

Multi-analytical approach for an archaeometric study on orichalcum coins



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Short note

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ABSTRACT

Orichalcum is a Cu-Zn based alloy known since the 1st millennium BC. The cementation was the ancient technique used for its production. The PhD project here presented aimed to characterise this alloy and to evaluate its degradation: for this purpose, non-destructive, nano-invasive and destructive techniques were used on a collection of ancient coins issued from the 1st century BC to the end of the 1st century AD. In particular, a multi-analytical approach was used: to investigate the patinas and their corrosive patterns, to study the alloy microstructures and their degradation, to describe the dezincification process and grouping the coins by emission. In addition, quantitative analyses allowed a complete characterization of this ancient alloy. The multi-analytical approach allowed to review the previous theories used for dating samples in orichalcum. This project wanted to contribute to the current knowledge on Roman coinage and to attempt to investigate the mechanisms of corrosive processes affecting ancient alloys.

KEYWORDS: Archaeometry, corrosion, alloy composition.

INTRODUCTION

Among all the ancient metallic objects, coins are the most common findings in archaeological excavations, due to their production in series, strictly related to their daily use. Nevertheless, there are some denominations that seem rarer than others, as they belong to peculiar issues or because they were coined in uncommon alloys. The Roman coins minted in orichalcum are a good example of this. Indeed, they were issued for a not so long period in a short number of specimens (Catalli, 2003), if compared to the large amount of different denominations simultaneously circulating in Roman territories. In addition, the orichalcum alloy was considered

a high value material by the ancient populations, for the aesthetic features as well as the difficulty in its production. The focus of this PhD project was the Roman orichalcum coinage and the aim was to characterize the ancient Cu-Zn based alloy, similar to the modern brass, and to define the technological level reached by ancient population to produce it. For this purpose, a representative number of samples from private collections were studied, using a multidisciplinary approach and, thus, multi-analytical methods. This resulted to be the best way to acquire new information about the cementation process (Bayley, 1998), because of the lack of scientific sources on the Cu-Zn alloy production.

Archaeological orichalcum samples suffer from dealloying of the patinas, i.e., dezincification (the loss of zinc) or, in the worst cases, decuprification (the loss of copper, usually following the dezincification), causing the formation of a porous layer, with different Cu/Zn ratio compared to the inner core of the object. For these reasons, all the chemical information obtained from the external layer of the artefacts or from a non-defined area of analysis cannot be considered as representative of the real composition of the ancient alloy. Information about orichalcum patinas can give evidences about the development of the dezincification process that can extend deep into the samples (Campanella et al., 2009). Moreover, quantitative data of the undegraded cores of ancient metal objects are almost absent in scientific literature. Therefore, the results of this study will allow to fill the scientific gap on orichalcum and could be useful for the study of different alloys. Indeed, new analyses will help to better understand the technological development of metallurgical processes in ancient times. Both destructive and non-destructive analyses were performed to characterize the whole set of samples, investigating both the

corroded external layers and the uncorroded core of the coins. Combining techniques as X-ray fluorescence (XRF), voltammetry of immobilized particles (VIMP), attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR) and focused ion beams – field emission scanning electron microscopy (FIB-FESEM-EDS), the organic and inorganic compounds of the patinas were identified. Moreover, the use of scanning electron microscopy (SEM-EDS), X-ray distribution maps of elements, high resolution field emission scanning electron microscopy (HR-FESEM) and electron microprobe analysis (EMPA) on cross sections of the coins allowed to characterize the real composition of the orichalcum. The information obtained in this way helped to distinguish different technological levels of cementation process achieved by the Roman in different historical periods. Information about the chemical composition of the patinas and of the uncorroded nucleus, in addition to the investigation of the micro and nanostructures of the orichalcum, were a powerful tool to understand where the corrosion and the degradation processes begin on this ancient alloy. This project aimed to contribute to the current knowledge about the orichalcum coinage during the Roman Empire and to deepen knowledge of corrosive processes of ancient alloys.

HISTORICAL BACKGROUND

The use of orichalcum both for coinage and for common objects is closely related to the production of copper-based alloys and, thus, to the knowledge of the georesources available and the achievement of the technological levels in metalwork. According to the limited historical sources and archaeological literature, among the zinc ore mines active in antiquity we can mention *Andeira* in Phrygia, (north-west of Anatolia, Turkey), the mining district of Laurion (southern Attic Peninsula, Greece) and Cyprus Island (southeast of the Mediterranean sea) (Alexakis, 2008; Caley, 1964; Craddock, 1998; Gale et al., 1985; Pyatt, 2001). Often, zinc can be found in association with copper. In this case, the pyrometallurgical extraction of metals caused the evaporation of zinc, due to its relatively low boiling point, with a consequent content of less than 3wt % in prehistoric or early historic artefacts (Craddock, 1978; Tylecote, 1992). During the Roman Era, metallurgical techniques (e.g., cupellation and cementation) were well known and this allowed the definition of accurate rules for the production of metal alloys.

The two main metals composing orichalcum are copper and zinc. The minimum temperature required to reduce zinc oxide by carbon is higher than the boiling point of the zinc itself at one atmosphere (907°C). Hence, it means that in open environment, or in presence of air in general, the zinc vapor so far produced is rapidly transformed into its corresponding oxide.

The difficulty in extracting zinc from ore deposits and the need of a close and reducing environment prevented ancient population to produce orichalcum in open crucibles or primitive furnaces (Caley, 1964). Using carbonate ores or oxides directly, zinc in vapour phase could be extract with charcoal under reducing condition. Instead, the sulphide ores required an initial roasting phase and this additional step caused the losing in environment of the vapour-phase zinc (Craddock, 1978).

To directly produce a zinc-based alloy from ores it should be employed a peculiar system “to trap” the resulting zinc vapour. For this reason, the so-called “cementation process” appeared to be the better way to produce copper-zinc alloys, probably since the prehistoric times (Caley, 1964). Despite the absence of archaeological evidences (Craddock, 1978) but according to historical sources, the cementation procedure adopted in Roman times was performed by using ceramic crucibles, sealed with more or less accuracy, in which zinc oxides or carbonates (calamines) were heated with charcoals and fragments of copper to a temperature between the zinc boiling point and the copper melting point (i.e., 900-1000°C); within this range of temperature, zinc vapour could diffuse in the non-completely molten copper that, further heated and stirred, formed the orichalcum alloy. In particular, the cementation involved as first step the calcination and the fine grinding of the calamine and then the mixing of the mineral with charcoal. According to historical sources (Tylecote, 1992), the mix was placed in a hot crucible, filled to one-sixth of its capacity. The crucible was than filled with copper and covered with other charcoal and, once the cementation reaction had completed, it was heated to the temperature necessary to melt and homogenise the vessel content (Bayley, 1998; Bayley & Rehren, 2007; Tylecote, 1992). With this method, the weight percentage of the zinc in the alloy unlikely could exceed 28-30% (Bayley, 1998; Newbury et al., 2004; Rehren, 1999; Thornton, 2007), although higher zinc values are attested (Bourgarit & Bauchau, 2010; Di Fazio et al., 2019).

In general, the use of a good-quality metal to produce ingots (Caponetti et al., 2017), and thus coins, was fundamental to ensure the commercial value of the coin itself. Indeed, the use of a specific metal or alloy, in addition to a standard weight of coins, was needed in ancient times as today to guarantee the authenticity and the value of each denomination in circulation (Smekalova, 2009). Probably, the first coins in orichalcum were minted in the Kingdom of Pontus and in the regions of Phrygia and Bithynia, during the reign of Mithridates VI (120-96 BC) (Fajfar et al., 2015; Smekalova, 2009). According to the current state of the studies (Amela Valverde, 2004; Catalli, 2003), the Roman coin production in orichalcum is limited to the Caesarean Era and to the phase of the Julio-Claudian dynasty, from the 23 BC reform to 68 AD ca; in particular, the use of brass to strike coins under the reign of Julius Caesar (from the beginning of his dictatorship in 49 BC until his death in 44 BC) can be considered as experimental (Crawford, 1974), as shown in the studies carried out by Amela Valverde (2004) on the emissions *C. Clovio, RRC 476* and *Q. Oppius, RRC 550*, and it was suddenly halted due to Caesar’s death in 44 BC. Julius Caesar’s emission in orichalcum probably derived from a meditated reform of the entire monetary system that has never been implemented (Catalli, 2003). The last phase of the Roman Republic was characterized by a remarkable monetary disorder, in which the production of coins was left to the initiative of the military Commanders, without control from central authority and, therefore, without respecting the characteristics of weight, dimension and alloy provided for each denomination. To solve this problem, in 23 BC the Emperor Octavianus Augustus carried out a complete reform of the monetary system, stabilizing the issues, establishing clear weight standards and organizing a precise and rigorous

exchange rate system between the values of all the denominations. As regard orichalcum, Augustus reform provided for the production of a ~27g *sestertius* and a ~14g *dupondius* with this alloy. Nero's new monetary reform, in 63-64 AD, defined again the standards of production and introduced the two new issues in orichalcum, i.e. *semis* and *quadrans*, previously minted in bronze and copper (Amela Valverde, 2004; Catali, 2003).

MATERIALS AND METHODS

Materials

A set of Roman orichalcum coins, in good state of conservation, from several samples of Private Collections were selected for this study. The comparison with numismatic dataset (Crawford, 1974; Sutherland, 1984) permitted to confirm that the selected coins were minted in a period of time spanning from Julius Caesar to Domitianus and that they belong to five denominations: asses, sestertii, dupondii, semisses and quadrantas. The coins come originally from unknown burial environments with no documented cleaning. Stereomicroscope examination does not show erosion features denoting sandblasting, nor smoothing associated to intense chemical cleaning. All the historical and numismatic information about the samples are reported elsewhere (Di Fazio et al., 2019, 2020).

Experimental methods

Preliminarily, analyses on the patinas were carried out by energy-dispersive X-ray fluorescence spectroscopy (EDXRF) (Department of Basic and Applied Sciences for Engineering, Sapienza University of Rome, Italy). The spectrometer consists of an X-ray generator (Amptek MiniX) with an anode target of rhodium and a beryllium window of 127 μm of thickness. The detector is a Peltier cooled silicon drift with integrated amplifier and multi-channel analyser (Amptek 123-SDD). It has a surface of 25 mm^2 , a thickness of 450 μm , a beryllium window of 12.5 μm of thickness, with 140 eV resolution at 5.9 keV (full width at half maximum). The incident and the revealed beams form an angle of 45° with respect to the surface of the sample. The analysed surface is distant 3 cm from the X-ray generator anode and 3.5 cm from the detector surface. The X-ray generator was equipped with a 2 mm diameter collimator and was powered with an accelerating potential difference of 35 kV and an electronic current of 15 μA . For each sample, three measures were obtained, with an acquisition time of 200s each.

ATR-FTIR spectra were obtained to determine the composition of the corrosion products (Constantinides et al., 2002; Doménech-Carbó M.T. et al., 2019) on microsamples of the corrosion layer of the coins using a Vertex 70 Fourier-transform infrared spectrometer with an FR-DTGS (fast recovery deuterated triglycine sulphate) temperature-stabilised coated detector and a MKII Golden Gate ATR accessory (Institut de Restauració del Patrimoni, Universitat Politècnica de València). Scans were collected at a resolution of 4 cm^{-1} and the spectra were processed using the OPUS/IR software.

SEM investigation and X-ray maps on cross sections were performed using a FEI-Quanta 400 (SEM-EDS) instrument, operating at 30 kV, equipped with X-ray energy-dispersive spectroscopy (Department of Earth Sciences, Sapienza University of Rome, Italy).

FIB-FESEM experiments were carried out with Zeiss (Orsay Physics Kleindiek Oxford Instruments) model Auriga compact equipment (Electron Microscopy Service of the Universitat Politècnica de València). To obtain a focused beam of Ga ions 30 kV accelerating potential and current intensity of 500 μA and 20 nA in the FIB were used. A voltage of 3 kV was used in the FESEM for photographs. X-ray linescans were performed in the trench operating with an Oxford-X Max X-ray microanalysis system coupled to the FESEM controlled by Aztec software. A voltage of 20 kV and a working distance of 6-7 mm were used.

EMP analyses for quantitative chemical analyses were performed using a Cameca SX50 electron microprobe equipped with five wavelength-dispersive spectrometers (CNR-IGAG, Rome, c/o Department of Earth Sciences, Sapienza University of Rome). The operating conditions were: accelerating voltage 15 kV, beam current 15 nA. Element peaks and background were measured with counting times of 20 and 10s respectively. Matrix corrections were calculated by the PAP method, with software supplied by Microbeams Services. The detection limits under the specified working conditions vary from 0.05 to 0.1 wt% with standard deviations from 0.02 to 0.04 wt%. The analytical error was ~1% rel. for the major elements.

Voltammetry of Microparticles were performed at 298 K in a three-electrode cell using a CH I660C device (Cambria Scientific, Llwynhendy, Llanelli UK) using air-saturated aqueous 0.25 M HAc/NaAc aqueous buffer solution (Panreac) at pH 4.75, selected on the basis of the Nernst Equation. A sample-modified graphite bar (Alpino, HB type, 3 mm diameter) was used as a working electrode, the three-electrode arrangement being completed by a platinum wire auxiliary electrode and an Ag/AgCl (3 M NaCl) reference electrode. The analysis of each sample was carried out by pressing a graphite bar onto selected spots of the coin surface (free from corrosion products) as described elsewhere (Doménech-Carbó A. et al., 2019). Depending on the number and extension of such spots, 3-5 replicate measurements were performed on each coin. Square wave voltammetry (SWV) was used as a detection mode determining successively the negative- and the positive-going potential scans using as parameters: potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

RESULTS AND DISCUSSIONS

XRF preliminary analyses

The XRF analyses were used to distinguish and, then, select the samples in orichalcum from the whole collection. Indeed, despite the numismatic examination and references, scientific non-destructive analyses can distinguish the value of unknown denominations and can reveal the variation in composition of the alloys used in the Roman mints over the years. This investigation was suitable to test the presence of Zn in the surface areas even

at low percentage, avoiding unnecessary destruction of samples not produced in orichalcum. Indeed, one can easily fall into error because of the similar appearance of corroded orichalcum to bronze (Fig. 1).

The surface XRF analysis revealed Cu and Zn as the two main alloy components, followed by Fe and Pb. Tin is also present in most Cu-Zn samples. Exogenous elements (Cl, Ca, S, Si, Al, P and Mn) can also occur, but in low amounts as highlighted by the low-intensity of their characteristic peaks (Fig. 1). They probably represent contaminants introduced from soils through the induced porosity of the external layer (Papadopoulou et al., 2016).

ATR-FTIR information from the patina

The ATR-FTIR investigation allowed to obtain the chemical information from the patina. Due to the low quantity of collectable material, the measurements were acquired on a limited number of coins. However, the results can be considered representative of the entire collection, as the properties of the samples taken from the patinas were observed throughout the collection. The IR absorption spectra revealed the presence of atacamite/clinoatacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) and malachite $\text{Cu}(\text{CO}_3)\cdot\text{Cu}(\text{OH})_2$ in the degraded patina. Furthermore, specific absorption bands can be assigned to

different components of the patina, such as clay materials ($\sim 3571\text{ cm}^{-1}$, Fig. 2), as burial contaminant, and copper carboxylates (band at 1585 cm^{-1}). The presence of copper(II) acetate can be explained by the resulting of the corrosion process due to old cleaning treatments by private collectors. However, the occurrence in the spectra of bands of organic compounds (bands at $\sim 2962\text{ cm}^{-1}$, $\sim 2923\text{ cm}^{-1}$, $\sim 2852\text{ cm}^{-1}$ and $\sim 2807\text{ cm}^{-1}$, Fig. 2) probably resulted from the contact with the human skin oils and the alteration products of oxalate type. Oxalates are the result of the degradation of lipids and subsequent complexation with metal ions over a long period of time: this indicates that the coin's original surface is preserved. In some spectra a band at $\sim 1738\text{ cm}^{-1}$, assigned to the C=O group (Di Fazio et al., 2020), may be detected as well. It can indicate the presence of lipids, which can again be ascribed to the contact of the coins with the hand skin oils of their ancient users (Doménech-Carbó M.T. et al., 2019).

SEM-EDS investigation

The analyses on the cross-sections allowed to investigate the microstructure and compositional variations along the whole thickness of the samples. The microstructure of the alloy showed the so called α -grains structure of the Cu-Zn alloys, which is

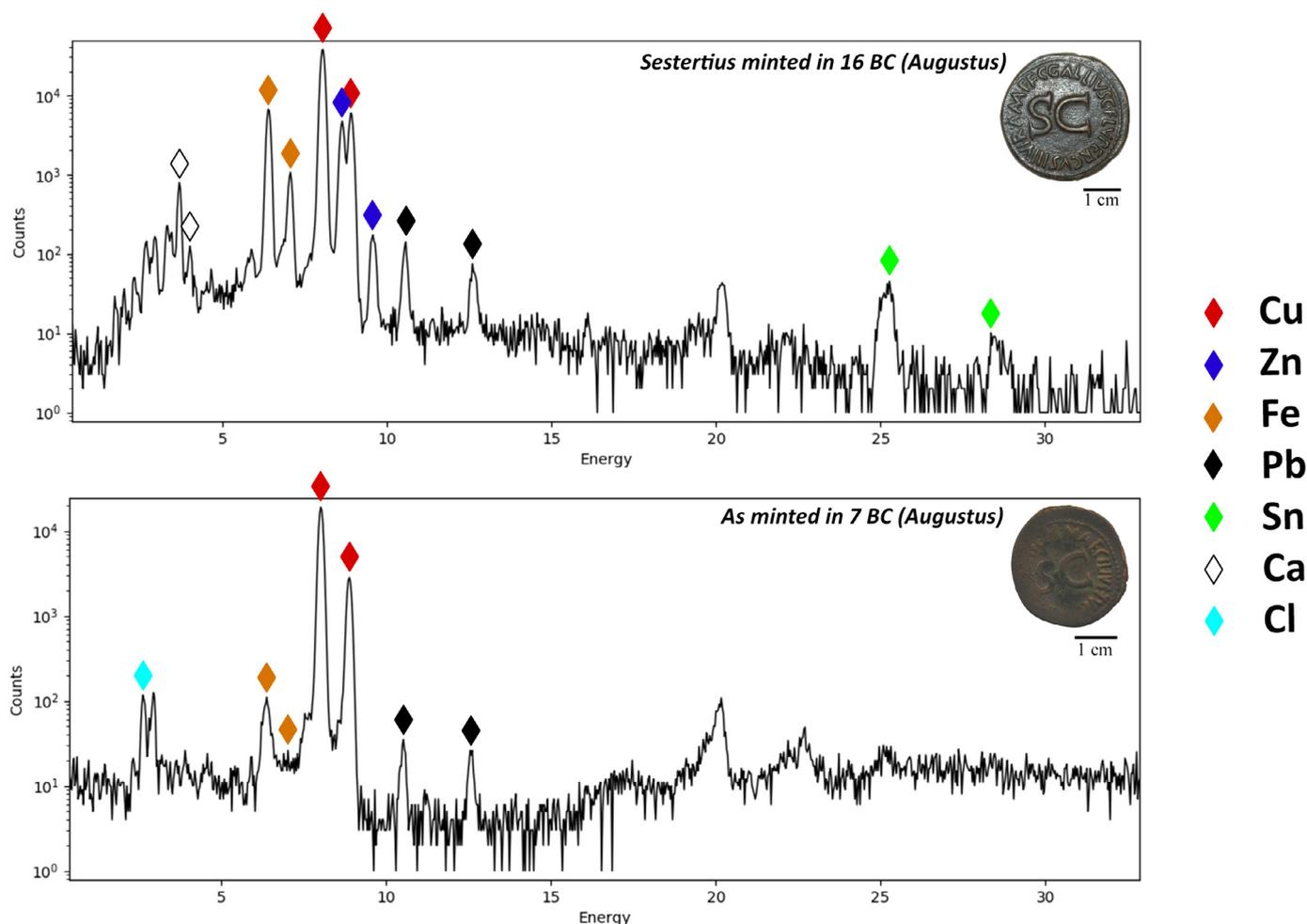


Fig. 1 - Comparison between two XRF spectra: an orichalcum coin (up) vs. a non-orichalcum coin (down). The main difference lies in the presence of zinc in the sestertius alloy.

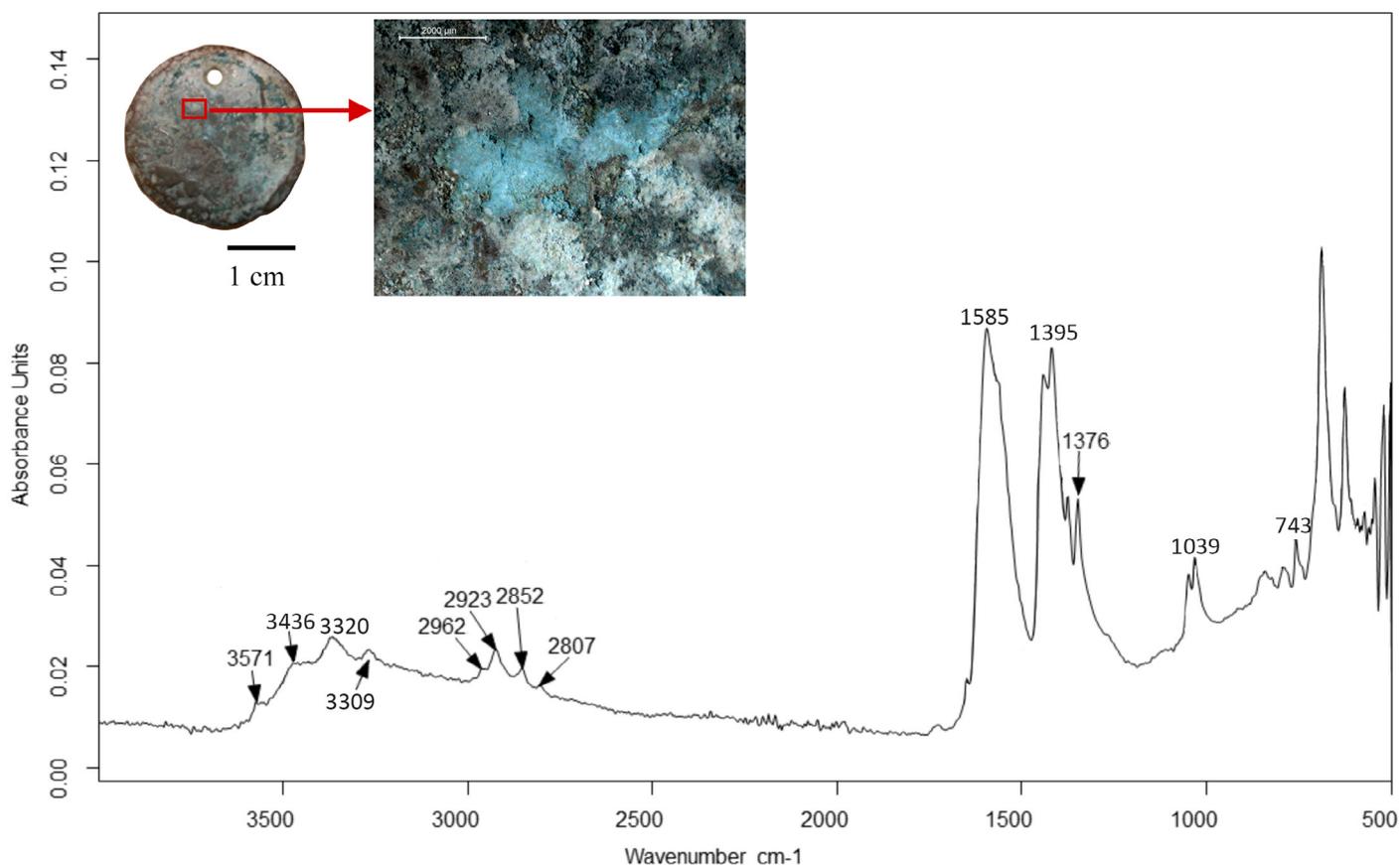


Fig. 2 - ATR-FTIR spectrum of an orichalcum coin and related point of analysis.

usually observed in archaeological brass samples. Due to the natural corrosive processes that occur during the long burial period, the grains structures are well visible in the more degraded samples, as the grain boundaries are easily susceptible to natural acid attack. This is true in particular close to the external rim of the samples (Fig. 3a). According to Scott (1991) this well-formed polygonal crystal structure is the result of an efficient casting-cooling practice, achievable using up to about 35% of zinc in the alloy and a good temperature control avoiding loss of zinc (see Historical Background). The presence of this structure suggests the conscious use of copper and zinc and a good control of the processing temperature and, therefore, a good control of the cementation process. Along the sections, the grain size varies from ~50 μm to ~200 μm, suggesting a non-rapid cooling speed. In figure 3a, a deformation of the grain's borders with the development of thin strain lines is observable. The distortion was caused by heavy cold-working, which provokes the slip of crystal planes, resulting in a series of parallel movements, observable as thin lines in section. In addition, the lines do not present further deformation, suggesting that coins were struck only once and did not undergo annealing (Scott, 1991).

SEM images revealed that the patinas can have an irregular thickness with different degree of dezincification, which can cause loss of material and induced porosity nearby the patina (Fig. 3b). In the studied orichalcum samples an important dezincification process occurs and, in some cases, this degradation process is extended up to 1.2 mm in depth (Di Fazio et al., 2019). The corrosion

proceeds from the external rim to the inner core with micro-areas of selective corrosion, driven by grain boundaries of the alloy (Barrena et al., 2008). The selective dealloying can be justified with the trans-granular stress corrosion, frequently observed in alloys with content of Zn between 20% and 30% (Sieradzki et al., 1987). Indeed, is reported in literature that the local strain due to cold-working could lead the acceleration of the corrosion cracking by stress, deformation of grain boundaries and the trigger of corrosion (Ulaganathan & Newman, 2014). Evolving, the dezincification process in the external layer formed a sponge-type structure, also observed in brass with low content of Sn, such as standard sample representative of archaeological brass (Constantinides et al., 2002).

X-ray maps of chemical elements provided information about their distribution along rim-core-rim cross-sections. The maps outlined from medium to high degree of dezincification of the patina (Fig. 3c, d). The cores of the samples showed in figure 3 present a homogeneous distribution of Cu and Zn. This pattern confirms the good technological skill in cementation process by Romans.

Nano-invasive FIB-FESEM

A group of selected samples were analysed using FIB-FESEM, a nano-invasive technique, to investigate the corrosion pattern occurring in superficial portion of the patina, performing a square trench of ~10x10 μm in the external layer. Despite the small area of samples under study, this technique enabled the characterization

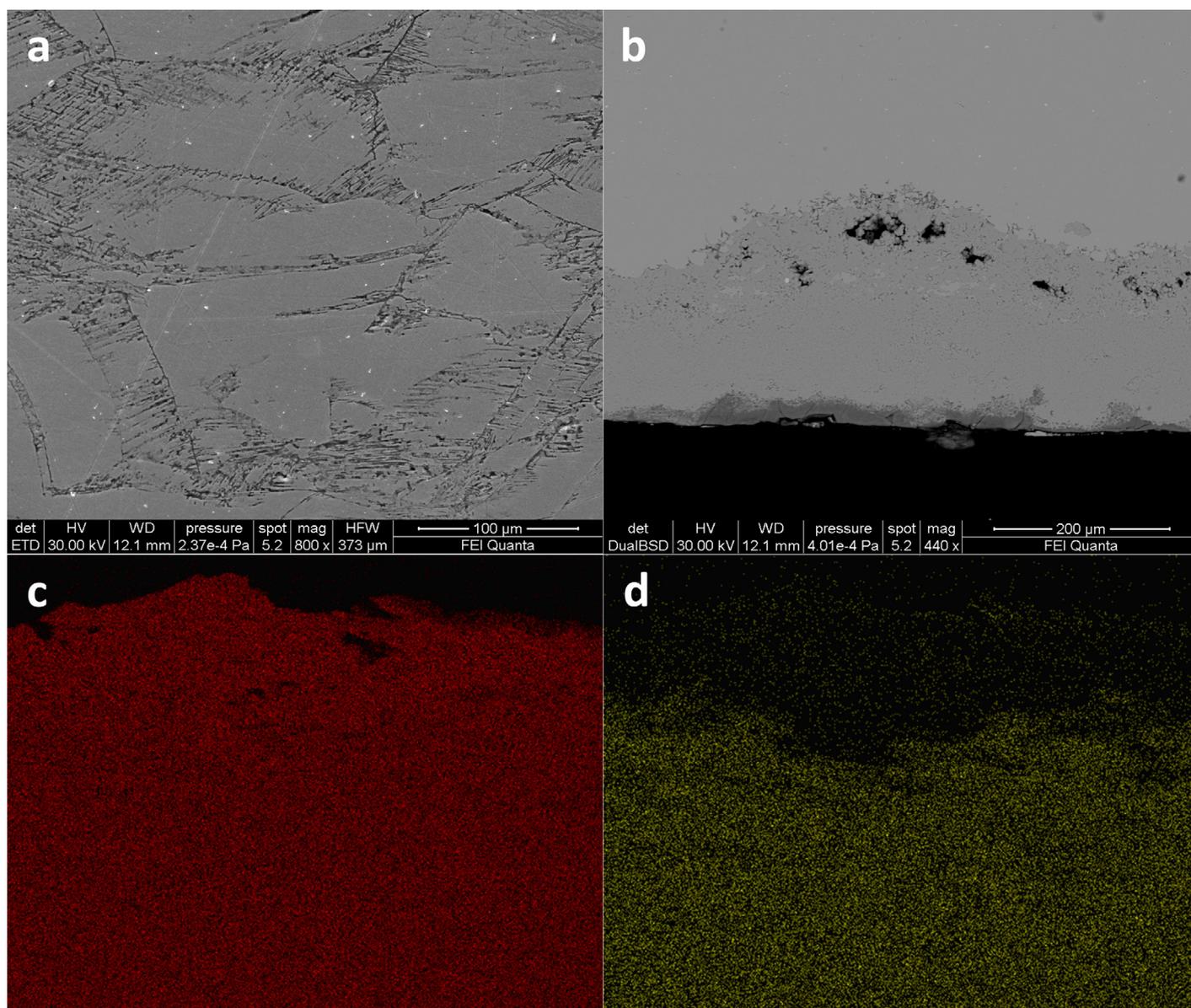


Fig. 3 - a) SE image of orichalcum grain structure of a dupondius minted between 37 and 41 AD (Caius); b) BSE image of a semis minted between 62 and 68 AD (Nero) showing the alloy degradation in the corroded external layer; c) and d) x-ray map of distribution of copper (in red) and zinc (in yellow) in section of a dupondius minted in 16 BC (Augustus).

of the first $\sim 10\mu\text{m}$ of the patina in depth even of those samples that cannot be cut. The samples presented a high corrosion degree in the external layer. Indeed, the first $3\mu\text{m}$ of the patina showed microdomains with low amount of Zn, due to a selective dealloying. The Cu and Zn segregation areas are well visible in the deeper region of the analysed patina (Di Fazio et al., 2020). The patterns described with FIB-FESEM are comparable to those previously observed (Di Fazio et al., 2019).

EMP analyses on uncorroded sample core

EMP analyses of the uncorroded nucleus allowed to obtain quantitative chemical information about the original alloy and permitted the reconstruction of the dezincification and decuprification patterns through the section. Moreover, EMPA allowed to determine the composition of the orichalcum alloy

without the influence of the corroded external surfaces (Di Fazio et al., 2019). Samples with a low degree of corrosion showed homogeneous distribution of Cu and Zn throughout the section (Fig. 4), whereas in the degraded samples the corroded layers have an amount of Zn that varies from 1.33 to 23.49 wt %. This confirms the high degree of dezincification for samples in a bad state of conservation. In particular, the sample B14 is an example of the progress of dezincification towards the uncorroded core of the coins. Indeed, the results of rim-core-rim point analyses performed with EMP showed Zn value below 1wt % at the interface between the corrosion patina and the core and, consequently, a related increase in Cu (Fig. 4).

Minor and trace elements showed a causal and non-homogeneous distribution along the whole cross section (Fig. 4), indicating a completely random and unintended presence of such metals in the alloy. For example, the low content and uneven

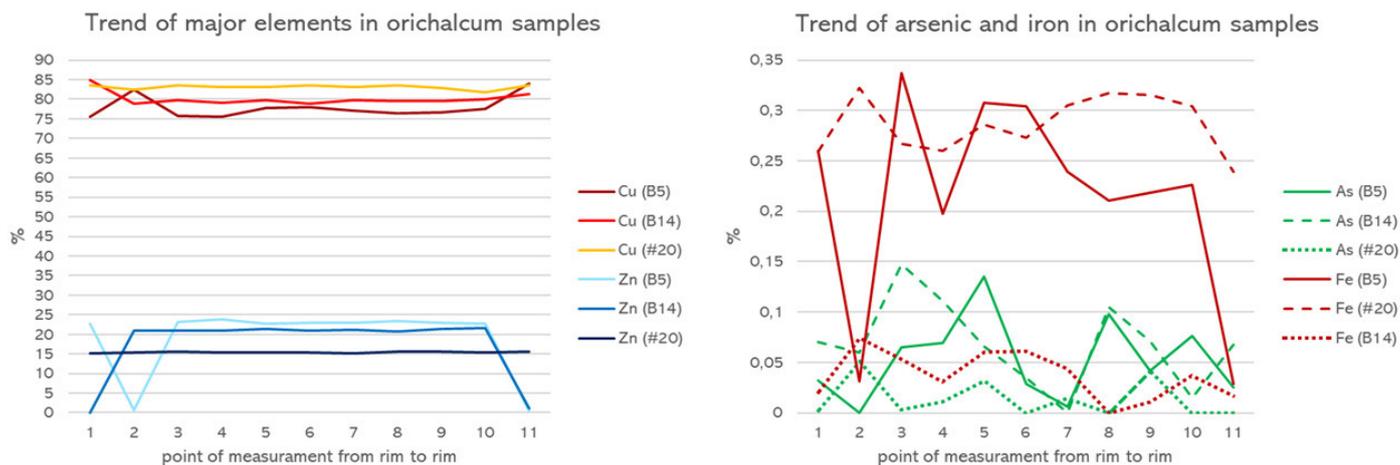


Fig. 4 - Comparison between the trends of the percentages of major (left) and minor elements (right) obtained by EMP by analysing the non-corroded areas of cross-section of the coins minted in different years.. B5: sestertius minted between 50 and 54 AD (Claudius); B14: semis minted between 62 and 68 AD; #20: sestertius minted between 81 and 96 AD (Domitianus).

distribution of Fe throughout the samples can suggest the use of chalcopryrite-rich ore for the extraction of Cu.

EMPA results of the uncorroded cores performed on the collection studied were compared with the results acquired in previous studies (Caley, 1955). The current data show an irregular trend of Cu and Zn during the orichalcum minting period, unlike the results obtained by Caley, which showed a regular trend of the data (with progressive decrease in the percentage of zinc). This variation of Cu and Zn percentage in the alloy can suggest difficulties in the regular supply of mineral raw materials, both for Cu and Zn, or a not regular control of the cementation process during the production of orichalcum ingots. Earlier researches (Caley, 1955) suggested the possibility to approximately date coins by the measured Zn content. It was described a decrease of the Zn amount from the oldest to the most recent coins. The chronological decrease of the Zn was justified with metal recycling. However, the coins here analysed show an irregular variation of the average Zn content, which fluctuates over time (Di Fazio et al., 2019). Moreover, in some cases Zn can exceed the value of 28%, which usually is considered the maximum quantity achievable in ancient brasses (Scott, 1991). This confirms that even using cementation it would be possible to exceed 28% zinc alloy (Bourgarit & Bauchau, 2010).

Voltammetric pattern and grouping

The voltammetric response of coin samples allow to describe the corrosion products on the patinas. In the negative-going potential scans, signals at 0.0 Volt can be assigned to the reduction of cuprite and other corrosion products (malachite-, brochantite-, atacamite-type minerals) to copper metal. The reduction of tenorite (CuO) occurs between -0.4 and -0.5 Volt (Doménech-Carbó A. et al., 2017, 2019). In turn, the reduction of zinc corrosion products will occur at more negative potentials, being indistinguishable from the hydrogen evolution reaction (HER) process under the experimental conditions (Di Fazio et al., 2020). In the positive-going potential scan voltammograms,

anodic signals between 0.0 and +0.20 Volt (A2) can in principle be attributed to the oxidative dissolution (anodic stripping) of the metal redeposition, as a result of the reduction of corrosion products formed at negative potentials. Minor signals at -0.60 Volt can describe the presence of Pb (and Sn) corrosion products (Doménech-Carbó A. et al., 2018). Interestingly, different spots of analysis on the same coin produced quite similar voltammetric profiles. Nevertheless, the relative height of selected voltammetric signals exhibits small but significant variations among different samples. Although displaying similar profiles, these variations highlight differences in the composition and differences in the “corrosion chronology” of the coins. Since the points selected for the analyses had the same degree of corrosion, the samples were grouped on the basis of the variations highlighted by the study of voltammograms. Plots of the ratio between anodic and cathodic signal values reveal differences both in composition and in degradation level: this information can be related to the different issuing authority. As an example, coins from the moneyers Asinio Gallo and Plotius Rufus define two tendency lines which differ from the trend defined by coins from the moneyers Casius Celler, Gallius Lupercus, Gnaeus Calpurnius Piso and Naevius Surdinus, which seems to have lower Zn and Sn contents (Di Fazio et al., 2020). These results illustrate the capability of VIMP measurements to discriminate between monetary emissions. Moreover, the voltametric response and related grouping of dated coins and for which numismatic information is available, will allow to obtain chronological and numismatic information from unknown samples.

CONCLUSIONS

This project aimed to improve and enrich the scientific knowledge on the production of the ancient orichalcum alloy and its degradation processes during time. The coin emissions in orichalcum, started as an experiment, represents the will of

the Imperial authority to reform the entire monetary system; this reform arose because the previous Republican rules on coinage had, in fact, been abandoned. With this purpose, ancient Roman orichalcum coins were investigated combining non-invasive, micro-destructive and destructive techniques. The application of a multianalytical approach allowed to evaluate the patterns of corrosion of the patinas and the chemical composition of the uncorroded metal cores.

This research demonstrated that the external layers of the orichalcum samples are deeply corroded and have a porous microstructure, when affected by dezincification and decuprification. X-ray maps analyses highlighted variations in the distributions of the main elements of the alloy in section, picturing enrichments and depletions of metals. In addition, the thickness reached up by corrosion layers rules out any possibility to obtain quantitative data from superficial investigation alone, as in the case of XRF analyses. Studying the inner portion of the coins with X-ray maps, it has been noticed that the uncorroded cores of coin are homogeneous in composition, indicating the technological expertise reached from Roman metalworkers. Scanning electron imaging analyses on cross sections, at different scales and resolution, showed a typical orichalcum microstructure with α -grain and evidences of hard cold-working to struck coins. From a quantitative point of view, results from the inner uncorroded cores evidenced an homogeneous distribution of Cu and Zn in the alloy, whereas the average amount of Zn in orichalcum during time showed fluctuations. This suggests that it is not possible to date undated coins by comparing the amount of Zn in the alloy, as previously reported in literature.

According to historical sources, the monetary reform of Augustus in 23 BC remained unchanged until the kingdom of Nero. However, this information is not confirmed by qualitative and quantitative analyses reported in this PhD project. Indeed, the research shows that the respect of the Emperors' dictations has not been strictly followed during times: the *tresviri monetales*, i.e. the issuers responsible for minting operations, probably modified the fineness of the coins based on the availability of the raw materials and/or according to the economic situation of the Empire during their govern. The results here presented could suggest the hypotheses about an historical event that induced Nero to promulgate a new reform in 63-63 AD, necessary to put order in the uncontrolled monetary system, as the Augustus reform bring order in the Republican economic organisation. To confirm this, using the data obtained from the VIMP methodology it was possible to group the coins by emission, evaluating the differences in composition between issues from different authorities.

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