Sinoie Lake, another containing the samples from Castrul 22 and two samples from Pâcuil lui Soare, while amphora PA14 from Pâcuil lui Soare seems to form a category of its own, being different from any of the former two groups. Possible interpretations of this clustering might be the production of the objects with similar composition in the same workshop, the use of the same raw materials or, a common origin for the recipients belonging to the same group.

In a further stage of this project, PIXE results will be interpreted in correlation with mineralogical analyses by petrographic methods (polarized light microscopy) and X-Ray Diffraction (XRD) or Raman spectroscopy, in a trial to achieve a comprehensive characterization of the Byzantine ceramics discovered in Romania. Summarizing, PIXE data obtained during the 2016 experimental campaign at LNL, INFN were employed to get hints about the ceramic manufacturing practices and raw materials employed in the Lower Danube area during the Byzantine period. In a broader perspective, it is expected that this on-going project will provide hard science evidences for the commercial exchanges between different settlements from the Lower Danube region. As this subject was just occasionally tackled in the archaeological literature, it follows that the study briefly reported here is one of remarkable interest for the scientific community.

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