Characterization of ancient Greek coins using non-destructive TOF neutron diffraction.

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Abstract. The characterization of ten ancient Greek silver coins from the Treasure collection of Gazoros (CH IX 61) found in Serres- North Greece; as well as two silver coin replicas, has been carried out using a polychromatic neutron beam of large cross-section to obtain diffraction patterns from the entire objects. The diffraction profiles indicate that there are three distinct categories of coins. The first one is a set of three coins consisting mainly of silver and copper alloy phases with high quantities of Cu₂O and CuCl. The second group is formed of coins with high silver/copper alloy ratio and the third is a collection of five coins consisting of very high purity silver. The comparison between the diffraction profiles of the original coins to those of the replicas present distinct variations that may be used to differentiate the different groups.

1. Introduction

Information about long gone societies is logged in archeological or historic objects. The deciphering of such recordings requires apart from comparative ethnographic, visual, aesthetic, textual, stylistic, morphological or epigraphic investigations primarily performed by the archeologists, extended scientific approaches and multi-analytical techniques that can look into the chemical-physical properties, the microstructure and the elemental compositions of the materials used during the fabrication. To this purpose, analytical methods may be employed to collect data from the surface as well as the bulk of the object, however, this involves sampling which is either completely forbidden or in some very rare cases acceptable, but absolutely limited to certain concealed areas of the object and in very minute amounts. These facts demand the use of noninvasive procedures that on the one hand are well suited for near-surface analysis and can be used “in situ” e.g. Laser induced break down spectroscopy LIBS [1-2], X-ray fluorescence (XRF), Proton induced X-ray emission (PIXE) [3], 3D MicroXRF [4-7], EDXRF-PIXE [8-9]. Although the portable methods are very useful to provide real time data at the site so that decisions for further investigation can be readily made, they are somewhat less specific as they are subjected to environmental conditions, absorption, X-ray production cross section etc., while the “ex situ” measurements are limited to several micro meters (~20-100 µm) of information depth. On the other hand, these constraints can be overcome by the use of High Energy PIXE [10] or neutron diffraction (ND) [11-17]. Neutron diffraction has been applied on metallic and ceramic artifacts and various objects at ISIS using a polychromatic pulsed neutron beam on ROTAX, ENGIN-X and GEM instruments, while later, the method has been extended in using monochromatic neutrons mainly on ceramics [18-19]. However, the time of flight (TOF) method is preferred to single wavelength neutrons for it requires smaller irradiation times. The crystal structure of each of the phases, the mineral and metal phase abundances, the grain sizes, orientations and, microstructures in materials can be examined. Surface anomalies and multifaceted articles can be overcome while the measuring time is cut down to minutes, reducing the irradiation time to a minimum, which in turn decreases the decay times of induced radioactivity levels on the isotopic...
compositions, to a few days for objects containing silver or copper. The (ND) technique can be employed to complement other long established analysis methods such as XRD, XRF, PNAA, EDX, PIXE in use by the archaeological science today as it can deliver information on the mineral phase abundances, by using both the Rietveld, or the two stage method of profile fitting, from the bulk rather than the surface of the object.

The present work focuses on fingerprinting selected silver/copper coins from the Treasure collection of Gazoros (CH IX 61) in Serres Greece, using a pulse neutron beam to obtain diffraction patterns from the entire sample.

2. Experimental

The selected coins shown in Figures 1 and 3(a-b), were discovered in a single grave at the archaeological site of Gazoros in Serres, North East Greece. They were considered to be representative of the coinage circulated in a rather wider area of ancient North East Greece and on the island of Thasos. Chronological estimation based on archaeological criteria in the style of the die-engraver, morphological details and other peripheral archaeological findings suggests that the samples were minted at the end of the 5th century B.C. Information on the archaeological classification of the objects is listed in Table 1. Given the archaeological importance of the coins, the surface of the coins were cleaned from all soil depositions and preserved with a silica gel cover in an attempt to prevent further environmental erosion. The two replica coins obtained from the Archaeological Museum of Kavalla were prepared using 950 high purity silver and a metallurgical mixture consisting of copper-tin-antimony-lead. These coins served as markers and standards.

The measurements were carried out on the ROTAX instrument, a medium resolution diffractometer, at the pulse neutron source at ISIS facility at the Rutherford Appleton Laboratory, England. The samples without any prior preparation were placed for support and protection in a pocket made of vanadium foil. The sample chamber was evacuated and the coins were exposed to a 15x25 mm² incident beam for 20-30 minutes. The overall measurements lasted 4 hours. Details on the experimental set-up are given in reference [11]. The resulting multi-bank diffraction profiles were analysed using the public domain software GSAS [20] with the EXPGUI [21] interface and the program Amphorae [19] which employs profile decomposition analysis to specifically determine and evaluate multi-phase diffraction profiles.

Table 1. Phase analysis (wt%) and data alloy composition (Sn wt%). Estimated error of ±0.5 wt%

| Silver plated copper coins | CuSn | (Sn) | Ag | Cu₂O | CuCl | AgCl |
|----------------------------|------|------|----|------|------|------|
| 01 Thasian stater triti     | 79.3 | 2.38 | 9.1| 10.6 | ~1   | +    |
| 02 Neapolis hemidrachmo    | 77.5 | 1.16 | 9.6| 11.9 | 1    | +    |
| 03 Thasian stater triti     | 79.7 | 1.04 | 10.8| 8.8  | 0.7  | +    |

| Silver coins              |      |
|----------------------------|------|
| 00 Replica                 | 99.9 |
| 04 Thasian hemiekto        | -    | -   | 96.9| -    | -    | 3    |
| 05 Thasian hemiekto        | -    | -   | 96.9| -    | -    | 3    |
| 06 Thasian hemiekto        | -    | -   | 99.8| -    | -    | 0    |
| 07 Thasian hemiekto        | -    | -   | 98.7| -    | -    | 1.3  |
| 09 Vergeo stater triti     | 2.4  | 0.72 | 96.6| -    | +    | ~1   |
| 10 Iona hemiekto           | -    | -   | 98.9| -    | -    | 1.1  |
3. Results and discussion

The collected diffraction data for all the samples at room temperature is plotted in Figure 1, along with the corresponding calculated profiles derived from the theoretical analysis of the mineral fractions produced using the software. Measured data is represented by crosses (+), the final calculated spectra correspond to solid lines (-). The starting model for the analyses of the observed data consists of Cu, Ag, Pb, Au, CuSn, Cu\(_2\)O, CuCl and AgCl, based upon earlier EDS-XRD measurements and on comparable Greek coinage data [22-25]. The structural parameters of the starting phases were taken from the Inorganic Crystal Structure Database and CrystMet [26-27]. Phase analysis was carried out by refining one overall Debye–Waller parameter and one common absorption parameter for all patterns. Pattern fitting procedures and mineral phase refinement has been described in [19]. The sum of crystalline phases was normalized to one. The profile decomposition process and the resulting

Figure 1: The coin images are shown on the right with their corresponding neutron diffraction profiles on the left. Bragg peaks for silver, Cu-alloy, cuprite (Cu\(_2\)O) and nantokite (CuCl) are displayed in the lower part of the diagram.
Figure 2: (a) Profile decomposition showing the individual calculated profiles of copper (Cu), nantokite (CuCl), silver (Ag) and cuprite (Cu$_2$O). (b) The neutron diffraction profile of the coin 01. Measured data is represented by crosses (+), the final calculated spectra correspond to solid lines (-). Bragg reflections for (Cu/Sn), (Ag), (Cu$_2$O) and (CuCl) are displayed in the lower part of the figure.
calculated pattern is illustrated in figure 2(a) and the measured and Rietveld refined profile of the coin No 01 is shown on figure 2(b). The reliability value of the refinement $R_{\text{Bragg}} = 4.4\%$.

From the diffraction profiles it is clearly observed that there are three distinct categories of coins. The first shown in Figure 3a, is a set of three items that present identical diffraction patterns consisting of two main phases, namely a copper-tin alloy and a pure silver and similar corrosion products phases. The pronounced copper alloy Bragg peaks originate from the core of the sample and are shifted with respect to pure copper Bragg reflections. These shifts can be linearly correlated with Sn wt% found in alloys containing up to 14 wt% Sn [28- 30]. The CuSn compositions were obtained by Rietveld refinement and the $\alpha$-bronze phase lattice parameters are in good agreement with literature. Additional smaller silver peaks result from the surface of the coin while high quantities of copper oxide (Cu$_2$O), small amounts of nantokite (CuCl) and silver-chlorine type compounds were also found. The presence of the various corrosion products developed on the coins is due to selective galvanic corrosion which is induced to metals of different electrochemical potential, namely copper (0.34) and silver (0.85), that are in contact or in very close proximity to each other [31-32]. In an electrolytic environment, the less noble metal (Cu) becomes anodic and consequently suffers a severe corrosion attack. The spread of corrosion is dependent on environmental factors, burial conditions, soil acidity or salinity and the micro-structure of the metals [33].

The second group consisting of coins with high silver to copper alloy ratio is illustrated in Figure 1 (Vergeo triti Ag/Cu –coin 09). These coins are very rich in silver and contain only a small fraction of copper-tin alloy with similar structural alloy characteristics as found in the first set. Copper chloride is also present, although in minute quantities. The third class group presented in Figure 3b, is a collection of five coins that display similar features on their diffraction profiles, presenting high amounts of silver content which are manifested by the prominent and slightly broad structured (111) and (200) Bragg reflections. Although these observations suggest the existence of additional phases such as gold (see ref. 26-27), Rietveld refinement carried out by assuming the presence of silver, gold and copper phases did not add to improving the theoretical profile or the reliability value of the refinement. The detected silver corrosion is identified as chlorargyrite (AgCl), and is considered among the most common alteration products of silver during burial in saline soils [29]. It is interesting to note (see figure 3b) that coins 04 and 05 are broken and are highly worn, coins 07 and 10 are pierced and slightly damaged, while coin 06 is in almost perfect condition.

The above observation may be correlated to the amount of AgCl found in each coin and reflects to the degree of damage and attrition due to corrosion. Although it is beyond the scope of this work, the archaeological and historic evidence suggest that the coins were issued during a period of Thasian domination and possession of the silver mining districts on the mainland, yielding enormous wealth to Thasians and their allies. The coins of the first group though referred to as being of Thasian origin, present a very careless style and differ significantly in silver / CuSn composition when compared to the genuine article such as found in group two, namely the coin 09. Therefore, these coins may be considered as poor imitations and they are more likely to be of local Thracian origin. The debasement of the stater triti and the Neapolis hemidrachmo further illustrate the deprivation of bullion in the particular local communities during the period the coins were minted. In contrast, the five Thasian silver hemiekto that chronologically coincide with the coins of group one, suggests an abundance of Thasian silver. Nonetheless, to avoid hasty deductions, one should try to analyze other similar coins.

The analysis of the replicas has shown that the inclusions of copper-tin-antimony-lead could not be detected, possibly due to overlapping with the main phase of silver and/or due to their small amount that was below the detection limit of the method. Additionally, the refined silver parameters obtained for the ancient and the replica coins differ from the pure silver parameters. This fact may signal the existence of metal inclusions (i.e. copper). At present a neutron diffraction investigation on laboratory prepared “silver and metal combinations” replicas are due, in order to complete a systematic calibration study.
Figure 3: (a) 3D representations of the neutron diffraction profiles of the coins 01, 02 and 03; b) Coins 04-10 and the corresponding measured data shown with solid lines (-). The prominent Bragg peaks are characteristic of the Cu-alloy in figure (a) and of the silver in (b). The corrosion products of cuprite, CuCl and AgCl are displayed in the lower part of each diagram.
4. Conclusions

Throughout this study ten ancient coins and two replicas have been examined using TOF -ND. The results of the analyses suggest that the coins can be classified into three categories according to the main metallic phases found, which confirms the initial hypothesis of the museum numismatists inferred from archeological sources. The fine style of coins constituting the third group along with the identical compositions, points to the same production technique. There is no apparent reason for a numismatist to suspect an imitation.

The comparison between the diffraction profiles of the original coins to those of the replicas, present distinct variations that may be used to differentiate the copies from the original items. As the results of this preliminary inquiry are encouraging, further analyses will probably help to further the comprehension of Thracian and Thasian coinage during the fifth century.

The above results also show the necessity in using complementary analysis techniques such as SR-XRD, High Energy PIXE and PGAA to separate the possible different phases, identify the elemental compositions, recognize additional trace elements and provide further information on minority phases which cannot be identified from the ND data, that has otherwise vanished into the background, or is lost due to the peak overlap.

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