

Roman coins from the “Brettii and Enotri” museum: a non-destructive archaeometric study by X-ray fluorescence spectroscopy and X-ray microtomography

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Abstract - Two of a group of thirty coins dating between to 1st century BC and 1st century AD, found in the so-called “Grotta delle Ninfe” near Cerchiara di Calabria (Calabria, Italy), and preserved in the display case of the Brettii and Enotri Museum in Cosenza (Calabria, Italy) have been under archaeometric investigation. This paper aims to understand the oxidation processes, know constituent material and find hidden signs or inscriptions on the coins by means of X-ray fluorescence (XRF) portable spectrometer and X-ray microtomography (X-ray μ -CT) in order to make the hypothetical inscriptions readable, to know the period of manufacture and their provenance. The coins collection will be analysed in future research to make the inscriptions readable and identify the coins’ provenience and typology.

Keywords: Roman coins; X-ray μ CT; XRF spectroscopy; archaeometry; non-destructive investigations

I. INTRODUCTION

At the base of Mount Sellaro, a limestone relief of the Pollino massif, there is the “Grotta delle Ninfe” (fig. 1), a cave of natural origin (Cerchiara di Calabria, Calabria, Italy). The “Grotta delle Ninfe” is an ancient source of sulphurous water, which flows at a nearly constant temperature of 30°C. Thanks to the therapeutic effect of sulphurous water, this cave is used for healing baths, also known as “Grotta dei Bagni”.



Figure 1: The red point represents the places where the coins under investigation were found (a); the interior of the “Grotta delle Ninfe” (b)

Archaeological studies [1] carried out at the “Grotta delle Ninfe” have demonstrated that in this place, there was a continuity of use and attendance since Prehistory. This is confirmed both by oral stories and literary sources [1] and by the natural context, characterized by the presence of caves and water sources. The cave looks like a votive deposit and a sacred place. Furthermore, the presence of the Sanctuary of the “Madonna delle Armi” - whose origin goes back to the 10th century and whose name recalls the presence of caves - indicates the persistence of worship in this area.

In 1905, a large group of oil lamps and coins from the Imperial Roman age were found in the “Grotta delle Ninfe” cave. These archaeological finds are now preserved at the Brettii and Enotri Museum in Cosenza (Calabria, Italy), and the coins are catalogued in Coins Collection Catalogue [2-3].

The type of oil lamps found is among the most widespread in Italy and in the Mediterranean area, between the Augustan age (44 BC - 14 AD) and the 2nd century AD [4].

It was possible to relate the finds to either the Julio-Claudian dynasty (27 BC – 68 AD) or the Flavian dynasty (69 AD – 96 AD) based on the contextual discovery of lamps and coins.

Here, we show how to characterize the alteration processes and analyse the constituent materials of the coins conserved in the Brettii and Enotri museum in Cosenza. Specifically, we focus on two of the thirty coins in the aforementioned collection. The samples labelled M73 and M75 are altered (see Fig. 2a-b). We compared them with a coin in relatively better conservative conditions (M94 in the catalogue). This coin, which is used as a reference sample, is shown in figure 2c-d.

Chemical and morphological studies were carried out by means of both an *X-ray fluorescence (XRF)* portable spectrometer and an *X-ray microtomography* apparatus (X-ray μ -CT).

The XRF investigations presented in this paper were performed by an “Artax400” portable X-ray spectrometer from Bruker at the X-ray and Raman Spectroscopy laboratory of the Department of Biology, Ecology and Earth Sciences (University of Calabria). This technique is one of the most common and straightforward used in archaeometry studies [5-6]. The XRF chemical investigation allow us to detect the coin’s chemical nature and to understand the alteration processes. Two measurement points were chosen for each coin and averaged between them. The parameters used to perform the XRF measurements are energy 50 keV; voltage 50 kV; current 700 μ A; collimator 0.65 mm; exposition time for each measurement 1200 s.

X-ray μ -CT, one of the most powerful imaging techniques for inspecting the internal morphology of an object, is a diagnostic method which is frequently used in different fields of science [7-9], and in particular, in cultural heritage [10–12]. One of the advantages of X-ray μ -CT is that it is a non-destructive method and it does not require a specific sample preparation. It is used to characterize material inner microstructure in three dimensions with a resolution of the order of microns [13–15]. Microtomographic measures were performed at the experimental station @STAR Lab at the University of Calabria, whose main components are a microfocus source (Hamamatsu L12161-07), a flat panel detector (Hamamatsu C7942SK-05), and a sample positioning and rotation system. The measurement parameters are voltage 150 kV; current 66 μ A; exposure time for each projection 0.5 s; scaled pixel size is 16.67 μ m. The tomographic reconstructions were performed by correcting by the ring artefact and the beamhardening compensation parameters [16–18].

Our results permit, on the one hand, to unveil the period of manufacture and provenance of the finds and, on the other hand, to reveal the presence of hidden signs, such as readable inscriptions.

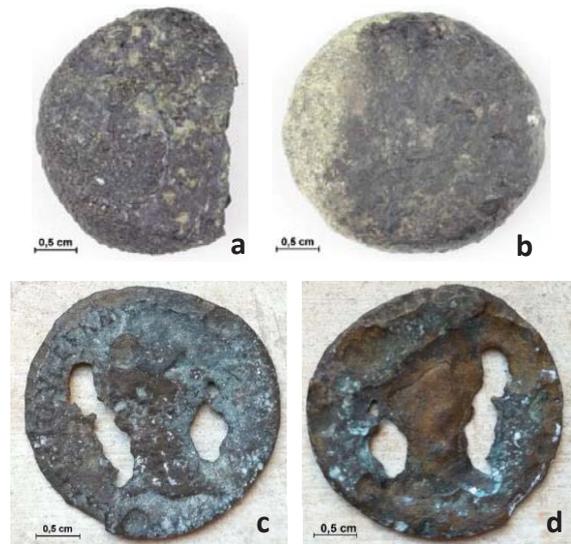


Figure 2: M73 (a) and M75 (b) coins; obverse (c) and reverse (d) of the M94 coin found in better conservative conditions

II. RESULT AND DISCUSSION

As a result of the XRF analysis, the chemical composition of each coin is very similar to each other, and then the average of each measure was calculated. The surface measurements revealed a copper and sulphur presence, whose relative weights are $(33.15 \pm 1.41)\%$ and $(66.44 \pm 1.35)\%$, respectively. Other secondary elements are present: Ti ($0.06 \pm 0.05\%$), Fe ($0.10 \pm 0.04\%$), Zn ($0.10 \pm 0.02\%$), As ($0.02 \pm 0.01\%$), Sn ($0.03 \pm 0.01\%$), Pb ($0.12 \pm 0.02\%$). In fig. 3 is shown a XRF spectrum representative of the M73 coin.

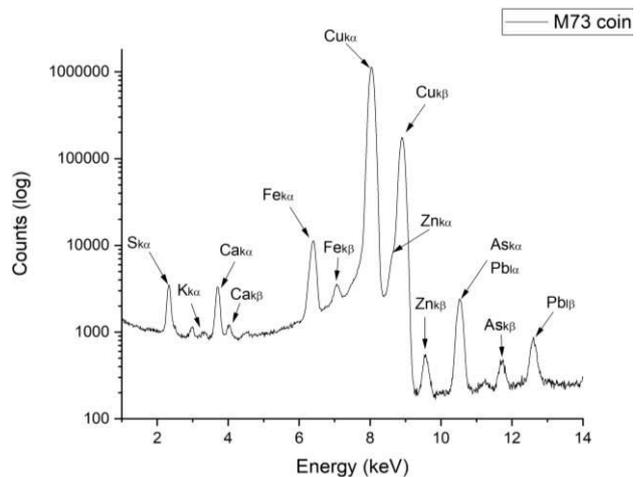


Figure 3: Representative XRF spectrum of the M73 coin

The long permanence of the Roman coins in sulphur water springs caused several chemical processes that formed a thick layer of black crust presumably made by copper sulphide minerals, like Chalcocite and Brochantite [19-21]. Further studies, like Raman spectroscopy and X-ray Diffraction investigations, can help to understand better the oxidation processes concerning the findings.

On this base, we can affirm that coins are mainly constituted of copper metal.

The X-ray μ -CT images shown in figures 4 and 5 report a longitudinal (a) and transverse (b) virtual section of the M73 and M75 coins, respectively. The outer sulphur-rich layer that covers the coins bulk is clearly discernible. In both cases, the internal coins thickness is 3.5 mm while the sulphur-rich layer thickness is 1.5 mm in average. The coin's diameter is approximately 28-30 mm. The coins thickness and diameter values are very close to those of the M94 coin.

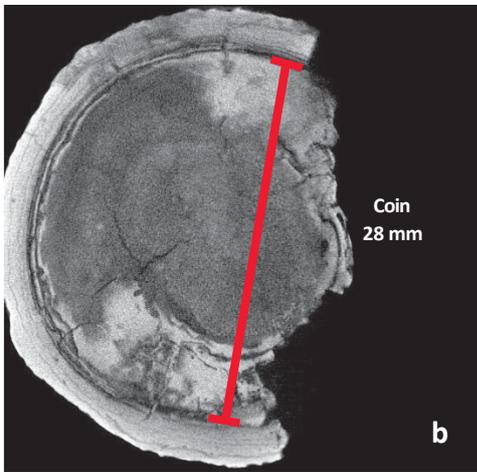
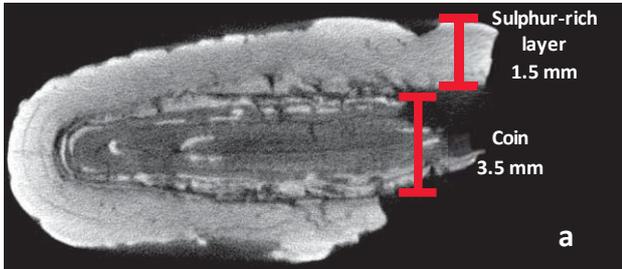


Figure 4: longitudinal (a) and transverse (b) grayscale slice of the M73 coin

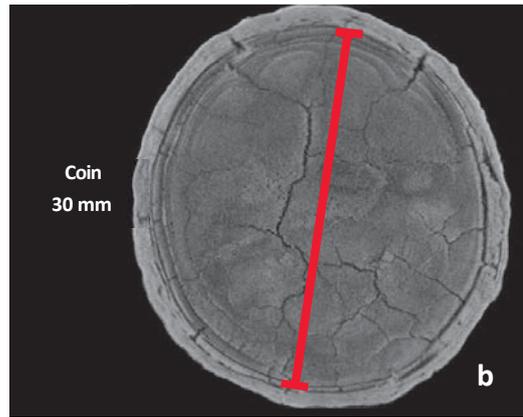
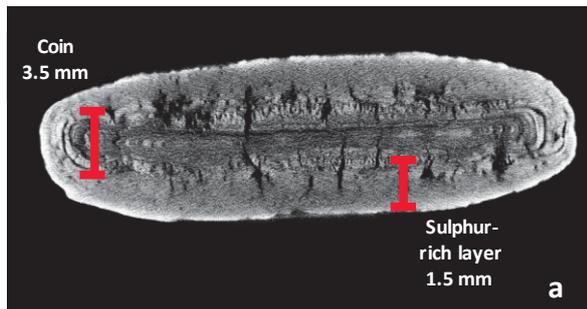


Figure 5: longitudinal (a) and transverse (b) grayscale slice of the M75 coin

The X-ray μ -CT surveys of the M73 and M75 samples revealed a series of signs like those found on the M94 coin's surface.

The M73 coin's grayscale cut (virtual section) shown in figure 5a own a profile of a thicker layer similar to the head profile present in the M94 coin, shown in figure 6b.

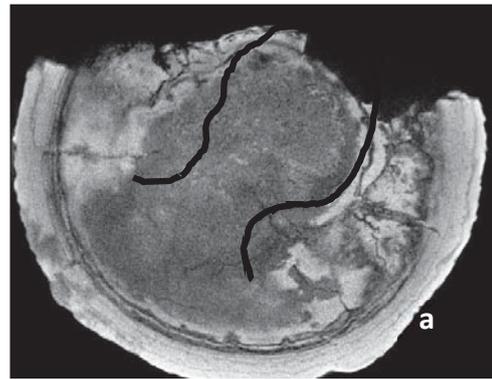


Figure 6: M73 coin's grayscale slice (a) show a profile similar to head profile in M94 coin (b)

Other marks are attributable to an inscription found in the M73 and M75 coins. The false colour slices of the M73

and M75 coins shown in figure 7b and figure 7c, respectively, show a series of marks similar to those constituents the inscription on the M94 coin (see the modified picture in figure 7a).

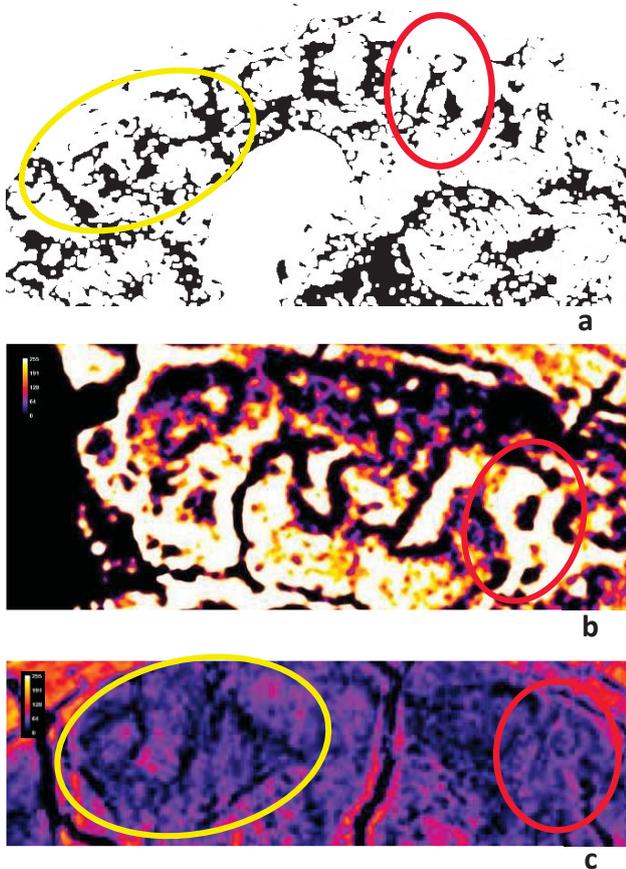


Figure 7: Area of the coin M94 modified picture in which inscriptions are visible (a); false colour slice of the M73 coin area in which relevant signs are visible (b); false colour slice of the M75 coin area in which relevant signs are visible (c).

III. CONCLUSION

M73 and M75 coins preserved in the Brettii and Enotri Museum in Cosenza have been studied by complementary physical methodologies means as X-ray μ -CT and XRF portable spectroscopy. These wholly non-invasive and non-destructive methods have allowed us to understand the oxidation processes, know constituent material, and find hidden signs or inscriptions.

Both coins are made of copper, and have followed an oxidation process due to the sulphur spring near the discovery site. Oxidation layers made the coins' inscriptions unreadable. Thanks to morphological studies by X-ray μ -CT, we could find signs and inscriptions compatible with the inscriptions on the reference coin. Therefore, we can say that the coins analysed belong to the same typology and we can confirm the archaeological hypothesis to relate the finds to either the Julio-Claudian dynasty (27 BC – 68 AD) or the Flavian dynasty (69 AD – 96 AD).

Then all the collection coins will be analysed in future research to make the inscriptions readable and identify the coins' provenience and typology.

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REFERENCES

- [1] M. Cerzoso, “I reperti di Cerchiara di Calabria al Museo dei Brettii e degli Enotri di Cosenza: contesto, materiali, funzione,” in “Tra Ionio e Tirreno: orizzonti d'archeologia. Omaggio a Elena Lattanzi”, M. L. Lazzarini, F. Lo Schiavo, R. Spadea (eds.), Casa Editrice Scienze e Lettere, Roma, 2020, pp. 253–266.
- [2] A. Polosa, “Le monete” in “Museo dei Brettii e degli Enotri - Catalogo dell'esposizione”, M. Cerzoso, A. Vanzetti (eds.), Rubbettino, Soveria Mannelli (CZ), 2014, pp. 649–669.
- [3] M. CERZOSO, F. QUONDAM, “La storia della collezione,” in “Museo dei Brettii e degli Enotri. Catalogo dell'Esposizione”, M. Cerzoso, A. Vanzetti (eds.), Rubbettino, Soveria Mannelli (CZ), 2014, pp. 5–19.
- [4] M. Cerzoso, “Le lucerne di Cerchiara di Calabria,” in “Museo dei Brettii e degli Enotri. Catalogo dell'Esposizione”, M. Cerzoso, A. Vanzetti (eds.), Eds. Soveria Mannelli (CZ), 2014, pp. 519–526.
- [5] K. Janssens, G. Vittiglio, I. Deraedt, A. Aerts, B. Vekemans, L. Vincze, F. Wei, I. De Ryck, O. Schalm, F. Adams, A. Rindby, A. Knochel, A. Simionovici, A. Snigirev, “Use of microscopic XRF for non-destructive analysis in art and archaeometry”, X-Ray Spectrom., vol. 29, no. 1, Jan. 2000, pp. 73–91.
- [6] A. Longoni, C. Fiorini, P. Leutenegger, S. Sciuti, G. Fronterotta, L. Strüder, P. Lechner, “A portable XRF spectrometer for non-destructive analyses in archaeometry”, Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip., vol. 409, no. 1–3, May 1998, pp. 407–409.
- [7] M. Ferraro, F. Mangini, Y. Sun, M. Zitelli, A. Niang, M.C. Crocco, V. Formoso, R.G. Agostino, R. Barberi, A. De Luca, A. Tonello, V. Couderc, S.A. Babin, S. Wabnitz, “Multiphoton ionization

- of standard optical fibers”, *Photon. Res.*, vol. 10, 2022, pp. 1394–1400.
- [8] P. Donato, S. Donato, L. Barba, G.M. Crisci, M.C. Crocco, M. Davoli, R. Filosa, V. Formoso, G. Niceforo, A. Pastrana, A. Solano, R. De Rosa, “Influence of Chemical Composition and Microvesiculation on the Chromatic Features of the Obsidian of Sierra de las Navajas (Hidalgo, Mexico)”, *Minerals*, vol. 12, no. 2, Feb. 2022, p. 177
- [9] S. Stelitano, A. Rullo, L. Piredda, E. Mecozzi, L. Di Vito, R.G. Agostino, R. Filosa, V. Formoso, G. Conte, A. Policicchio, “The DeltaH Lab, a New Multidisciplinary European Facility to Support the H₂ Distribution & Storage Economy”, *Applied Sciences*, vol. 11, no. 7, 2021, p. 3272.
- [10] R. G. Agostino, S. Donato, T. Caruso, E. Colavita, F. Zanini, A. D’Alessio, D. Pisarra, A. Taliano Grasso, “Microtomographic studies as a tool in the identification of a new ceramic class: The metal-imitating pottery as grave goods among Brettians and Lucanians” *Microchem. J.*, vol. 126, May 2016, pp. 138–148.
- [11] M. López-Prat, R.G. Agostino, S.R. Bandyopadhyay, B. Carrascosa, M.C. Crocco, R. De Luca, R. Filosa, V. Formoso, C. Lancelotti, N.A. Noori, A. Pecci, J. Simón-Cortés, D. Miriello, “Architectural Terracotta Sculptures of the Silk Roads: New Conservation Insights Through a Diagnostic Approach Based on Non-Destructive X-ray Micro-Computed Tomography”, *Stud. Conserv.*, Jan. 2021, pp. 1–13.
- [12] M. P. Morigi, F. Casali, M. Bettuzzi, R. Brancaccio, V. D’Errico, “Application of X-ray Computed Tomography to Cultural Heritage diagnostics”, *Appl. Phys. A*, vol. 100, no. 3, Sep. 2010, pp. 653–661.
- [13] A. Kak, M. Slaney, "Principles of Computerized Tomographic Imaging", Society for Industrial and Applied Mathematics", IEEE Press, New York, 1988.
- [14] A. Lin, S. Stock, R. Guldberg, "Microcomputed tomography", Springer Handbooks, 2019, pp. 1205-1236.
- [15] E. N. Landis, D. T. Keane, “X-ray microtomography”, *Mater. Charact.*, vol. 61, no. 12, Dec. 2010, pp. 1305–1316.
- [16] V. Veikutis, T. Budrys, A. Basevicius, S. Lukosevicius, R. Gleizniene, R. Unikas, D. Skaudickas, “Artifacts in computer tomography imaging: How it can really affect diagnostic image quality and confuse clinical diagnosis?” *Journal of Vibroengineering*, vol. 17, no. 2, 2015, pp. 995–1003.
- [17] Y.-W. Chen, G. Duan, A. Fujita, K. Hirooka, Y. Ueno, “Ring artifacts reduction in cone-beam CT images based on independent component analysis”, *IEEE Instrumentation and Measurement Technology Conference*, May 2009, pp. 1734–1737.
- [18] R. Schulze, U. Heil, D.D. Bruellmann, E. Dranischnikow, U. Schwanecke, E. Schoemer, “Artefacts in CBCT: a review”, *Dentomaxillofacial Radiol.*, vol. 40, no. 5, Jul. 2011, pp. 265–273.
- [19] D.A. Scott, "Copper and bronze in art: corrosion, colorants, conservation", Getty Conservation Institute, LA, USA, 2002, pp. 145-167.
- [20] V. Muros, D. A. Scott, "The occurrence of brochantite on archaeological bronzes: a case study from Lofkënd, Albania", *Studies in Conservation*, vol. 63, no. 2, 2018, pp. 113-125.
- [21] A.G. Kitai, I. F. Gablina, A. O. Bol’shikh, "Formation of Elemental Sulfur during the Oxidation Leaching of Chalcocite", *Russian Metallurgy*, 2022, pp. 463-474.