Characterisation of Ancient Coins Made in Silver-Copper Alloy by Means of Micro-PIXE

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INTRODUCTION

A study to analytically characterise ancient coins has been started by the Solid State Physics group of the Torino University and INFN in 2010 [1,2]. This topic is particularly interesting for numismatic and archaeometry, because it allows to evaluate commercial exchanges among tribes, to hypothesise relative chronologies, to verify the presence of a debasement along the years and to investigate the exchange ratios among different emissions of coins. Until now the study has been focused on coins made of a silver-copper alloy in the Roman and pre-Roman period. The samples made of this material are often characterised by surface silver-enriched layer and, for this reason, some silver coins have been cut to study their microstructure and especially to assess the absence or the presence (and in this case also the size), of corrosion layers, enriched layers and inhomogeneity between surface and bulk. Some papers in literature have already discussed the topic [3,4] and some preliminary measurements on one coin have already been performed at LNL in last years [5].

MATERIALS AND METHODS

The 13 analysed coins are: victoriati (4) and quinarii (6), minted by the Roman Republic between II and I century B.C., and Illyrian drachmas (3) minted by the cities of Apollonia and Dyrachium in the same period. They come from a private collection and have been prepared using a standard metallographic procedure. All the coins have been cut with a rotating diamond wheel and one of the cut parts have been mounted in resin. Subsequently, the surfaces were polished with papers having different grit and with a diamond crystal paste (with grains 6-3-1 μm). A carbon coating has then been applied to make the sample surfaces (section of coin in resin) conductive, so to allow measurements in vacuum avoiding charging effects.

Micro-PIXE measurements were carried out on these cross-sections at the AN2000 microbeam facility of INFN-LNL, using 2 MeV protons. The beam was focused to a spot size of ~5 μm and raster-scanned over large areas of the samples (from one side to the other of each coin), analysing both the surfaces and the bulk. Quantitative analysis has been carried out by means of the Gupixwin software (version 2.1.3), calibrated using 3 Ag-Cu alloy standards and 5 modern coins of known composition (Netherlands, 25 Cents 1925; UK, Schilling 1945; Sweden, Crown 1946; USA, 1/2 Dollar 1968; Italy, 500 Lire 1959), as shown in figure 1.

RESULTS AND DISCUSSION

The presence of a very thick surface silver-enriched layer (up to 250 μm) has been confirmed on the victoriati and Illyrian drachmas, while almost all the quinarii do not appear to be affected by this phenomenon (figure 2). Area and profile measurements carried out on victoriati show that silver content is clearly higher in the surface layer, suggesting an intentional depletion occurred with acid chemicals before minting operations, as reported in [3].

The added value provided by \textmu-PIXE, however, concern the distribution of minor and trace elements along the section. A selection of coins has been analysed acquiring PIXE spectra of different areas (raster scanning the beam on 40x40 μm², then moving the sample of 40 μm and repeating this operation from one side of the coin to the other) obtaining the distribution profiles of all the detected elements.

Representing the ratio of each minor element in relation to the main ones (Silver and Copper) it is possible to understand where each element comes from: if the ratio on Silver is constant along the profile, one can suppose that the element was present in the raw material containing Silver (for example Gold in figure 3); the same for Copper. If both the ratios vary along the profile, the element can be entered in the coin during its burial time, coming from...
earth or water around the sample (for example Bromine in figure 3).

In the coins elements like Bromine, Chlorine and Iron, commonly present in soil and water, are detected mainly close to the surface and can be therefore linked to alteration phenomena due to the bury conditions. On the other hand, Gold is clearly linked to Silver, as it appears mostly present in the silvery layer. Nickel and Zinc seem, on the contrary, to be correlated to Copper, since their presence is concentrated in the bulk.

CONCLUSIONS

The elemental analysis of ancient coins by means of micro-PIXE showed to be useful to study the different elemental distribution between surface and bulk. A thick silver-enriched layer (up to 250 μm) has been found on different kind of coins, confirming that the victoriatus coin series is strongly characterized by the presence of thick surface silver-enriched layers, as shown in recently published data [6].

The strongly different Ag-Cu distribution between surface and bulk implies that compositional analyses carried out with surface techniques (e.g. XRF) on untreated surfaces on silver-copper alloys are not reliable to provide fineness of ancient coins.

Finally minor and trace elements seem to be differentially correlated either to Silver or Copper or coming from earth and water during the burial period.