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**Advanced Analytical Methods and Technologies for the
Conservation, Diagnostics and Archaeometry of
Copper-based heritage items**

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Abstract

The study of ancient metals is of great importance, given the interest they present from many point of view, from production technology and corrosion science, to the history of society and economy.

Archaeological copper-based alloys, in particular, are extremely abundant in our historical heritage, but still nowadays they present major scientific challenges to be addressed. The strong opacity of copper-based materials towards optical probes, as well as the extreme complexity risen by metallic bulk and corrosion features make their investigation extremely challenging without recurring to physical cross-sections. The missing knowledge about their corrosion mechanisms and the inability to define the conservation status of each single item in a time-efficient and non-invasive way makes even the formulation and implementation of tailored protective treatments tricky and inconsistent. On top of this, there is the fact that copper-based items are found in enormous amounts during archaeological excavations, also determining concern on the management and handling of such number of artifacts.

This research successfully responds to these challenges starting from the observation of real current practise and of the current limitations in protection and investigation of archaeological metals, then pushing the technological limit towards new standards. More in detail, this has been achieved by exploiting advanced analytical techniques for the study and long-term preservation of archaeological copper-based objects, by defining new protocols, and by designing new experimental procedures and hardware components.

In particular, a new XCT-based protocol for the rapid investigation of archaeological copper-based coinage is tested. A new form of silver corrosion, never identified before on ancient metals, is observed and deeply investigated by making use of X-ray Photoelectron Spectroscopy (XPS) and Scanning Photoelectron Microscopy (SPEM). Focused Ion Beam coupled with SEM (FIB-SEM) is here used for the first time to produce deep trenches, in order to attain subsurface and near-bulk information in a micro-invasive way. Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) is also applied to the same goal, and its potential and limitations are highlighted. Towards conservation purposes, both the preparation of mock-up samples mimicking burial conservation conditions, and the testing phase through Electrochemical Impedance Spectroscopy (EIS) are addressed. In particular, a new EIS setup specifically devoted to archaeological copper-based items is designed and tested, allowing for the non-invasive investigation of the residual corrosion activity on highly corroded artifacts.

The focus of the methodologies and procedures developed in this work is on small items completely covered by thick corrosion *patinas*, and their further application to other kind of samples is not straightforward. Nonetheless, this research have implications that from the specific research topic, affecting many other fields of Heritage Science and, in particular, the real practise of archaeologists,

conservators and conservation scientists. In detail, the FIB and LA-ICP-MS protocols investigated here have the potential evolve the way archaeometric and diagnostic study of archaeological copper-based objects is conceived today. At the same time, the adoption of the designed μ XCT and EIS methodologies may strongly impact on the management of large collections of archaeological find. Moreover, the artificial aging procedures developed can support the activity of conservators, in testing new treatments in conditions closer to the ones of a real sample. Additional implications regard the detection of forgeries, as well as novel insights in the peculiar phenomenon of metallic whiskering.

By applying a modern concept of integration between advanced technologies and real on-field practise, this work scores multiple achievements which can positively impact the way archaeological copper-based metals are studied and manipulated today, ensuring a more thorough extraction of useful information without the sacrifice of entire artifacts, and enhancing their long-term preservation for future generations.

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List of abbreviations

4E	Four-electrode (EIS setup)
μ-XES	Muon X-ray Emission Spectroscopy
μXCT	X-Ray Computer Microtomography
at.%	Atomic percentage
BH	Beam Hardening
BSE	Backscattered electrons
BTA	Benzotriazole
CB	Carbon-brush (EIS setup)
CE	Counter electrode
CF	Counterfeiter (aging)
CPE	Constant Phase Element
CPE_{dl}	Double layer CPE
CPE_{pat}	Patina CPE
CS	(FIB-milled) Cross-section
CT	Computed Tomography
EC	Equivalent Circuit
EDS	Energy-Dispersive Spectroscopy
EL	Electrochemical (aging)
EIS	Electrochemical Impedance Spectroscopy
FCC	Face-Centred Cubic
FIB	Focused Ion Beam
FTIR	Fourier-Transformed Infrared Spectroscopy
ICP	Inductively Coupled Plasma
IR	Infrared

LA	Laser Ablation
MS	Mass Spectrometry
NIR	Near-infrared
OCP	Open Circuit Potential
OM	Optical Microscopy
R	Resistance
R_{CT}	Charge transfer resistance
R_{el}	Electrolyte resistance
R_{pat}	Patina resistance
RE	Reference electrode
RIS	Reflectance Imaging Spectroscopy
ROI	Region of Interest
SE	Secondary electrons
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectrometry
SPEM	Scanning PhotoElectron Microscopy
SR	Synchrotron Radiation
TCEIS	Two-cell EIS
THz	Terahertz
UV	Ultraviolet
VIS	Visible (light)
VOC	Volatile Organic Compound
WE	Working electrode
WOT	Wash-out time
wt. %	Percentage by mass
XCT	X-Ray Computed Tomography

XPS X-Ray Photoelectron Spectroscopy

XRD X-Ray Diffraction

XRF X-Ray Fluorescence

Introduction

The possibility to study objects that have been manufactured thousands of years ago has an undeniable appeal, as it allows to delve into the intricate narratives of ancient civilizations. This is even truer when speaking about ancient metals. Thanks to the combination of their material composition (which provides insights into technology and economy), their intricate corrosion patterns (retaining the memory of the object's personal history), and aesthetic features (offering valuable social insights), ancient metals stand as a remarkable intersection for the collaboration of materials science and humanities.

This work has a single focus: archaeological copper-based alloys. In this thesis, the term "copper-based alloys" is consistently used instead of "bronze", the latter being a term typically employed by historians and archaeologists to describe any historical item containing copper as the primary component. This decision reflects a commitment to adhere to a more rigorously scientific nomenclature, and reserves the term "bronze" for alloys with specific metallographic features.

During the Roman era, copper-based alloys and iron were the most widely used metals. However, while iron objects usually degrade into powder in a short time, copper-based object more often survive the passing of centuries. For this reason, copper-based objects are among the most common archaeological artifacts, and are found in large amounts during archaeological excavations and surveys. This, together with the high content of information they store within, make them a unique key to penetrate the history of the humankind.

This thesis is motivated by the observation that, despite significant scientific efforts invested in technological solutions for the study and conservation of copper-based artifacts, the practises currently employed by conservators and conservation scientists, both in the field and in the lab, have shown limited advancements compared to previous decades. These considerations are particularly relevant to artifacts originating from a buried environment. Unlike objects that are stored in outdoor conditions, archaeological metals have spent centuries in soil and are typically stored in indoor conditions after their retrieval. This determines important differences in their corrosion pattern and conservation needs.

The need for new protocols and strategies arise from the current limitations in the way archaeological copper-based alloys are currently handled. In particular, the large number of finds to be processed, the absence of non- and micro-invasive procedures for their investigation and the limited number of studies specifically devoted to their conservation entail negative consequences for our common heritage. Thousands of archaeological copper-based artifacts (mostly comprising coins, ornaments and tools) are left in deposits in uncontrolled nditions, lacking any kind of attention, including both their

characterisation and preservation. Many others have been sacrificed during the years, because there was a lack of methodologies to extract the invaluable information they were storing within without physically cross-sectioning them. In order to capitalise this massive hidden inheritance and guarantee its long-term preservation, the development of new protocols for their analysis and protection is required.

Indeed, archaeological artifacts present some peculiarities that make this goal challenging to achieve. In particular, the optical opacity of their *patinas* and metallic bulk makes most of the common non-invasive characterisation protocols unfeasible, due to the low penetration depth of typical non-invasive probes (such as VIS-to-THz electromagnetic waves). Moreover, the complexity of their conservation state, with thick and highly heterogeneous *patinas*, is hard either to investigate and to replicate. The development of new technologies and the upgrading of current ones offer an interesting opportunity to be caught in order to respond to this challenge.

The present thesis aims to fill this gap and exploit these opportunities, paying particular attention to propose solutions that can be implemented, with significant and tangible improvements, in the daily working routine of conservators and conservation scientists. More in detail, the final goal is to set the world of conservation and archaeometry of copper-based items towards more advanced and modern standards of performance, efficiency and non- and micro-invasiveness. This goal is pursued by acting on three fronts: the investigation of advanced technologies that to date have never or rarely been applied to metallic heritage, in order to assess their potential and limitations in this field; the development of new, more efficient and versatile protocols for well-established and widespread techniques, in order to overcome technological limitations that have restricted their use up to now; the advancement of new strategies for the development and testing of protective treatments.

In detail, this thesis comprises five experimental units, dealing with the main challenges regarding archaeometry, diagnostics and conservation of archaeological copper-based heritage: from coin identification, to the evaluation of latent corrosion and the testing of new treatments, passing through the micro-invasive investigation of internal and surface features. All of this is achieved by applying a wide variety of complementary techniques. Special focuses are devoted to Focused Ion Beam coupled with Scanning Electron Microscopy (FIB-SEM), Laser Ablation coupled with Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) and Scanning Photoelectron Microscopy (SPEM) as they represent techniques relatively new to the field of archaeological metals. They are investigated for their potential and limitations in the analysis of this kind of samples. For FIB-SEM in particular, a protocol for its efficient use in the micro-invasive investigation of sub-surface and near-bulk feature is proposed. New methodologies are designed and validated also for techniques already diffused in the field, such as X-ray Computed Microtomography (μ XCT) and Electrochemical Impedance Spectroscopy (EIS).

Finally, novel protocols for the reproduction of mock-ups mimicking the conservation state of archaeological samples are evaluated.

The design of methods and procedures proposed herein takes into account as much as possible the current practises adopted by conservators and conservation scientists and the applicability to their daily working routine.

The present thesis is structured as a single, multifaceted but coherent manuscript. It consists of four chapters, each divided into sections and paragraphs.

Chapter I provides the reader with the basic notions and the state of the art of the literature that are needed to follow the unravelling of the PhD project across the subsequent chapters. It first features a description of the material nature of Roman copper-based alloys and their corrosion pattern in burial environment. The focus then moves to the current practise in the field of archaeometry, diagnostic and conservation of archaeological copper-based alloys. At the end of the chapter, the experimental work conducted during the PhD project is described in detail, making explicit reference to the critical issues identified in the current literature.

In **Chapter II**, materials and methods applied across the experimental research are described. They are organised in five sections, following the structure of Chapter III.

Chapter III presents the experimental results achieved during the PhD project. The chapter is divided into five sections, representing the five topics faced by this project. Each section starts with a brief description of the specific work, and then takes a deep dive into the results of the research, which are thoroughly discussed.

Finally, in **Chapter IV** the general conclusions are drawn, illustrating the impact of the achieved results on the world of copper-based heritage, and depicting the potential for further studies to follow.

An **Appendix** is provided at the end of the thesis, reporting preliminary investigation towards the development of a protective treatment.

The world of materials science and humanities will be always more intertwined. This PhD project foster this relationship by proposing new connections, for the mutual benefit of both worlds.

Chapter I State of the art

I.1 Archaeological Copper-based alloys

Copper had a role of primary importance in the human history. The diffusion of the copper smelting process, starting from the late 6th/5th millennium [1], traditionally marks the transition from the Stone Age to the Metal age. The later intentional production of the first alloys (Cu-As and, after, Cu-Sn) marked a huge technological advance for the production of tools and equipment, implied in the definition of Bronze Age (ca. 3rd to 1st millennium BCE). Nowadays, Copper has lost some of its previous functions, while raising strong interest for industrial applications, such as semiconductors [2] and superconductors [3].

In the Roman age, copper-based alloys covered important roles in the life of the society, from daily life (tools, *fibulae*, rings, and other decorative items [4–7]) to monuments (especially statues [8–11]), making them a distinctive aspect of Roman society in both technological and socio-cultural terms. However, it was in numismatics that copper alloys saw their widest use.

Copper-based coinage was, as it is today, the lowest level in the value scale of Roman coinage, behind gold and silver. This implies that it was the most widespread currency in terms of numbers of coins in circulation. It must be underlined that, being so widespread among the population and created to be exchanged between people, coins also served as an ideal means to convey official propaganda through the “types” (the figures) and the “*legendas*” (the text) embossed on them. Thanks to these features, to modern scholars, coins have become an essential source of socio-historical information about the period in which they were issued [12]. Moreover, their material composition sheds light on contemporary technology [13], and the variation in copper percentage over time in the alloy is an invaluable source of economic data [14].

The relative abundance of copper-based coinage is reflected in their prominence as archaeological artefacts. Copper-based coins are not only almost ubiquitous in archaeological contexts, but they are also found in large numbers [15,16], thus making them one of the most common archaeological finds. The number of coins resulting from surveys, excavations, and occasional findings is so large to represent for archaeologists, conservators, and conservation scientists almost a limit to their study and preservation, calling for tailored time-efficient solutions.

Next paragraphs give the historical and scientific context on the kind of archaeological samples, copper-based Roman coins, which are featured in all the experiments in this thesis.

I.1.1 Copper-based coinage in the Roman era

The age of coinage in the Roman history is commonly traced back to the *aes rude* [17,18]. Rather than an actual coin, *aes rude* was an irregular piece of bronze (which was called *aes* in Latin), without any specific mark or nominal value, which was traded based on its weight (Figure 1 a). Around the end of the 6th – 5th century, the shape of the metal ingots became gradually more and more regular, also featuring a distinctive mark of production: the *aes signatum*. This rudimental form of copper-based “coinage” (Figure 1 b), made by casting liquid metal into a mold, was the only circulating in the Roman territory when, exceptional minted silver coinage series started to appear around 300 BCE, most probably initially produced in the federated city of Naples and intended for commercial exchanges with the Greeks [17,18].

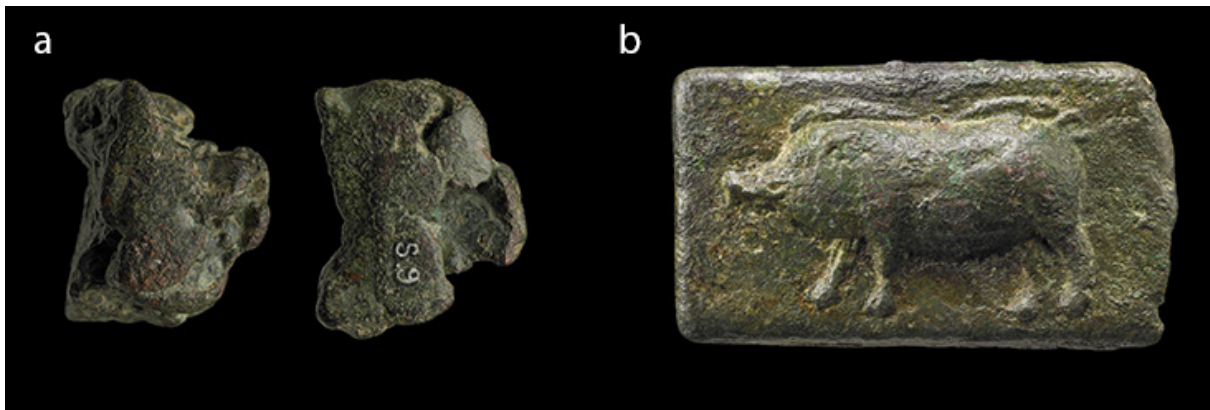


Figure 1 a) *aes rude* (34.38 g, ca. 500 BCE) and b) *aes signatum* (1746 g, ca. 280BCE-250BCE). © The Trustees of the British Museum

Soon after, Rome started casting its first regular coin-like currency, the *aes grave*, which originated a full bronze coinage system. Romans kept using cast coinage for internal use until the late 3rd century BCE when the *aes grave* eventually gave way to the struck *as*. Over the century, the *aes* weight had rapidly fallen from the original ca. 300 g to ca. 50 g, while the production technology had slowly moved from casting to minting [17].

Unlike casting, minting implies melting the metal into an even plate from which planchets (flans) are obtained. These blank coins are placed between the anvil, bearing the obverse die, and the punch, bearing the reverse die, and then struck by hammering (Figure 2). The planchet could be annealed prior

to striking in order to ease the flow of the metal in the smallest details of the negative figure on the die [18].

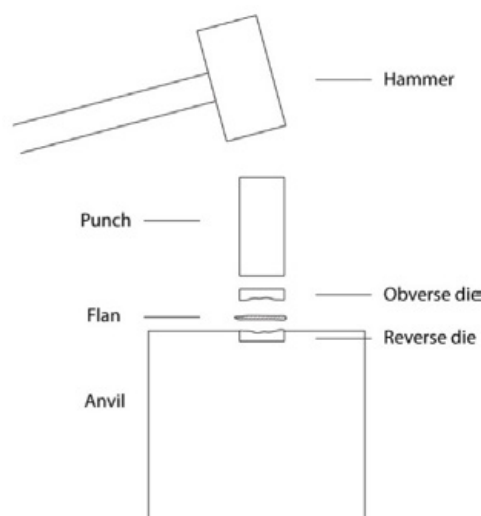


Figure 2 Schematic example of coin minting.

Around 211 BCE, the first proper Roman silver coinage was introduced: the *denarius*, which became the main currency. At the same time, the standardised struck *as* became the reference “unit of account”, i.e. the unit of money used for expressing the value of other coins, or goods. For instance, originally, a *denarius* was equal to ten *asses* [19].

Following a couple of centuries of constant devaluation both of *as* and *denarius*, now equal to sixteen *asses*, Augustus’ reform (23 BCE) revolutionised Roman currency by establishing a tri-metallic system. As for the copper-based coinage, two main groups were identified: *as* (and its submultiples), in pure Cu, and the higher-value *sestertius* (and relative submultiples), in *orichalcum*, which was the Latin term for brass. Furthermore, Augustus formally put the minting of gold and silver currency under the exclusive control of the Emperor, while leaving the copper/bronze coins supposedly as a prerogative to the *Senatus* [17,20].

It must be noted that precise alloy compositions cannot be associated univocally to either of these coin types. In fact, the amount and type of alloying elements greatly varied during the centuries, and even from mint to mint, not to mention the presence of many secondary elements (such as As and Sb) that we are not considering in this dissertation. The main driving force behind this variation was the progressive debasement of the coins following the degrading power of the Roman Empire. For instance, both *asses* and *sestertii* became smaller and smaller, while *sestertii*’s Zn content gradually decreased. Zn and Sn were rarer and thus more valuable compared to Cu and Pb. This is why there has been an increase in the use of Pb across the history of Roman coinage, in place of Zn and Sn [21].

Starting from Nero (60 CE), the general decline of the economy of the Roman Empire also affected the silver *denarius*. The nominal Ag content went from 98% pre-Nero, to 93.5% under Nero, to ca. 70% under Commodus (161-192 CE), and then fell below 50% under *Septimius Severus* (ca. 197 CE). After this period, the *denarius* can be mostly defined as a copper-based coin, from the point of view of the material [22]. Moreover, under Septimius Severus and his successors, there is evidence that some mints resumed casting [23], even if in a minority of cases. Cast coins will last until Constantine (310 CE), which banned the casting technique given the high risk of forgeries.

In order to avoid further debasement of the *denarius*, Caracalla introduced in 215 CE a new silver coin (with only 50% of Ag content), called *antoninianus*, which gradually replaced the *denarius*. This, however, did not stop the debasement trend of the *denarius*, which almost disappeared as currency around 240 CE together with *as* and *sestertius*, although it remained as a unit of reference [17].

In the second half of the 3rd century CE, due to the instability of the political period, copper-based coinage also gradually underwent changes, and saw the use of alloys increasingly contaminated by secondary elements, the progressive reduction of the Ag content, and a greater use of Pb. This was accompanied by the increasingly widespread practice of re-melting old coins to mint new smaller ones [17,18].

From then until the end of the Western Roman Empire (476 CE) Roman coinage became even more dispersed and less standardised in terms of coin types and alloy compositions. Aurelianus (274 CE) reformed the old *antoninianus* by setting it at 4 g with ca. 5% Ag. This coin was also known as *aurelianus* or *radiatus*, because of the radiate crown on the Emperor's obverse profile. Diocletian (294 CE), on the other hand, tried to stop the devaluation trend by introducing both a new silver coin, *argenteus* (95% Ag), and a new copper-based large coin (4% Ag), called *folles*, commonly known as *laureatus*, because the Emperor's portrait is wearing a laureate crown. Both *radiati* and *laureati* coins and their submultiples were made of complex bronze alloys (usually with Pb or even Zn) and tiny amounts of Ag, which debased to just traces after few decades [23]. After this period, Roman copper-based coinage was made primarily by complex bronze alloys, often with minimal amount of Ag, or pure copper [24]. In this period, the numismatic nomenclature is so little standardized, with terms like *folles* and *nummi* being often used as generic reference for copper-based coins, to the point that 4th and 5th century coins are usually defined by numismatics just on the basis of their diameter and not by a proper name.

I.1.2 Copper-based alloys in the Roman coinage

Due to the elevated complexity and scarce standardisation of copper-based Roman coinage across centuries, for the sake of the topics involved in this thesis it is more convenient to classify coins type in macro-group of different alloys. The following classification is based on the archaeometric studies present in the current literature.

As stated in the previous paragraph, *asses* and its submultiples were mostly made of pure copper, starting from Augustus' period. Cu, as pure metal, solidifies in a Face-Centred Cubic (FCC) system, which in cross-section resembles like equi-axial hexagonal grains (Figure 3a). However, the presence of impurities commonly determines the growing of Cu grains in form of dendrites during the solidification process (Figure 3c,d). A partial or complete recovery of ideal hexagonal conditions can be attained by annealing (Figure 3b). Other common features of copper are inclusions of Cu_2O or CuS , and porosity.

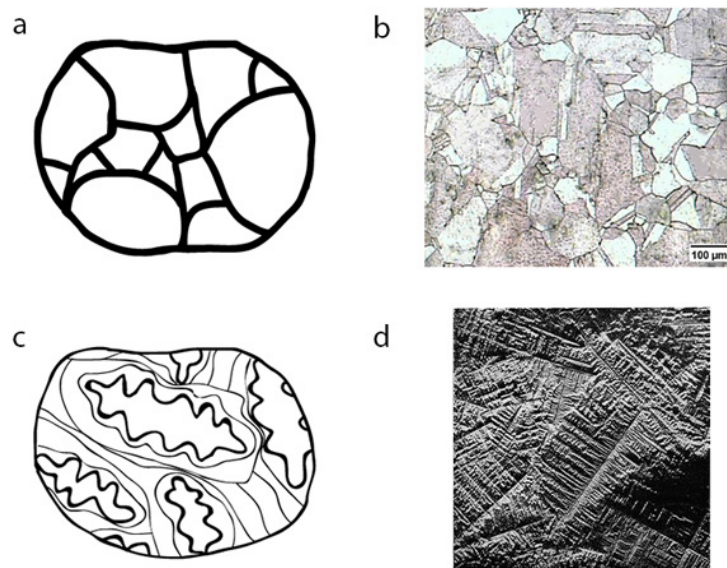


Figure 3 a-c) Schematic example of an equi-axial hexagonal texture of an FCC system, and of a dendritic structure. b) Micrographic example of an annealed pure Cu [25] (Reprinted upon license from [Springer Nature](#)). d) Micrographic example of a dendritic structure (magnification 5x) [26].

The alloy that is most intended as “bronze” is actually a binary Cu-Sn alloy, more correctly defined “binary bronze”. Binary bronzes were scarcely used in Roman coinage after the Augustus' reform. However, their thermodynamics represents the basis for describing more complex ternary and quaternary bronzes, which have been more diffused in the Roman coinage.

Roman coins contained percentage of Sn below 15-20%, which is a threshold to separate low-Sn to high-Sn bronzes. Consequently, we do not deal with the microstructure of high-Sn bronzes in the following discussion. Low-Sn bronzes usually present a so-called “eutectoid” structure, which forms during the cooling of the alloy across multiple steps [26–28]. Looking at the phase diagram (Figure 4), over the temperature range 1080° - 800° C, a dendritic α phase starts nucleating to form a solid solution made of FCC-Cu containing fractional amounts of Sn, while the residual liquid metal enriches in Sn. Below the peritectic temperature (800° C), residual liquid solidifies as an infill made by $\alpha+\beta$ phases, where β is a different solid solution richer in Sn and stable only at high temperature. When temperature decreases below 520° C, β phases decompose directly into a $\alpha+\delta$ system, where δ is an intermetallic compound with a specific stoichiometry ($\text{Cu}_{31}\text{Sn}_8$), while the intermediate decomposition to γ phase usually does not take place.

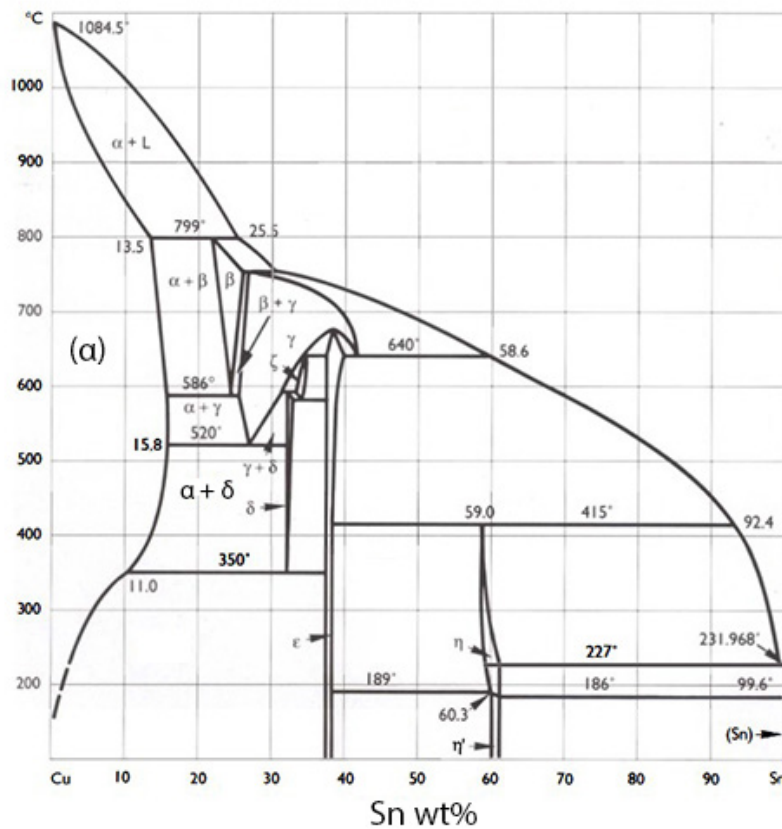


Figure 4 Cu-Sn phase diagram.

The final structure will then have a cored dendritic phase, with an infill of peritectic - or secondary - α phases (richer in Sn compared to α dendrites) and small inclusions of eutectoid $\alpha+\delta$ grains (Figure 5). In this way, the concentration of Sn will increase going from the centre (dendrites) to the periphery (eutectoid phases), marking a so-called “inverse segregation” process. In this kind of systems, it can

happen that α -dendrites and peritectic α can interdiffuse, creating a region near the dendrites where elemental composition is more homogeneous.

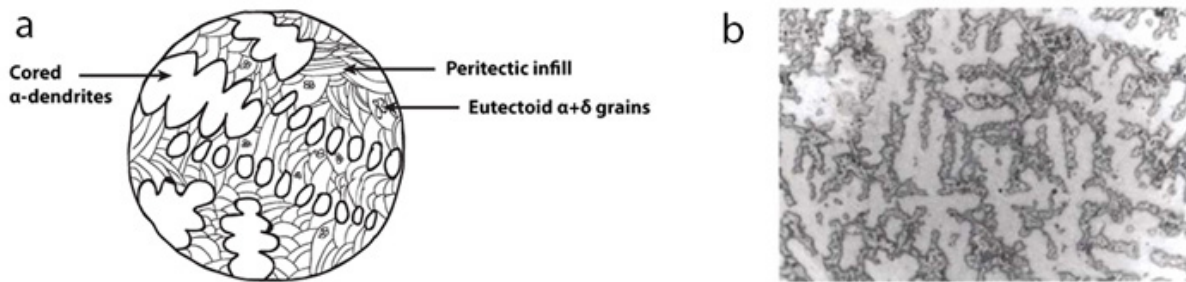


Figure 5 a) Schematic example of a eutectoid structure of a binary bronze. b) Micrographic example of a binary bronze (original magnification $\times 120$ [27], © 1991 J. Paul Getty Trust).

It must be noted that, if the alloy is annealed after casting, δ phases tend to disappear into α phases, which tend to homogenise in composition towards an ideal hexagonal structure without dendrites. There is evidence that Romans performed coin annealing before or after striking [13].

Cu-Zn alloys, which Romans called *orichalcum* and today are called “brass”, are eutectoid alloys quite similar to the Cu-Sn system. The main difference is that Zn is even more soluble in α -Cu, determining a higher threshold (ca. 32.5 wt% of Zn) for the appearance of β phases (Figure 6a). *Orichalcum*, as used for coinage of *sestertii* and *dupondii*, rarely surpassed the 20 wt% in Zn [20,29], thus the expected microstructure would be more similar to the one of pure copper in Figure 3 rather than the one in Figure 5. Due to the similarity in behaviour between Sn and Zn and given the better solubility of Zn in the α -Cu, ternary Cu-Sn-Zn bronzes (with limited amounts of Sn + Zn) can be compared with binary Cu-Sn bronzes in which the amount of Sn is equal to Sn + $\frac{1}{2}$ Zn, as far it concerns the alloy microstructure [26].

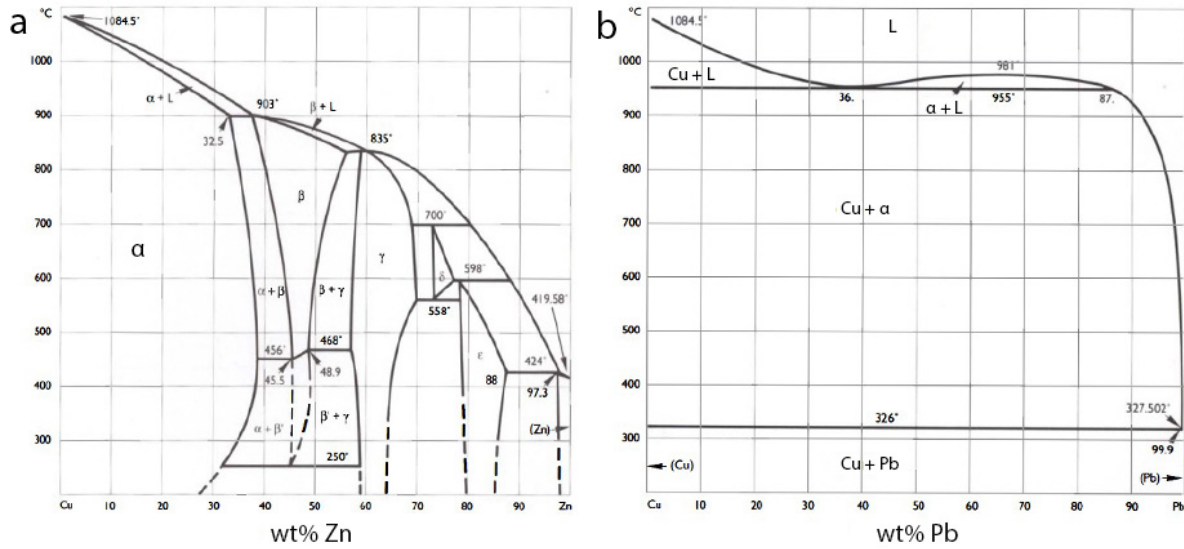


Figure 6 a) Cu-Zn phase diagram and b) Cu-Pb phase diagram.

Rather than a real alloying agent, Pb can be regarded as an additive for Cu, bronzes and brasses. The reason is that Pb is totally immiscible into Cu, Sn and Zn, always segregating at grains border as clusters of almost pure Pb during crystallisation (Figure 6b). The size of these clusters strictly depends on cooling speed after casting (Figure 7). Macro-segregation, usually along the external surface, can also occur, which can be particularly misleading when performing point analyses like X-ray Fluorescence. Pb was added into Cu-alloys to substitute more precious Sn and Zn, in order to lower the melting temperature and increase workability. There is evidence that Pb was present in the major part of the copper-based Roman coinage, especially in the one of the Imperial era [13].

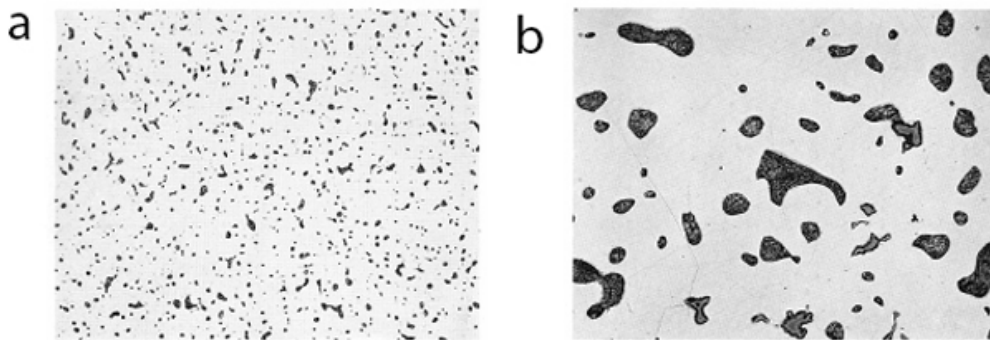


Figure 7 Micrographic examples of quaternary bronzes with ca. 10% of Pb after rapid (a) or slow (d) cooling (original magnification 200x) [26].

The Cu-Ag system is, instead, a eutectic one (Figure 8). Generally speaking, a Cu-Ag alloy with less than the 70 wt% of Ag can be regarded as the Cu-Sn system, with α dendritic cores and an infill of eutectic $\alpha + \beta$. In this case, β will be an Ag-rich phase (>90 wt% Ag) (Figure 9). This type of alloy is sometimes referred to as “billon”, and it is characteristic of debased *denarii* and *antoniniani*.

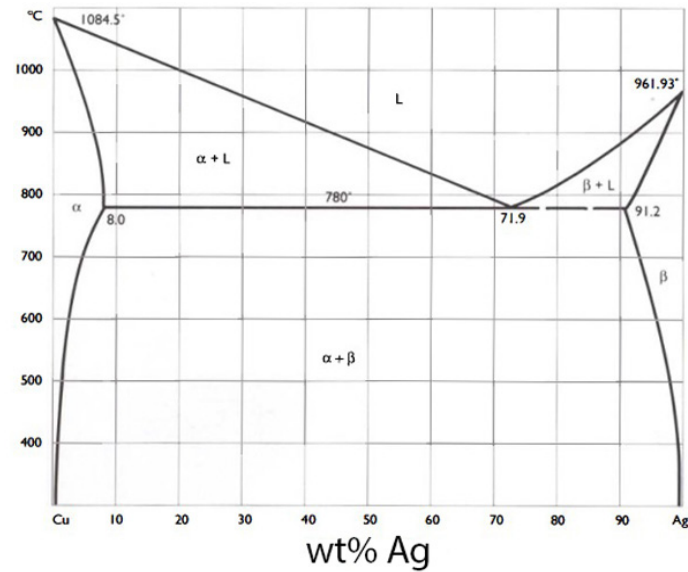


Figure 8 Cu-Ag phase diagram.



Figure 9 a) Schematic example of a Cu-Ag eutectic structure. b-c) Micrographic example of a 40% Cu - 60% Ag alloy. *α* dendrites and *α*+*β* eutectic infill are clearly visible ([27], original magnification: x35 (b), x100 (c), © 1991 J. Paul Getty Trust).

In late Imperial coinage, the Ag content rarely exceeded 5 wt% [23], being added in complex bronzes, like ternary Cu-Sn-Pb or even quaternary Cu-Sn-Pb-Zn ones. What can be expected in this case is the presence, in casted alloys, of some *β*-Ag grains in the peritectic or eutectoid areas, and tiny amount of Ag solubilised into the *α*-Cu phases. This is the case of heavily debased *denarii* and *antoniniani*, as well as *laureati*, *radiati*, *nummi*, *folles* and related issues.

Lastly, as described in the previous paragraph, most of Roman coins were struck. The effect of plastic deformation from the cold working on the microstructure of the alloy can be drastic [30]. One example is reported in Figure 10, depicting the elongation of grains along the deformation axis. Other effects can see the formation of twinned grains or strip lines, while annealing after cold working can partially reverse such modifications.

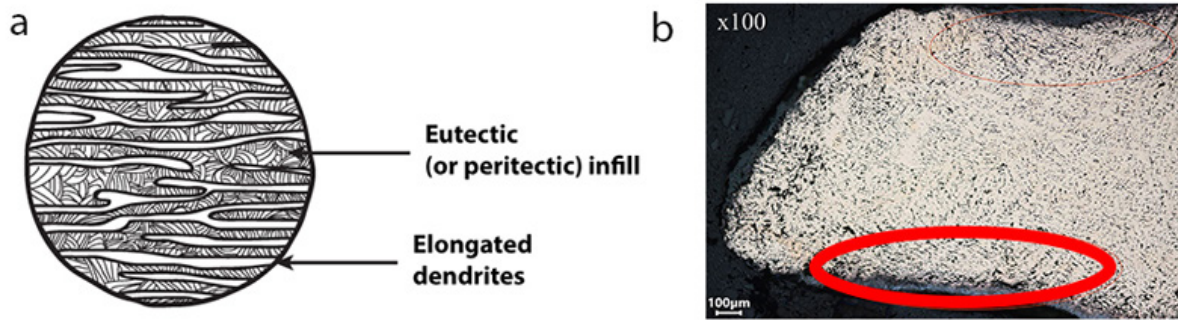


Figure 10 a) Schematic example of the elongated structure of a binary alloy following cold working. b) Micrographic example of a struck Roman coin. Red circle marks an area where effects of cold working are evident [13] (Reprinted upon license from [Springer Nature](#)).

I.1.3 Copper-based alloys and burial environment

Although considered as a noble metal, copper (and its alloys) presents a lower resistance to corrosion in respect to other coinage metals, gold and silver. This is especially true when speaking about artifacts that have rested for centuries in a burial environment. In common burial conditions, in fact, copper alloys develop corrosion layers (hereafter, *patina*) that can grow inward towards the bulk metal by running through porosity or grain boundaries, and outward by re-precipitation of leached-ion salts, englobing extrinsic compounds (e.g. soil), etc [31,32].

The exact corrosion pattern greatly varies from item to item, mainly depending on the specific corrosion environment, alloy composition and working process the artifact has subdue. For instance, cold working can drastically increase grain boundary density, creating new preferential patterns for corrosion to grow [27,30]. A subsequent annealing, instead, can reduce grain boundaries and contextually reduce compositional gradient between different phases, which can represent another attacking point for selective corrosion [33].

As regards the conservation environment, there are five major factors influencing the corrosion of metals during burial [26,33], namely: the moisture level in soil and its degree of oxygenation, because water and oxygen are usually directly involved in the corrosion mechanism; the electrical conductivity of the soil and presence of stray currents; soil composition, especially in terms of chemical environment, presence of aggressive ionic species and micro-organisms [26,33]. The last factor is the anthropic one. It is particularly relevant for items found in fields devoted to agriculture. There, soil is periodically ploughed, giving to the artifact a cyclic exposure to burial, sub-aerial and aerial environments, which

can result in very harsh conditions for a metal [26]. Moreover, the rise in the use of fertilizer and pesticides in last decades may also play a role in their corrosion [34].

In this regard, all the coin samples analysed in this thesis come from a near-lagoon environment, and specifically from farmed fields in the countryside of the ancient city of Aquileia (northeast Italy). Some fields where the coins have been found have been recently studied [35], revealing a more clayey composition and near-neutral pH (6.8) if located close to the lagoon, while the ones few kilometres inside the mainland showed a more carbonaceous composition and basic pH (>8). All soils showed a high conductivity (300–400 $\mu\text{S}/\text{cm}$) and a high Cation Exchange Capacity (CEC) (30–40 cmol/kg), indicating a high capacity of the soil to exchange ions with materials buried in it.

The large variability of concerned factors determines that each artifact has its own different *patina*. However, copper-alloy *patinas* subjected to a long exposition to burial conditions usually present some common characteristics. First and foremost, *patina* covers the whole object; it is thick (from tens to hundreds of μm) (Figure 11); its structure is highly complex, with a severe degree of heterogeneity both along its surface and across its section, on a small scale.

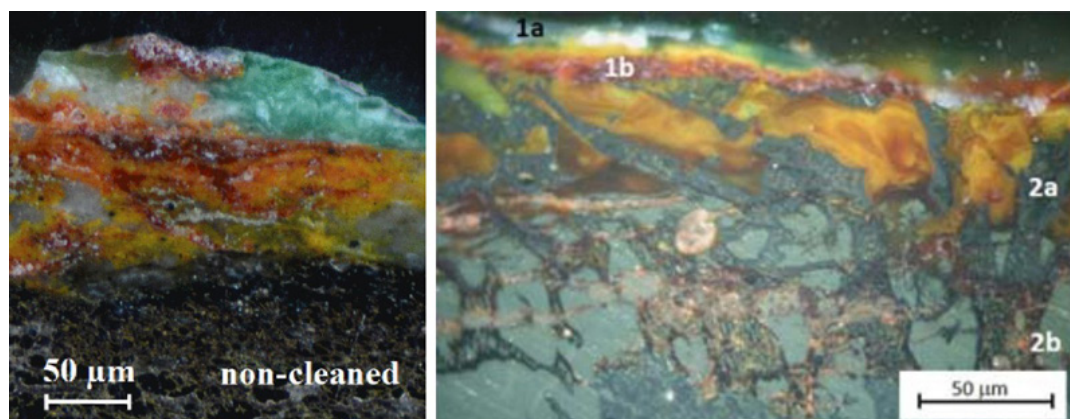


Figure 11 Examples of thick patinas on archaeological copper-based items seen under optical microscope (original magnification: unknown (left), 500x (right)) [36,37]. Image on the left is reprinted from [36], with permission from Elsevier.

In soil conditions comparable to the one in Aquileia, the most common compounds that are generated by the interaction of Cu and soil are: oxides, such as cuprite (Cu_2O) and tenorite (CuO); hydroxycarbonates, especially malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$) and more rarely, azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) [26,31,38]. The reason for that is clearly explained by thermodynamics (Figure 12). In common soil conditions, cuprite and malachite are the stable compounds. Azurite has a narrow range of stability at slightly acidic conditions, which gets smaller with the reduction of carbonates concentration. However, an increased concentration of carbonates usually rise the pH towards basic conditions. For such

thermodynamics reasons, azurite is less common of malachite as corrosion compound in burial environment [38].

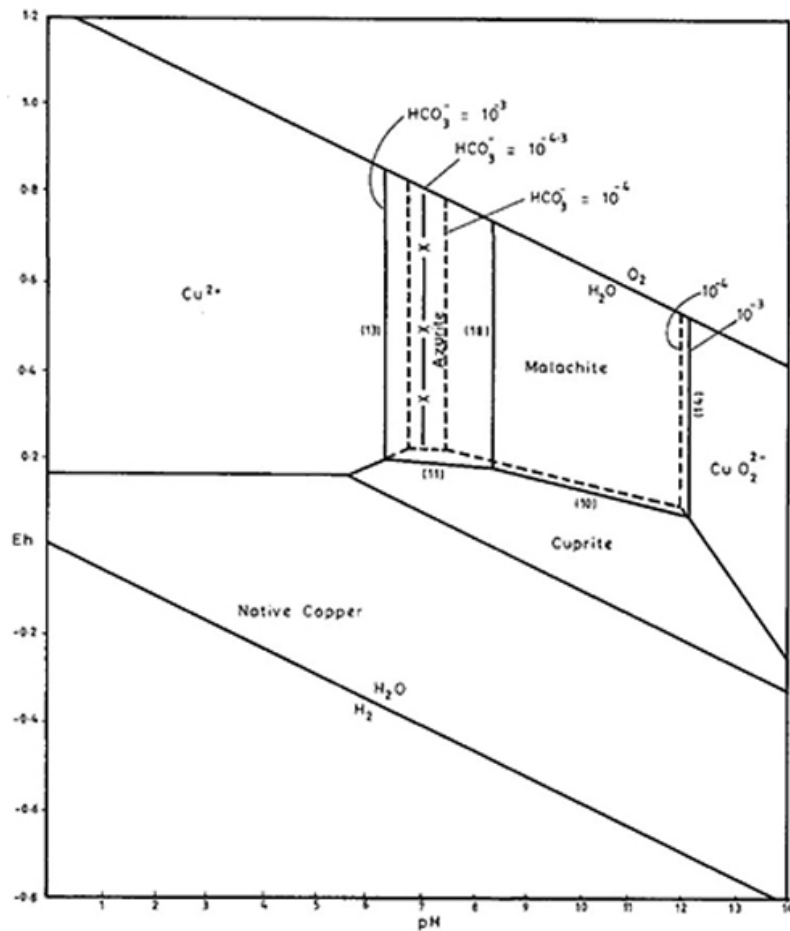


Figure 12 a) Pourbaix diagram (Eh-pH) of the system Cu-O-H-HCO₃⁻ at 25° C and 1 atm. Total dissolved copper ion: 10⁻⁶ mol/kg. Straight lines: log(HCO₃⁻) = -3 mol/kg. Dashed lines: log(HCO₃⁻) = -4 mol/kg. [38] (2018© Cambridge University Press, reproduced with permission).

Their presence also governs the aesthetics of copper-based artifacts (Figure 13). Most commonly, such *patinas* have a stratified structure with a thick layer of cuprite close to the bulk, covered by a malachite overlaid. Curiously, but not unexpectedly, cuprite and malachite represent two of the main natural sources for copper smelting too, together with copper sulphides and few others [39]. Others Cu compounds less commonly found in burial conditions (but frequently in outdoor conditions) are sulphates (such as brochantite, Cu₄(SO₄)(OH)₆) and sulphides (such as covellite, CuS, and chalcocite, Cu₂S) [1]. Particularly appreciated by collectors and valued by the market is the *patina* type colloquially called “desert”, which is due to the presence of silicates covering surface inlets, while the details are exposed and thus highlighted due to mechanical wear.



Figure 13 Examples of different kinds of patina aesthetics on copper-based roman coins, from top left to bottom right: cuprite red (ID 587202), tenorite black (ID 570103/1), malachite green (ID 579679), azurite blue (ID 20.S239-2.2569) and silicate “desert” [40] patinas. Coin images are not to scale. Coins 587202, 570103/1 and 579679 are reproduced upon permission of the Ministry of Culture, Regional Directorate of Museums of Friuli Venezia Giulia. Coin 20.S239-2.2569 is reproduced upon permission of the Ministry of Culture, General Directorate of Archaeology, Fine Arts and Landscape of Friuli Venezia Giulia. Any further reproduction of such images, duplication by any means, as well as downloading and subsequent manipulation, is strictly prohibited.

In binary bronzes, the presence of Sn usually determines the formation of cassiterite (SnO_2) inside *patina* layers. Moreover, binary bronze is also the only class of copper alloys with an established corrosion mechanism and nomenclature, as proposed by Robbiola *et al.* [32] (Figure 14). He designed a double route that a tin bronze can follow when corroding in soil, depending on local conditions. If soil conditions are mild, a layer of Sn oxides forms on the surface of the object, which first slows down the corrosion process and then regulates the selective dissolution and leaching of Cu ions, determining a tin-enrichment (or “decuprification”) inside the *patina* (Figure 15). This kind of *patinas* are defined as type I. Type II *patinas* forms, instead, in aggressive environments, which determine a fast initial dissolution of Cu and do not allow for Sn oxides to cover the object’s surface. In this case, the corrosion is more severe and brings to the complete disruption of the original surface details.

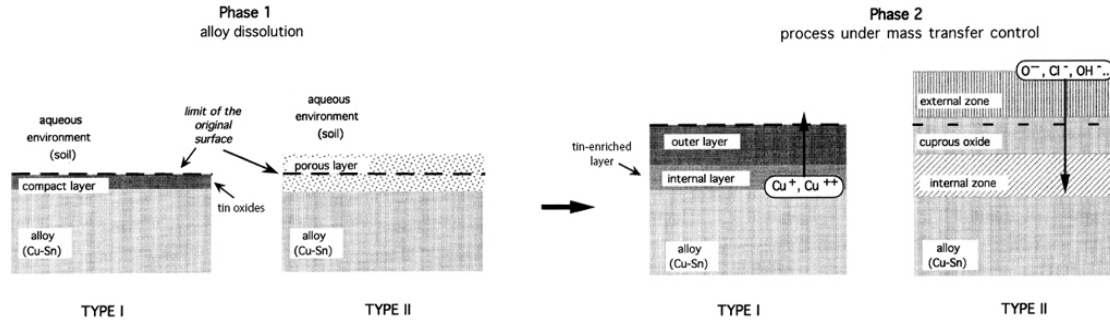


Figure 14 Type I and type II patinas for Cu-Sn binary bronzes, as defined by Robbiola et al.. Reprinted from [32], with permission from Elsevier.

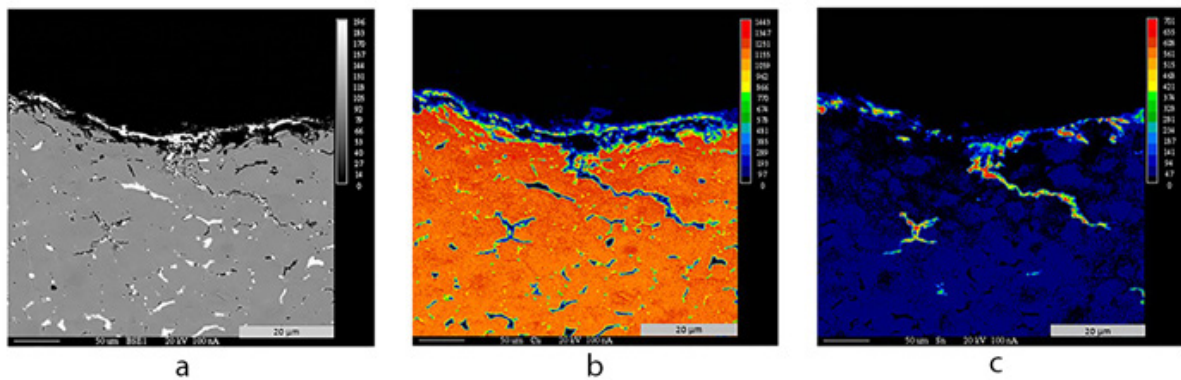


Figure 15 Example of tin-enrichment (decuprification) inside patina. a) SEM-SE image of a cross-section of a late imperial coin. b) EPMA map of Cu. c) EPMA map of Sn [23]. Reprinted upon license from [Springer Nature](#).

At the microstructural level, some common phenomena may happen in binary bronzes and extend to other copper-based alloys. For example, $\alpha+\delta$ eutectoid phase are often preferentially corroded in respect to Cu-rich dendrites (Figure 16a,b). Metallic Cu can redeposit inside *patina*, due to over-saturation in Cu ions generated from the corrosion process (Figure 16c). Another highly interesting feature is the pseudomorphic replacement of original alloy grains by corrosion products [27] (Figure 16d). Pseudomorphic replacement means that corrosion products grow in place of original alloy phase, mimicking their shape. This can happen in the primary corrosion layer, which grows inward. Consequently, by studying corrosion morphology a lot of information on the original alloy microstructure, its composition and processing can be retrieved [27].

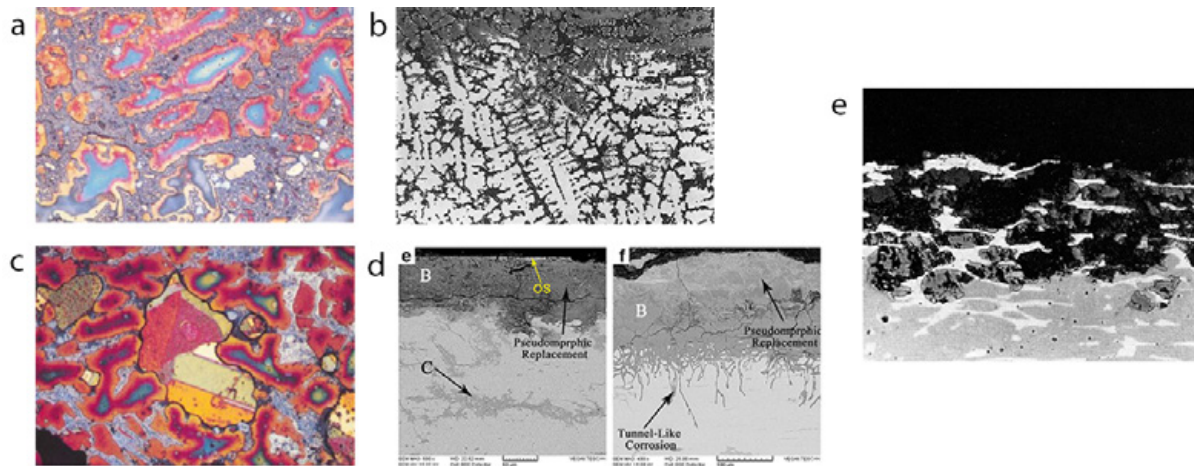


Figure 16 Examples of: a-b) preferential $\alpha+\delta$ corrosion (interdendritic attack, original magnification: x350 and x500, respectively), c) Cu reprecipitation (x420) and d) pseudomorphic replacement in bronzes (Reprinted upon license from [Springer Nature](#) [41]). e) Preferential attack of Cu-rich phases in a Cu-Ag alloy (x500). Iridescent areas in (a) and (c) images mark metallic areas after thiosulfate-acetate attack, and are reproduced from [27], © 1991 J. Paul Getty Trust. Images (b) and (e) are reproduced from [26].

Zn can form oxides and sulphides, but can also cooperate with Cu to form mixed carbonates and chlorides. Moreover, Zn tends easily to be ionized and leached out of the system, due to its low resistance to oxidation. One corrosion feature that is specific for brass is the zinc depletion or “dezincification”, which refers to the reduction of Zn content in *patina* layers in respect to its bulk content [27,42] (Figure 17). There are two different mechanisms proposed for explaining dezincification: first, preferential leaching of Zn against Cu; second, contextual leaching of Zn and Cu, with redeposition of metallic Cu due to oversaturation [43].

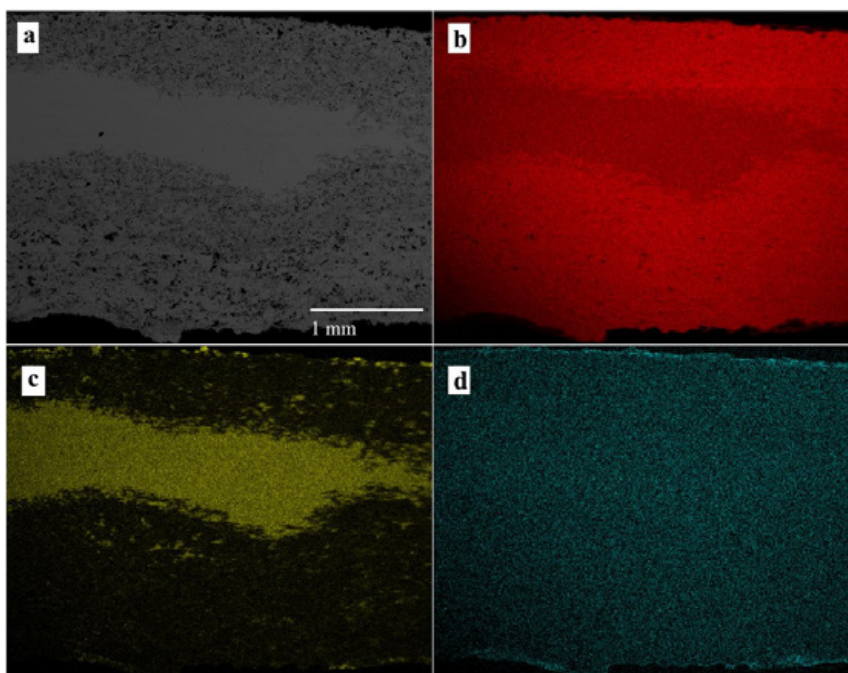


Figure 17 Example of severe dezincification in a sesterius. a) SEM-BSE image of a cross-section. b-c-d) EDS maps of Cu, Zn, Fe, respectively. Reprinted from [42] under [CC BY 4.0 DEED](#).

Pb is known to form a great variety of corrosion compounds, such as: litharge (PbO) and plattnerite (PbO_2), cerussite (PbCO_3) and hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$), cotunnite (PbCl_2), anglesite (PbSO_4), galena (PbS), not to cite organic salts.

The role of Pb in corrosion at the microstructural level is rather obscure and little investigated until now, even though present in relevant amount across Roman bronze metallurgy. The same applies to Ag, when added in limited quantity in copper or bronzes. It has been observed a silver-enrichment phenomenon similar to what happens for Sn[44]. Furthermore, it can be hypothesized that Cu-rich phases preferentially degrade in respect to Ag-rich phases, as the electrochemical series and some case studies would suggest (Figure 16e). However, specific interaction between Ag and Cu and the holistic behaviour of Cu-Ag alloys has been little investigated and mostly for the case of Ag-rich alloys, such as sterling silver [45,46]. Nonetheless, Ag most commonly degrades in oxides (Ag_2O), sulphides (Ag_2S) and chlorides (AgCl) [1,47].

Most of the corrosion products listed in this paragraph are quite stable in indoor conditions, which represent common storage conditions for objects after their excavation and eventual cleaning. When the metallic bulk is completely covered by stable corrosion products, its interaction with the oxidising agents present in the surrounding environment is hindered, cutting down the corrosion rate. In such conditions, the metal/alloy is called in a *passive* state. However, for copper-based alloys, there is one

specific corrosion mechanism that is well known to cause permanent corrosion activity until all bulk-Cu is depleted (*active state*), which is the “bronze disease”.

Bronze disease is an autocatalytic process in which Cu reacts with environmental oxygen, water and chloride ions [31,48–51]. The first step sees the formation of nantokite (CuCl) at the interface between metallic bulk and environment (or *patina*). Nantokite does then trigger the autocatalytic dissolution of bulk Cu, following the path of further degradation to tri-hydroxychlorides (such as atacamite, $\text{Cu}_2(\text{OH})_3\text{Cl}$, and its polymorphs) (1) [48], producing HCl as by-product which in turn attacks the metallic Cu to form more CuCl (Figure 18):

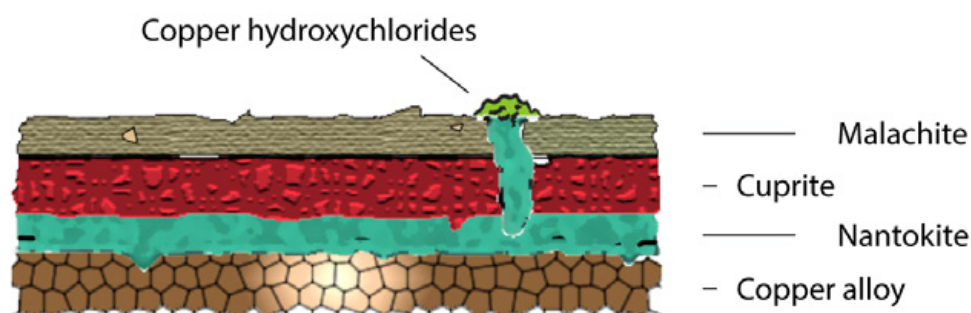
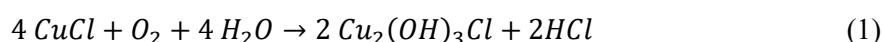


Figure 18 Schematic representation of bronze disease.

When still in burial conditions, the growth of bronze disease can be limited by anoxic conditions. For such reason, most effects of this process do manifest after excavation, when the artifact is exposed to a higher amount of oxygen [52]. Visually, bronze disease results in powdery and de-coherent light-green by-products and in the cracking of the surface due to large volume change following chemical reactions.

Bronze disease has been largely studied in literature and it is still attracting much experimental efforts [53–56], being the only one clear and well-defined concern for archaeological copper-based alloys in terms of long-term stability. However, far less attention has been devoted to the investigation of other potential critical factors, such as surface porosity and their concerns for long-term conservation, as well as to diagnostic methods to evaluate and monitor these factors on a routine-basis. Moreover, treatments for the generic protection of metal artifacts are still based on the same dichotomy (coating-BTA) by decades now, approach that has proven many limitations (see par. I.4.1). This scenario calls for more research on corrosion mechanisms and products, on fast and reliable diagnostic methodologies, and on new strategies for long-term conservation. All these topics are central in this thesis.

I.2 From excavation to cleaned coins: Standard workflow for coin identification

Ancient coins are a primary source for understanding the human past, as they provide invaluable information about the economy, politics, and society of the time [57–59]. To be used as a source of documentation, coins must be correctly identified from a numismatic perspective. This involves analysing various aspects of the coin, such as its size, weight, shape, inscriptions, symbols, and images, in order to determine its origin, date of production, and the historical context in which it was produced and used. Without proper numismatic identification, the historical significance of a coin may be lost or misinterpreted, making it less useful as a means of acquiring relevant knowledge.

Coins that are discovered in direct contact with soil are often in a compromised state of conservation [60,61]. Long-lasting exposure to burial conditions can cause them to deteriorate due to the interactions with the surrounding environment. This can lead to the development of thick *patinas* and pronounced soil deposits on their surfaces, making their identification challenging [62,63].

After being discovered, coins may undergo one or more treatments to recover numismatic information, each with potential consequences. Coins are usually subjected to an initial superficial cleaning just after their recovery, to remove soil materials and allow for a quick screening [64]. However, this preliminary physical cleaning process may fail to retrieve residual surface details, leaving significant information hidden. In some cases, it may even lead to an irreversible loss of important details [65–68], or cause additional degradation of the bulk metal. For instance, this can happen to copper coins due to the occurrence of bronze disease, which can be triggered by the direct exposure to environmental oxygen of copper chlorides that may be concealed inside or beneath corrosion *patina* and encrustations [48,51]. Less frequently, coins undergo micro-excavation and cleaning operations in laboratory settings by hand of conservators [69]. However, this approach is time-consuming and not practical for large numbers of copper coins [69–72], to the extent that often only coins intended for display in museum exhibits are cleaned and restored, while the rest remain stored away in their state of recovery or only partially cleaned, unable to reveal the information they hold [73].

This scenario calls for a time-efficient, non-invasive method for coin identification that can protect against the loss of valuable information during physical cleaning and facilitate the examination of coins on a comprehensive scale.

I.2.1 Remote identification by X-ray Computed μ Tomography

X-ray Computed Microtomography (μ XCT) is a powerful technique, that exploits X-ray capabilities to penetrate in most materials. Basically, a sample is placed between an X-ray source and a detector. A radiography (i.e. an “X-ray photograph”) of the object is taken, then sample rotates of a small angle and again another radiography is recorded. The sample is scanned this way step by step through a certain solid angle (usually, 360°), collecting a number of radiography at variable angle. All these data are then processed through a mathematical algorithm, which is capable to reconstruct from them a 3D volume of the object (Figure 19).

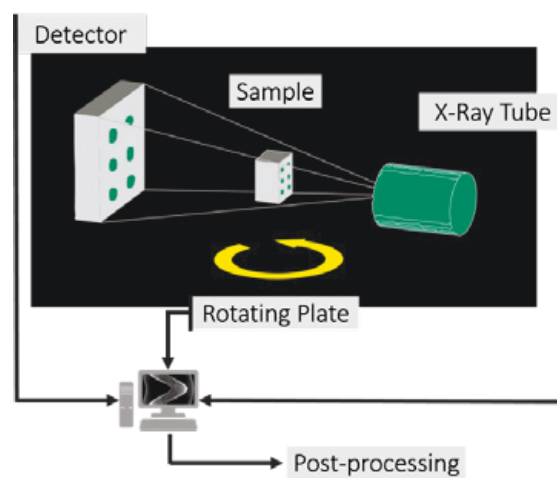


Figure 19 Scheme of an XCT setup.

Several studies have been conducted to test remote recognition methods for coins using X-ray Computed Microtomography (μ XCT) [62,63,74–80]. This technique is widely acknowledged for its powerful capability in revealing hidden features, its mature technology, widespread deployment in many fields (such as medicine and engineering), and non-invasive nature, making it a valuable tool in various fields of research. In particular, μ XCT has been utilised to support the identification of uncleaned silver [74–78] and, to a minor extent, copper coins [62,63,79,80]. For instance, Miles et al. have used μ XCT to virtually open a pot containing a block of silver Roman coins and further identify those coins [77]. This was well expected for thin silver coins, which experience far less issues of surface disruption from corrosion. Bude and Bigelow, instead, showed how nanoXCT could retrieve information on the original surface morphology of two heavily corroded copper-based coins [80].

However, there is currently a lack of direct comparison between μ XCT and traditional cleaning methods for coin identification, which introduces uncertainty regarding the degree of equivalence or difference

in the outcomes of these two types of approaches. A comprehensive comparison needs to be conducted to evaluate the specific reduction in identification times compared to cleaning practises. Additionally, μ XCT has mainly been applied to individual objects and has not been tested on a large scale, making it unclear whether the method is suitable across the broad spectrum of Roman copper coinage, due to large variety in size and elemental composition between different type of copper coins.

I.3 From cleaned coins to laboratory: Analytical techniques for Archaeometry and Diagnostics

I.3.1 The persisting need for an invasive approach

From the previous paragraphs, it is evident that a metallic artifact can store precious information both in the original components and in the corrosion *patina*, from an archaeometric and diagnostic point of view. Regrettably, the complete and detailed extraction of such information is still today achieved by invasive means, i.e. by sacrificing parts of the objects in a visually impactful manner. For small items like coins, cutting out even a small piece determines an irremediable damage to its integrity as archaeological artifact (Figure 20).



Figure 20 How sampling can visually impact on coins [81,82]. Both coins in figure have been cut in order to allow the investigation of their bulk and of their corrosion layers, at a high cost in terms of aesthetic impact on the sample. The black arrow points toward the cut side. Image on the left is reprinted from [82], with permission from Elsevier.

The capability of non- and micro-invasive approaches to replace invasive methods is under debate in the metallic heritage literature. Already Cope [21], Ponting [44,83] and Metcalf [18], in their milestone works on ancient coinage, have reiterated this aspect. However, the situation has evolved little in the last decades, and even the most recent published works in this field make extensive use of invasive sampling for their investigations on corrosion and bulk features [13,14,23,30,36,42,60,81,82,84]. De

facto, the current golden standards are still cross-sectioning (i.e. cutting out a sample from the artifact, by coring (Figure 21) or direct cutting (Figure 20)), and core-drilling, preferred when just bulk powder is requested for composition studies.



Figure 21 (left) Core cutter [26] and (right) core drilling [14].

The reasons for this lies in the thick and complex alteration layers that characterise archaeological metals, as described in par. I.1.3, but also in the kind of interaction that metals have with optical and particle probes.

It must be noted that metals are strongly opaque to both optical and X-ray radiations, and this reduce their interaction volume inside metallic artifacts (i.e. their penetration depth). Moreover, even the bulk alloy itself see the presence of strong segregation effects, as highlighted in par. I.1.2. All these factors strongly limit the representativeness of the volume probed.

Standard non-invasive methodologies are mostly based on surface techniques. This means that they analyse only a small volume of the whole sample, which is located on or near its surface. Due to the intense corrosion copper alloys are subjected to, such a measurement would be strongly distorted, either if you are looking for bulk or corrosion information. This happens even if the technique does probe millimetres down from the surface, because the altered layer will still represents a significant portion of the total volume analysed.

In addition to that, spatially resolved data are needed to extract most of the useful information contained in metallic alloys (e.g. to study their microstructure). Only certain neutron-based techniques do allow non-invasive 3D chemical imaging inside metals, but they have other drawbacks (see par. I.3.2).

For such reasons, attaining a detailed, depth- and spatially resolved analysis of archaeological metallic samples without relying on invasive methods is considered a much-anticipated achievement, but also an utterly challenging task [18,21,44,83].

To carry out this task, many attempts have been reported in literature [85,86] (Table 1). The next paragraph briefly reviews non- and micro-invasive techniques that have been applied to this end, highlighting their achievements and failures, before moving to a detailed literature review on the techniques specifically investigated in the present thesis.

Invasivity	Probe type	Technique	Information	Information level	Depth of information
None	Optical	RIS/FTIR/Raman spectroscopies	Chemical	Corrosion layer	nm to μm
		THz-TD	Chemical and Structural	Corrosion layer	tens of μm
		OCT	Structural	Corrosion layer	nm to μm
		XCT	Structural	Corrosion layer & Bulk	μm to mm
		XRF	Elemental	Corrosion layer & Bulk (mixed)	hundreds of μm
		XRD	Chemical	Corrosion layer & Bulk (mixed)	tens of μm
		GRT	Elemental	Corrosion layer & Bulk (mixed)	mm
		XPS/SPEM	Chemical and Elemental	Corrosion layer	nm
None*	Particle	SEM-EDS (surface)	Morphological and Elemental	Corrosion layer	nm to μm
		PIXE/PIGE/RBS	Elemental	Corrosion layer & Bulk (mixed)	μm
		PGAA/NAA/NRCA	Elemental	Corrosion layer & Bulk (mixed)	mm
		TOF-ND	Chemical and Structural	Corrosion layer & Bulk	mm
None	Electrochemical	μXES	Elemental	Corrosion layer & Bulk	mm
		EIS	Corrosion activity	Whole sample	-
Minimal	Optical	LIBS	Elemental	Corrosion layer & Bulk	hundreds of μm
		LA-ICP-MS	Elemental	Corrosion layer & Bulk	hundreds of μm
	Particle	SIMS	Elemental	Corrosion layer	< μm
		FIB-SEM-EDS	Morphological, Structural and Elemental	Corrosion layer (potential for Bulk)	Up to 150 μm
	Electrochemical	VIMP	Elemental	Corrosion layer	Sampling-dependent

Table 1 Non- and micro-invasive techniques applied to the investigation of archaeological copper-based metals. The techniques investigated in this thesis are marked in red. The depth of information is an estimation for a typical archaeological copper-based sample. *Neutron-based analyses can make copper-based samples radioactive for some time.

I.3.2 Brief overview of non- and micro-invasive techniques and their limitations

Most classical non-invasive techniques with proven application on archaeological metals are based on optical probes. Among these, one can distinguish between a low/mid-energy radiation-based group, and another group based on high-energy radiation.

To the first group belongs those technique that is based on infrared (IR), near-infrared (NIR), visible (VIS) and ultraviolet (UV) light. Most notably, we are talking about Fourier-Transformed Infrared Spectroscopy (FTIR) and Raman Spectroscopy, which are extremely informative, being able to detect the presence organic and inorganic compounds, and of specific crystalline species [87,88]. In this group also falls Reflectance Imaging Spectroscopy (RIS), whose definition includes all kinds of VIS-NIR multi- and hyper-spectral techniques, and colorimetry [89]. RIS can be partially informative, especially because most of the Cu corrosion products present strong colours. Optical Coherence Tomography (OCT) shares with the previous techniques the same operative frequency range, but represent a completely different technology, being able to reconstruct from the reflected beam information the 3D mechanical structure below the surface of the sample [90].

What all the above-mentioned techniques have in common also represent their common limitation, i.e. the use of low-mid frequency light as probe. Depth of penetration of UV-to-IR light is very limited, even in partially opaque materials. Metals do represent one of the most opaque materials for this kind of light, with a penetration depth in the order of nm. Consequently, the sampling depth of such techniques is unsuitable for a satisfactory analysis of archaeological metals, without resorting to sampling. Terahertz spectroscopy, for instance, can be compared to FTIR and Raman as functioning, but it makes use of longer wavelengths than IR, showing thus a larger probing depth. However, its development is still at early stage specially on metals [91].

Techniques that exploit higher-energy radiation are usually based on X-rays, and less commonly on γ -rays. Among X-ray techniques, X-ray Fluorescence (XRF) is by far the most applied for metals characterisation, thanks to its ability to detect and quantify multiple elements, even if present in small amounts [92]. Another plus of XRF is the large availability of easy-to-use, portable and relatively cheap instrumentations, which allows its wide diffusion in most conservation laboratories. The main downsides of XRF: the single spot-nature of the measurement, meaning that only a small, finite portion of the sample will be probed each time (with all concerns regarding bulk segregation discusses in the previous section); the depth probe of the X-ray beam, which is not only limited, but also variable as a function of the element probed and of the matrix in which it is immersed (i.e. the alloy or corrosion

phase). Consequently, even though qualitative analyses are commonly performed and relatively informative, it is difficult to extract detailed quantitative information from an XRF analysis that take into account all the distortions introduced by the presence of a heterogeneous corrosion layer. In other words, with XRF you can hardly decouple the information coming from the bulk alloy from the one coming from the corrosion layer.

XRF can be applied in several ways to partially mitigate the above drawbacks. For instance, using polycapillary optics to reduce the spot size (μ XRF) adds 2D-spatial resolution to the output data, which can be helpful in the investigation of the outer shell of the sample [93]. In order to extract depth-resolved information from an XRF dataset, Monte-Carlo simulations can be used (MC-XRF) [94], even though modelling and fitting data from complex samples is everything but straightforward. In general, only relatively small improvements in data extraction can be obtained by such methods.

X-ray Diffraction (XRD) can help in detecting specific corrosion products and, less commonly, bulk alloy phases, thanks to its capability to identify crystalline phases [95]. The usual co-existence of a large number of different corrosion compounds, with variable crystalline size, and other un-idealities like rough surfaces and presence of amorphous compounds, make XRD data from archaeological metals extremely challenging to interpret [95]. Moreover, XRD suffers from similar drawbacks as XRF, with a limited probing depth [96] and even without the affordability and easy to use of related instrumentation. Even if attempts of coupling XRD and XRF to maximise the output information have been made [97], the complexity of archaeological metals seems to hinder such possibility.

Gamma Ray Transmission (GRT) have also been applied to ancient metals [98]. It exploits high-energy high-penetrating γ -rays to collect elemental information from a volume of analysis that goes through the entire sample, with a diameter of 6 mm. Even if promising, the results were far from enthusiastic in terms of accuracy and precision [98], and the experiment represented an isolated case without further developments.

Apart from light-based ones, there is another category of instruments that has been applied for the non-invasive investigation of metallic heritage, which are the particle-beam techniques.

The most common example of particle-beam technique is the Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS). SEM exploits the interaction of an electron beam with the sample surface to investigate its morphology. EDS is a spectroscopy usually found in combination with SEM. EDS exploits the characteristic X-ray light emitted by a sample during SEM irradiation. As a microscopy and elemental imaging technique, SEM-EDS grants excellent spatial

resolution. However, its probing depth is limited at the μm level, making it a strictly surface technique [99].

There are specific particle-beam techniques that require large-scale facilities, like accelerators, synchrotrons, or spallation sources, but also grant superior performances in terms of sensitivity, data resolution and depth of investigation. Among these, Particle Induced X-ray Emission (PIXE), Particle Induced γ -ray Emission (PIGE) and Rutherford Backscattering (RBS) share the same probe, i.e. an ion beam accelerated on a linear particle accelerator. All of them have been applied for the investigation of bulk composition of ancient metal objects [100,101], achieving good results, even if relative error in the measurements is quite high, due both to the technique and the heterogeneities in the samples. Moreover, to achieve better results, high-energy sources (e.g. HE-PIXE) [102–104] are required, in order to have most of the sampling volume inside the bulk of the alloy. At the same time, they give little information on corrosion, nor spatial or depth resolution, still requiring quite advanced instrumentation such as a linear particle accelerator.

Neutron-based techniques look very promising in terms of information output. In fact, metals are quite transparent to neutrons [105]. Prompt-gamma Activation Analysis (PGAA), Neutron Activation Analysis (NAA) and Neutron Resonance Capture Analysis (NRCA) all exploit different kinds of interaction between a neutron source with the sample to investigate bulk composition [106,107]. Nevertheless, it is with Time of Flight – Neutron Diffraction (TOF-ND) that neutrons reach their highest potential [108]. Using TOF-ND it is possible to achieve volumetric XRD-like information. This allows also for 3D texture and corrosion analysis, all of which in a completely non-invasive manner [109–112]. The most impactful drawback of neutrons is that they tend to activate copper-based samples, making them radioactive for some time (weeks or even months). This, together with the limited amount of spallation sources available across the world, and the long acquisition time needed for this kind of acquisition, strongly limit a wide application of TOF-ND.

Finally, the last few years have seen interesting applications of Muon X-ray Emission Spectroscopy (μ -XES, where “ μ ” stands for “muon” and not for “micro”) to ancient metals [113–116]. A Negative muon can be seen as a heavier electron particle (x206 the mass of an electron). When interacting with an atom, it can implants in an excited atomic orbital to relax soon after to a 1s orbital. This relaxation generate an X-ray, which is characteristic of the atom, similarly to XRF. Characteristic X-rays generated by muons are, however, much more energetic (and thus more penetrating) than the XRF ones, because of the higher binding energy that the heavier muon have towards atomic nuclei, compared to electrons. This enables μ -XES to achieve far higher penetration depths compared to XRF. In fact, the limited probing depth of XRF is due to the inability of fluorescence X-rays to exit from far inside a sample, rather than to the penetration of the primary X-ray beam. Thus, using negative muons, the above limit

can be partially overcome. By tuning muons' momentum, the probing depth can be adjusted in order to perform depth-profiling-like experiments. However, it must be noted that the limit of detection is far higher than XRF. μ -XES also shares with neutron-based techniques the need for a very peculiar and uncommon source to operate, while not showing the same issues on sample activation side. Furthermore, only a handful of experiments have been reported in literature so far, so there are still many uncertainties on the actual contribute it can give to the archaeometry and diagnostics of ancient metals.

Given the complexity of conducting a fully non-invasive characterisation of archaeological copper-based samples, other techniques that only requires minimal invasivity or sampling have been tested or developed, in order to avoid the need for cross-sectioning.

One example is the Secondary Ion Mass Spectrometry (SIMS). SIMS is a micro-invasive technique based on the analysis of ions generated by an ion sputtering from the surface of the sample. SIMS can grant highly depth-resolved information on surface elemental composition [117], however the usual sputtering rates achieved (nm/h) do not match with the scale at which useful information are usually attained in ancient metal systems (from μm to mm).

Similarly to SIMS, Laser Induced Breakdown Spectroscopy (LIBS) exploit an ablation process (by a laser) to micro-sample the artifact and retrieve elemental information. In respect to XRF, LIBS is micro-invasive but grants direct depth-resolved data. However, the probing depth is still limited by the difficulty of lasers in ablating deep drills, and suffer from many data artifacts [118,119].

Landing to the electrochemistry world, Voltammetry of Immobilised Particles (VIMP) has proven capability for different application in the recent past [120,121]. It uses small amounts of powdered sample to discriminate and quantify both elements and their state of oxidation, based on their voltammetric pattern. Even though interesting for corrosion studies, its scope is quite limited to a handful of elements, whose voltammetric behaviour is well known [120,121]. Moreover, it has been only applied with rudimental sampling methodologies, which did not allow to achieve a good depth-resolution by subsequent sampling, and a more rigorous standard of micro-invasivity.

As clearly emerges from this brief review, the analysis of ancient alloys is such a challenging task to have pushed the application of the most advanced technologies, such as neutron- and muon-based ones, towards the Heritage Science field. However, a method to extract all the desired archaeometric and diagnostic information from within an ancient metal, without physically cross-sectioning, is something that has not been achieved yet, even in a micro-invasive way. Only small pieces of information can be reconstructed by combining multiple analytical techniques into one single methodology, such as bulk

elemental composition. Conversely, still today little can be achieved in terms of depth- and space-resolved information on corrosion composition and bulk alloy structure, without recurring to invasive sampling. The present work tries to overcome this limitation by investigating the potential application and by defining efficient protocols for some advanced techniques scarcely applied to archaeological copper-based object, such as FIB-SEM, LA-ICP-MS and SPEM. The following paragraphs critically analyse such techniques, their past and potential applications to heritage metals.

I.3.3 Focused Ion Beam coupled with Scanning Electron Microscopy

Focused Ion Beam (FIB) is a technique employed to remove materials from a substrate for nanofabrication or sample preparation purposes [122]. Its working principle lays in the use of an ion beam (usually, Ga^+) to mill small digs on the surface of the sample. A flux of Ga^+ ions is accelerated from an ion gun towards the sample, which is placed in a high vacuum chamber (Figure 22). The interaction between Ga^+ ions and the surface determines an extremely fine ablation process with a precision of the order of nm [122,123].

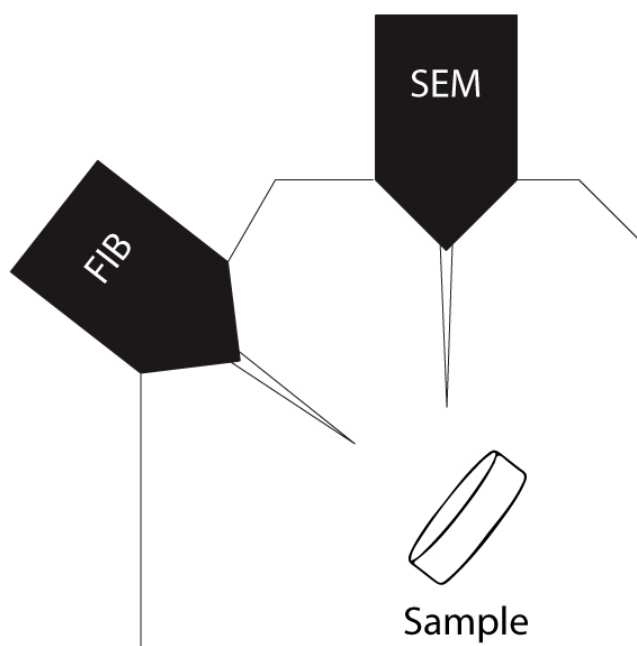


Figure 22 Simplified scheme of a FIB setup.

FIB is commonly adopted in microelectronic laboratories as a nanofabrication tool [124,125]. Another common application, which is the one of interest in the case of the present thesis, is micro-invasive cross-sectioning [126]. In this modality, milled digs have the shape of a trench, with a well-defined wall

perfectly perpendicular to the sample surface, and a ‘ramp’, which visually opens the way for an SEM column to analyse what is present on the surface of the wall. In practice, the trench wall is a micro-invasive cross-section of the subsurface structure of the sample. A third common application of FIB is the preparation of thin lamellas for TEM analysis, obtained by milling a double ramp in opposite direction and leaving just a thin wall in between [125,127].

Even if primarily belonging to the field of photonics and electronics, FIB trenching has seen some very recent applications in the field of Cultural Heritage as sample preparation technique for subsequent in-situ analyses. For instance, Doménech-Carbó et al. have used FIB-milled cross-sections to investigate the corrosion of tin-glazed ceramics [128]. Coming to metals, Manukyan et al. have extensively applied FIB trenching to a collection of silver *denarii*, to investigate the role of surface manipulation and silver enrichment [129]. Again, Doménech-Carbó and her collaborators have applied FIB trenching to a variety of coins, from Roman [130] and Polish *denarii* [131], to a series of copper and bronze coins from various periods [42,132–136].

Being able to see what is behind the surface of an artifact is an extremely seducing perspective. However, the standard approach to FIB trenching followed by the cited works has a strong limitation, namely, the low depth of trenching achieved, which is up to few tens of μm . In fact, no cases are reported in Cultural Heritage literature of FIB trenches that go beyond this threshold.

Such operative parameters have been inherited from the microelectronic applications, where one is interested in nano-to-micro sized features. They are also ideal for the production of lamellas, which have to be thin and small but extremely well defined, in order to be properly analysed under a TEM. However, they are only partially appropriate for analytical scale required by archaeological copper-based items.

As underlined in par I.1.3, copper-based alloys feature very thick *patinas*, whose investigation cannot be just limited to few μm . Moreover, this would not allow to attain information from the direct observation of the bulk. In addition, the limited lateral aperture commonly adopted is comparable to the scale of common grain size in ancient copper-based alloys (20 μm [13]), thus such standard approach would even miss to observe bulk-like features preserved in the corrosion layer due to pseudomorphic substitution, whenever reached by the depth of the trench. In this regard, it must be noted that FIB can also adopt different beams than Ga^+ . Most notably, the Xe-plasma gun (Plasma-FIB) can be a valuable alternative, since it allows to create big trenches much faster than Ga-FIB. Regrettably, Plasma-FIB is a quite recent technological breakthrough. It has being commercialised only about 10 years ago and its spread, even in specialised labs, is still limited. For comparison, Ga-FIB is been invented in 1974 [137] and still struggles to find active applications in Heritage Science. For such reason, Plasma-FIB

applications to Cultural Heritage objects is anticipated, but still far from being a viable option in the near future.

A FIB can also operate in a modality called FIB-Tomography [138–140]. In this case, after the milling of a trench, a set of data is recorded from the cleaned wall (commonly, a SEM image or an EDS map). Then, another thin layer of material is milled from the wall of the trench, and data is recorded again. This process is performed multiple times, and then all data recorded are fused in a single dataset. The output is a 3D reconstructed volume, somewhat remembering the one made using XCT. The possibility to micro-invasively mill a volume of material and reconstruct its feature in a 3D dataset represents an extraordinary outlook for the study of complex features such as corrosion and metallic microstructure. Still, such a strategy requires, as a prerequisite, the digging of bigger trenches than what is currently available in the literature.

From the above considerations, it appears that establishing a procedure for the reliable preparation of deep and large FIB-milled trenches would represent a significant step forward for the micro-invasive investigation of ancient metals.

I.3.4 Laser Ablation - Inductively Coupled Plasma – Mass Spectrometry

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is becoming a versatile and mature analytical technique for quantitative determination of major, minor, and trace elements in solid samples [141]. In particular, for cultural heritage samples, LA-ICP-MS is a well-established method to generate bulk chemical data, able to provide information on provenience of raw materials used for manufacturing process, which vary widely according to historical period and/or geographical area [142–144].

LA-ICP-MS analysis is based on the direct micro-sampling of a solid sample with the generation of an aerosol, which is then transported, vaporized, atomized, and ionized within the ICP for the quantification of elements via mass spectrometry. The instrument configuration generally employed involves the ablation of sample placed in the ablated chamber using a pulsed laser (wavelength typically 193, 213, 266, 532, and 1064 nm) focused on the surface of sample. A flow of argon and helium transports the ablated material, in the form of particles, out to the cell to the plasma torch, where the material is decomposed and ionized. The generated ions are then separated and quantified in a mass analyser (quadrupole, sector field, or time of light). LA-ICP-MS is considered a micro-destructive

technique, requiring minimal or no sample preparation, while providing higher sensitivity/lower detection limits (in the ng/g range) [141].

Two different ablation modes can be used for quantitative analysis: spot drilling and line scanning. In the first case, the sample is still, and a crater is formed on the surface by a continuous laser. This mode of operation can be used to obtain depth profiles of elements concentration within a sample. In the second approach, the sample is moved at a constant speed while shooting. Both modes can potentially be applied in a raster-scan framework to generate 2D elemental maps, and in multiple per-point ablations to obtain 3D maps (Figure 23).

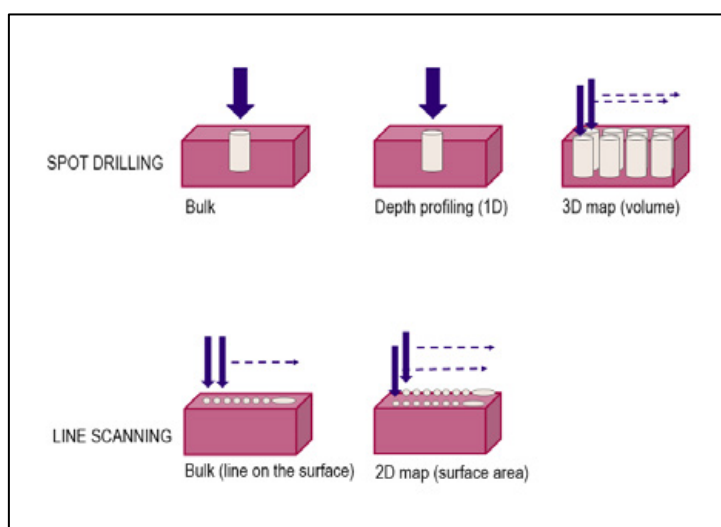


Figure 23 Laser ablation modes of operations: (top) spot drilling and (bottom) line scanning.

To achieve optimal LA-ICP-MS analysis, several factors need to be considered. The type of laser, ablation cells, and transfer line significantly influence the performance of the system. In addition, for optimizing ICP-MS parameters for maximum analyte sensitivity and minimal mass interference, parameters like power density, beam spot size, tracking speed, ablation line length and magnification should be tested before application, as laser operating conditions strongly impact results [145].

In the study of archaeological metals, LA-ICP-MS can represent an enabling technique thanks to its ability to monitor trace elements, its high spatial resolution and its limited invasiveness, even though the actual depth of penetration in function of the spot size used has still to be ascertained on archaeological metals. In recent years, LA-ICP-MS has been effectively used to investigate trace elements in ancient gold. Pd, Pt, and Rh enabled the discrimination between Russian and Ottoman gold coins [146]. Sn, Sb, and Pt, instead, facilitated the definition of three geographical macro-clusters for South American gold mines [147]. Dussubieux and Van Zelst [148] demonstrated the reliability of this

technique in determining Au concentrations, proposing a procedure using internal and external standards. The method's accuracy was validated by comparing it with other techniques like X-ray fluorescence and Proton Activation Analysis (PAA).

For what concerns silver objects, and specifically coins, it has to be acknowledged the existence of the ongoing EU-funded Advanced-ERC project “RACOM” [149], which aims, among others, to understand the problems caused by macro- and micro- heterogeneity in the LA-ICP-MS analysis of silver coinage, highlighting the current high scientific and social interest for LA-ICP-MS applications to Cultural Heritage.

A relatively small number of researches involved copper-based alloys, and all focused on the investigation of the original bulk alloy. For instance, Dussubieux et al. [150], demonstrated how it is possible with LA-ICP-MS to distinguish American native from European smelted brass artefacts. Basset et al. [151] followed the same protocol to further expand the investigation to copper trade networks between North America and Europe. Quantitative outcomes were achieved in literature by comparing sample signal intensities of the investigated samples with those of the same elements in standard reference materials. In this approach, adapted from Gratuze [152], copper was used as the internal standard. Additionally, Peterson et al. [153] studied late prehistoric metalwork, demonstrating the benefits of LA-ICP-MS for the analysis of variance in alloy composition for a large assemblage of copper-based artifacts.

A different approach was considered by Sarah et al. [154]. They applied a resolved analysis acquisition mode for depth profiling in ancient silver coins, using a silver–copper alloy as the reference material. Depth profile analysis has proven to be an efficient approach for removing the silver surface enrichment layer and characterizing the underlying unaffected alloy, without causing visible damage. As last, in-depth analyses using LA–ICP–MS successfully revealed details about the plating method in late Roman coins and identified Hg associated with the plating layers [155].

It must be noted that the major limitation of the above reported literature examples is that in no cases LA-ICP-MS has been applied to the investigation of *patina* layers or corrosion phenomena. When speaking about corrosion, it must be taken into account that monitoring the concentration of certain ions (such as Cl, F, C, S, and O) is not feasible due to their presence in the non-inert atmosphere of the ablation chamber. This limitation could affect the quantification of chemical compositions in ancient materials, particularly those with surface corrosion products (organic and inorganic salts, carbonates, sulphates, etc.).

Moreover, the calibration strategy is an issue to be addressed, as solid calibration standards with compositions that closely match with those of the examined materials are seldom available, even less so if the focus is the corrosion layers rather than the bulk metal. This is due to the fact that the composition of a calibration standard has to be as known and uniform as possible, two attributes that is hard to achieve from naturally or artificially corroded samples.

Finally, the investigation of metal alloys is challenging due to their bulk heterogeneity. Copper-based artifacts, in fact, have complex microstructures made of distinct phases, which may strongly vary according to their elemental composition as well as their production process [27]. Therefore, the results of LA-ICP-MS analysis on a portion of an artifact, which is typically only micrometers in size, must be approached with caution. This factor is even more severe for corroded metals, in which there is a strong heterogeneity not only within the bulk material but also within the corrosion layers, both in-depth and in-plane.

Moving the LA-ICP-MS from a 0D-point to a multidimensional technique may be the key to address the latter issue. In particular, the 1D-depth profiling approach could be a way to overcome the heterogeneity issue along the depth axis and achieve useful information on the corrosion layers. 2D and 3D mapping, instead, may give the most complete output about the composition but also the localisation of different corrosion phases in a limited area/volume of the sample. However, to our knowledge, all these approaches are currently unexplored.

I.3.5 X-ray Photoelectron Spectroscopy and SPEM

X-ray Photoelectron Spectroscopy (XPS) is the leading technique to evaluate the speciation at the atomic level, and the chemical environment of an atom [156]. In an XPS analysis, a sample is placed in a high vacuum chamber and irradiated with a monochromatic X-ray source (Figure 24). By photoelectric effect, electrons are emitted from the first atomic layers of the sample (Å to nm). The XPS detector then counts such electrons together with their kinetic energy. This kinetic energy, in fact, is directly linked to the binding energy the electron had in its atom of origin, which in turns is not only characteristic of a specific element, but of an atom in specific conditions such as oxidation state, chemical environment, and so on.

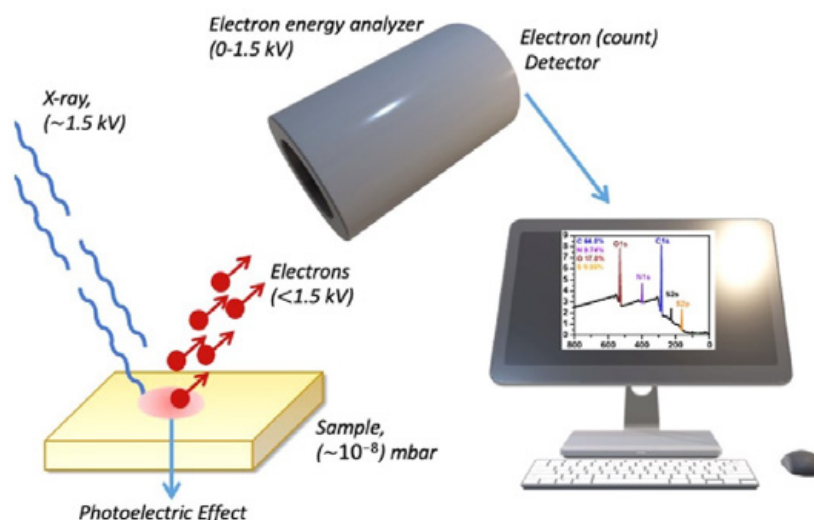


Figure 24 Scheme of an XPS analysis. Reprinted from [157], with permission from Elsevier.

XPS analysis is often coupled with a charge neutraliser, which irradiates the sample with slow electrons during the acquisition [158]. Its use is meant to avoid the accumulation of surface charging on insulating samples, because it would cause photoelectric electrons to deviate and slow down, altering their kinetic energy.

XPS has been applied in the past to the study of archaeological metal-based artifacts [159], offering crucial evidence and valuable insights into the elemental composition of the external corroded layers present on such objects [47,160,161], but also on the manufacturing technology [162], leading to recommendations for restoration and preservation. XPS has been also applied to monitor the development of corrosion products over time during artificial aging. Thanks to its superior sensitivity to surface phenomena, it excels in detecting and identifying alteration compounds as they form on the sample, supporting the understanding of the fundamental mechanisms behind corrosion [163]. XPS is also suitable for the combined and complementary use with other techniques, such as SEM-EDS [160] or Laser Ablation - Mass Quadrupole Spectrometry (LAMQS) [162].

Despite its low probing depth (nm), its diagnostic potential towards corrosion products makes XPS of high interest for application on copper-based archaeological items. However, the standard spot size boasted by traditional XPS lab-based equipment, which is of hundreds of μm up to mm, limits its applicability, because corrosion products on the outermost part of *patinas* can be very heterogeneous on a smaller scale. Having in a single spot of analysis many different compounds made by the same elements can cause severe difficulties in reading an XPS spectrum, due to the overlapping of many low signals that cannot be deconvoluted properly.

To overcome this limitation, XPS has been coupled with a microscopy setup (μ XPS) in order to achieve spot size down to the nm. Instruments boasting such coupling are also able to generate maps, usually by scanning the sample surface [164]. For this reason, the technique is generally called Scanning Photoelectron Microscopy (SPEM) (Figure 25).

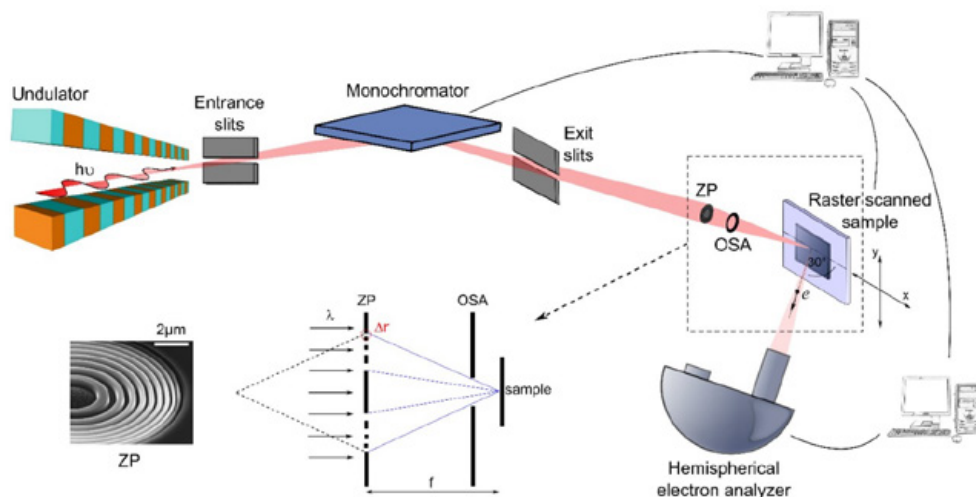


Figure 25 A schematic representation of SPEM setup at the ESCA microscopy beamline at ELETTRA Synchrotrone Trieste.

The operative conditions of SPEM focusing setup, based on Zone Plate diffractive optics, requires the use of a high-brilliance partially coherent primary X-ray beam [165], which is only available at synchrotron facilities. This clearly limits its adoption on a large scale, but what it is capable to achieve is rather unique in the spectrum of analytical techniques.

As far as it is known to the author, SPEM has been applied to ancient metals in just one case [74]. In this article, the authors performed SPEM on a fragment of a late Bronze Age metallic artifact, and specifically on an area at the interface between a slightly corroded region and a strongly corroded one. By doing so, have acquired insights into the multi-scale corrosion phenomena of Cu and Sn that occur in the framework of bronze disease.

Thanks to its microscopic and mapping capabilities added to XPS performance, SPEM may fill an interesting spot in the investigation of surface corrosion of archaeological copper-based alloys and other ancient metals. As XPS, it is non-invasive and have a depth of penetration in the order for the nm. Moreover, its use can be combined with other sample preparation methods, such as laser ablation, to achieve depth information in a micro-invasive way. However, the actual potentialities and limitations of the SPEM application to ancient metals have yet to be assessed, due to missing literature. Further experiments on that are thus required.

I.4 Conservation of archaeological copper-based alloys

One of the key missions of Heritage Science is preserving the material nature of heritage objects through time. The need for that is granting to future generations the right to access, study and enjoy our common heritage in the same way we are doing. To achieve such prominent goal, conservation scientists have spent much effort in developing treatments to be applied to heritage objects to enhance their long-term preservation. At the same time, procedures for their accurate and reliable testing have been developed. In fact, each heritage object is considered as a *unicum*, and thus cannot be directly used as a testing surface prior to having cumulated sufficient evidences of good behaviour of the treatment on replica substrates.

The present section presents a brief review of the literature on the conservation of ancient metals, providing critical remarks for what concern the conservation of archaeological copper-based items.

I.4.1 Traditional protective treatments and recent trends

After their retrieval, cleaning and study, archaeological copper-based artifacts can undergo a stabilisation treatment, in order to remove or convert chemically unstable phases such as nantokite and related chlorides, and finally are subjected to a conservation treatment [166].

Alteration of archaeological copper-based objects in indoor environment, as well as other metals, is mainly due to electrochemical corrosion processes, which are fed by the interaction between the object and oxygen, moisture, Volatile Organic Compounds (VOCs) and other aggressive contaminants naturally present in air. Consequently, the usual approach to curb corrosion phenomena is to cover the object with a layer of exogenous material, to act as a barrier towards these contaminants. The same approach is frequently adopted at the industrial level, but Cultural Heritage application presents some additional requirements. It is demanded that the treatment does not present aesthetical impact on the artifact. It should be easy to apply and safe for both operators and environment. It should present predictive performance and long-term durability, while being reversible or, at least, re-applicable [167].

It has to be noted that, even in the small realm of anti-corrosion treatments for heritage items, no treatment has been developed specifically for samples coming from an archaeological environment, and destined for conservation in indoor conditions. Most of the time, design and testing is performed on bare metal and outdoor *patinas*, real or artificial ones.

The products applied to the scope by conservators in their daily work have seen little evolutions across last decades. Currently adopted solutions are waxes, acrylic coatings, and the combination of the two, and this independently from the specific alloy, conservation state or conservation environment [168,169]. The use of waxes for the protection of copper-based object, especially outdoor monuments, has been attested already in Renaissance [170]. Their use is widely attested today, in the form of microcrystalline commercial formulations like Cosmoloid and Renaissance wax [167], although their limitations have been clearly assessed. Waxes present limited protective efficiency towards corrosion, while having poor barrier properties and a limited life-span (lower than a year), while at the same time being prone to UV-photodegradation, accumulation of dust and subsequent darkening [171–175].

Acrylic resins are a modern alternative to waxes, thanks to their higher resistance to weathering which grant them a life-expectance of few years [176,177], and together with high transparency, mechanical and adhesion properties. To this class belong the Paraloid™ family (especially Paraloid B-72) and Incralac®, which are the most preferred solutions today [167]. Incralac has been developed by the International Copper Research Association (INCRA) in the sixties, by creating a formulation with the most effective acrylic resin on copper substrates, Paraloid B-44, and the best performing corrosion inhibitor, benzotriazole (BTA), together with other additives. Such a combination effectively grants superior protective performance against corrosion [178]. The highest concern against the use of Incralac, in particular, is of safety nature. BTA is a suspected carcinogenicity agent [179], while many components and additives of the formulation (levelling agents as well as solvents) show a considerable level of eco-toxicity [169].

Another strategy, widely adopted by conservators, is the combined use of waxes and acrylic resins in a bi-layer or even sandwich wax/resin/wax tri-layer [180,181]. The idea behind this strategy is to use wax as sacrificial topcoat against possible damage of the acrylic layer due, for instance, to handling. At the same time, wax can also be used as a primer, in order to enhance reversibility and limit the consequences of the different thermal expansion coefficient between the metal and the resin.

Apart from the actual conservation practice, a number of alternative treatments have been proposed in literature, even though designed and optimised for outdoor *patinas*. They can be classified into three categories, based on their chemical composition: carboxylates, silanes and fluoropolymers.

Carboxylate treatments are based on the interaction between fatty acids with metallic ions to form metal salts. Due to their decreasing water solubility with the organic chain length, long-chain carboxylates have been mostly investigated, with decanoic acid and relates salts as the most common choice [182–186]. High eco-friendliness represents a strong plus of this class of treatments. However, poor protective efficiency and significant aesthetic changes have been observed [187], discouraging application in real

case scenarios. Silane coatings are sol-gel coating prepared using alkoxysilanes. 3-mercaptopropyltrimethoxy-silane (PropS-SH) is the most notable example of silane coating applied to copper substrates [188–196]. Thanks to the thiolate group, PropS-SH proved to strongly bond to metallic substrates and this is complemented by good protective performance in different environments [192,195,197–199], but it is questionable if the same can be achieved on highly corroded archaeological surfaces. This kind of treatment also presents other concerns, such as UV-photodegradation [200–203]. Fluoropolymers, such as polyvinylidene fluoride (PVDF), are well renowned for their inertness, high repellence towards both water and oil, and UV-stability [204,205]. However, due to their extremely poor adhesion properties towards the substrate to protect, fluoropolymers in conservation science have been only investigated in blend with other compounds or with a basecoat, which had the role of enhancing adhesion [204,206]. The strongest observed drawback of these coatings has been a detrimental interaction between the fluoropolymer layer and the basecoats, creating dangerous conservative conditions [207]. Another severe drawback of fluoropolymers is their high environmental impact [208].

It must be noted that, together with the specific treatment applied, also the application method does strongly influence the final protective efficiency. However, such aspect is less investigated, and reviewing the related literature is out of the scope of this thesis.

Most recent trends are giving increasing importance to the ecological aspect, prioritising the research of treatments that are safe for the operator and have small footprint on the environment, both from their use and their production. The most notable example is the biopolymer chitosan, which attracted much interest in past years [209], but without established applications up to now. Other trends see the early stage development of functionalised coatings, containing encapsulated corrosion inhibitors [210–212].

Another point to make is that the concept of “protective treatments” has until today mostly matched with “protective coatings”, in the meaning of covering the object with an external shell made of an exogenous material (commonly polymers), eventually added with a corrosion inhibitor. The reason for that may be found in the requirement for “reversibility” of the treatment [213]. Under the constrain of reversibility, in fact, any direct alteration to the surface of the sample was usually avoided, thus pushing the research in the direction of polymeric coatings. In recent years, reversibility is being gradually dismissed in favour of the more rational “retractability” concept, which opens the way to new approaches to conservation. One of these new approaches may be represented by the conversion of the outermost nanometric-thick layer of the corroded object into a different phase showing higher protective properties (i.e. compact and without porosity, enhanced chemical stability, etc.), but still made of an inorganic mineral-like nature as *patina* compounds. In this way, a longer-term stability may be expected compared to polymeric materials, with positive consequences in terms of cost and time-effectiveness, as well as less adhesion problems and subsequent localised corrosion issues [214–216].

Clearly, chemically acting on the surface of an ancient object is risky by many points of views. First, eventual archaeometric information contained in the converted layers would be lost. Second, the outermost layers of the sample are determinant to its global aesthetics, so that their modification may result in sensible changes to the visual appearance of the object. For all these good reasons, the eventual conversion reaction must be extremely controlled and should not involve harsh conditions (temperature, pH, environment, etc.). This last requirement is the most limiting, because making the inorganic mineral-like *patina* compounds dissolve, react and re-precipitate usually requires harsh conditions. A smart alternative can be exploiting the chelating properties of dicarboxylic acids [217] to initially facilitate the reaction with *patina* compounds (in particular, with Cu^+ and Cu^{2+}), and then form *in-situ* highly stable “organic minerals” with physico-chemical properties close to the pre-existent *patina*. Moreover, short-chain dicarboxylic acids dissolve in water, thus avoiding solvent toxicity-related issues. A dicarboxylic acid that shows such features is, for instance, oxalic acid.

I.4.1.1 Oxalic acid: properties and use in Conservation Science

Oxalic acid, also known as ethanedioic acid, is that represents the simplest dicarboxylic acid. It has a good solubility in water (95.5 g/L), and a relatively strong acid behaviour, with a $\text{p}K_{\text{a}1} = 1.27$ and a $\text{p}K_{\text{a}2} = 4.27$. Given its dicarboxylic nature, in water solution can be present in three different forms as function of the pH (Figure 26).

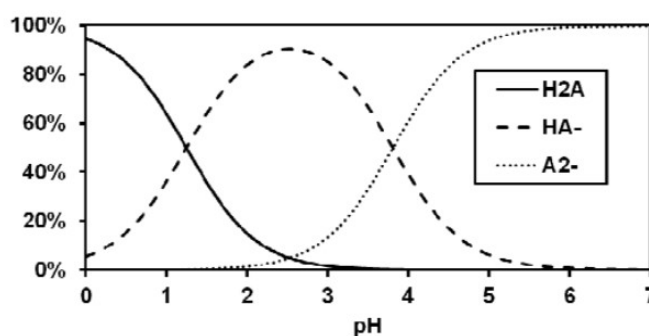


Figure 26 Percentage of the ionized species of oxalic acid with pH. H_2A = oxalic acid, HA^- = partially dissociated, A^{2-} = totally dissociated ([218], © The Electrochemical Society. Reproduced by permission of IOP Publishing Ltd. All rights reserved).

Oxalic acid is a mild chelating agent for metallic ions [217]. With copper, it forms highly stable and insoluble Cu(II) oxalates [219–221], which can appear in nature in the mineral form of Moolooite ($\text{Cu}(\text{C}_2\text{O}_4) \cdot n\text{H}_2\text{O}$, $n < 1$) [222]. Moolooite has been theoretically demonstrated to form from malachite

in presence of oxalic acid (Figure 27) [223]. Cu-oxalates have been also observed to form from Cu powder and CuO [224].

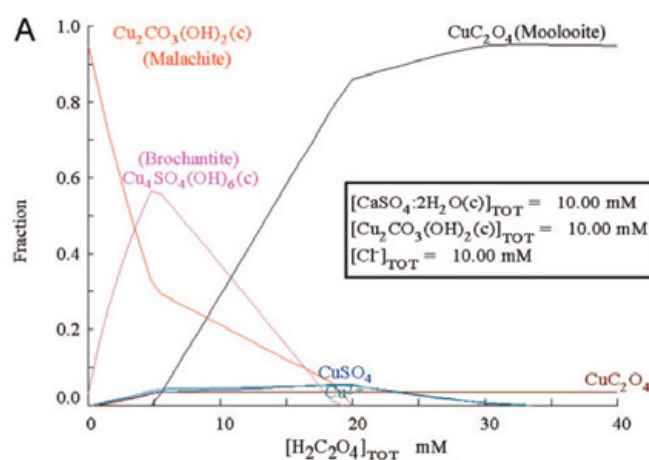


Figure 27 Equilibrium diagram of Cu species in presence of copper hydroxycarbonate, sulphate and of chloride, at increasing concentrations of oxalic acid. Brown line labelled as CuC_2O_4 is a different mineral form of copper oxalate taken into account in this simulation. Reprinted with permission from [223]. Copyright 2008 American Chemical Society.

In the context of Cultural Heritage, oxalic acid and oxalates play manifold different roles, depending on the specific substrate considered. On one hand, on marble and stone the presence of calcium oxalates can be associated with a biological attack and is commonly considered as “time patina”, even though sometimes the biological attack can be more harsh and evolve into a dangerous and undesirable degradation process [221]. Cu-oxalates of biogenic origin has also been reported as degradation product of Cu-based pigments [223].

On the other hand, oxalic acid has been used in restoration since the half of the past century, as a mean for the removal of iron rust [225]. On copper substrates, sodium oxalate has been proficiently tested as stabilisation treatment for bronze disease [55,226,227], and oxalic acid has been already applied to the conservation of outdoor copper heritage, both directly [228,229] and indirectly. In particular, the use of *Beauveria bassiana* as biological agent for the conversion of outdoor copper-alloy patinas into more stable copper oxalates has been investigated [214–216,230–236]. Positive results have been obtained in terms of protective efficiency [233,235] and aesthetic impact [215,233], even showing better stabilisation effects on bronze disease than BTA [233,234]. Furthermore, this treatment demonstrated to be effective in presence of tin-enrichment, forming tin oxalates, even if porosity-related issues have been reported [214]. Finally, mixed Ag-Cu oxalates were also recorded to form on Ag-Cu alloys [232]. The design of this treatment can be considered as a step forward in respect to polymeric coatings. Experiments have first focused on bronze disease neutralisation and on outdoor patinas, investigating the conversion of sulphates and chlorides to oxalates. Recent investigations have involved the

application to archaeological substrates [236–242], evidencing how this kind of treatment has a positive effect on the long-term stability even for this kind of samples, comparable to the action of BTA. However, further investigations are still needed to fully unravel the interaction between the components of archaeological *patinas* and oxalic acid, to enlighten its inhibition effect, and to fully address the slight colour shift caused by the treatment.

I.4.2 Challenges in the testing of novel treatments

The protective treatments currently used by conservators on ancient metals are mostly the same as decades ago. Even though lot of research has been spent in the development of new alternatives (see par. I.4.1), conservators has not grown confidence towards these new solutions and are held back from adopting them in their work.

One reason for this is that most of such research are often scattered studies. For instance, they often miss the long-term evaluation of treatment effects (durability, degradation effects), or they perform test on a small number of non-specific samples, using scarcely reproducible methodologies and producing data not comparable with third studies.

The next two paragraphs revise the latter two topics, namely the preparation of replica substrates and the reliable testing of anti-corrosion performances, with a special focus on applications to copper-based archaeological samples.

I.4.2.1 Reproducing archaeological substrates: a missing piece of literature

The study of the *patina*–copper alloys system within the context of archaeological burial presents significant challenges, as widely discussed in previous paragraphs. Still, being able to replicate this process is pivotal for conservation purposes. In fact, only testing a treatment on a substrate that mimics not only the chemical and mineralogical composition, but also the microstructure and aesthetics of a real archaeological sample, can give reliable information on its protective efficiency and aesthetic impact [243].

Particularly difficult to replicate are the multilayered structure and micro-porosity of the alteration compounds, given that the core part of the corrosion process occurs at the interface between the *patina* and the metal bulk [244]. Some types of corrosion are latent, activated only in specific environmental conditions, including humidity, moisture outdoors, and volatile organic compounds indoors. For archaeological objects, this can happen after their retrieval, during storage. Moreover, the porosity of

the altered layers mediates the interaction between bulk metal and the conservation environment, controlling part of the corrosion process. Thus, the reproduction of mock-ups in which such conditions are represented becomes a crucial step in the development of anticorrosion treatments.

Physical and chemical alterations may also involve the corrosion compounds that make up the *patina*, such as dissolution, leaching, cracking or chemical instability leading to further reactions and by-products. Nonetheless, in the specific case of archaeological copper-based artifacts, alteration compounds such malachite and cuprite are considered as mostly stable in standard indoor environments, excepting the case of bronze disease [32].

An ideal aging procedure for the production of replica mock-ups should present certain characteristics. For instance, it should allow to produce of a significant number of samples in a limited time. This large sample size is essential for statistically testing conservation methods. The process must also be reproducible, ensuring chemical and morphological uniformity among replicas. Numerous works in literature focus on *patina* reproduction, covering various copper-based alloys and using different aging methods [245,246].

Studies involving the reproduction of outdoor conservation conditions are prevalent in literature, given the criticality of developing protective coatings for this type of corrosion and the ease of reproducing it with accelerated outdoor stress, such as acid rain exposure [247–249] or other aqueous solutions [250–252], even adopted for simulating indoor environments [253]. While acid rain simulation and aqueous solutions are effective for outdoor and indoor *patinas*, they prove inadequate for reproducing burial *patinas* due to their more incoherent and pulverulent microstructural morphology and the different chemical composition of the resulting corrosion products.

Faithful reproduction of archaeological corrosion has been attempted by burying samples in specific corrosive environments, even in the same soil as the original objects (Figure 28) [254–257]. Although accurate in morphological and stratigraphic aspects, this method is time-consuming, with controlled burial corrosion experiments spanning several years. In contrast, accelerated corrosion through electrochemical methods offers convenience in terms of timing and reproducibility, making it a viable option for conservation and restoration research after determining suitable operating conditions and the electrochemical cell setup [258–260].

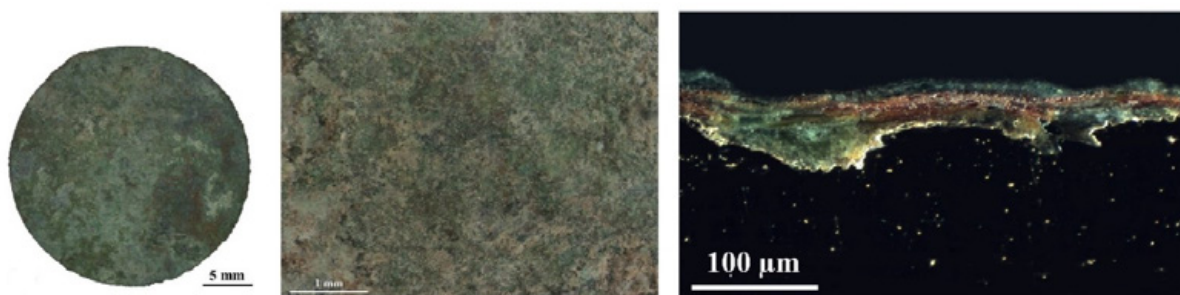


Figure 28 A bronze coin replica, made through 15 years of burial in soil [256].

The primary advantages of employing an electrochemical method to replicate ancient *patinas* extend beyond the expeditious nature of the process, which is determined by the current density over the exposed surface area. Notably, this approach allows for the deliberate selection of stable mineralogical phases at specific applied potentials on the working electrode, i.e., the sample to be aged. The precision in controlling the electrochemical parameters enables the reproduction of complex stratifications found in authentic archaeological *patinas* [261]. Furthermore, the method offers consistency and reproducibility across multiple samples. The ability to tailor experimental conditions, including electrolyte solution composition and applied potential, ensures the faithful replication of environmental factors relevant to distinct archaeological contexts. The efficiency of electrochemical reactions also expedites the aging process, providing a valuable advantage for experimental and research purposes. Promising results have been obtained on the replica of the conservation state of archaeological copper-based items [244,261,262]. However, much experimental effort is needed to deeply characterise such replicas, compare with real artifacts and ensure the replicability of the aging procedure.

The reproduction of realistic conservation conditions through accelerating aging is also exploited for less noble purposes, namely counterfeiting [263–266]. Archaeological items are the most counterfeited objects on the market, with coins making out the vast majority of seized cultural heritage objects, as found by a recent Interpol survey [267]. The circulation of forgeries and counterfeited items, and especially coins, is not only relevant in terms of frauds, but it can also negatively contribute to the work of archaeologists, if such items are eventually labelled as legit.

It is thus of primary importance to build tools for the identification of counterfeited objects, in order to ease the fight against illicit trafficking. At the same time, the experience of counterfeiters may represent an unexpected resource for conservation scientists to exploit.

I.4.2.2 Measuring corrosion: Electrochemical Impedance Spectroscopy

The analytical evaluation of the residual corrosion activity and of the protective efficiency of a novel treatment on a metallic artifacts is performed through a relatively narrow number of techniques, primarily of electrochemical nature (such as Tafel plot analysis [268] , Open Circuit Potential measurement and Potentiodynamic curves [269]) along with few others (water contact angle, nano-indentation). However, the most adopted technique is by far Electrochemical Impedance Spectroscopy (EIS) [270,271].

EIS is a powerful technique for characterizing electrical behaviour of systems in which coupled electrical processes occur at different rates [272]. In an EIS measurement, an alternate voltage signal is applied to a working electrode, and its response in terms of alternate current is registered. The input signal is then scanned over a range of frequency while recording the current, hence its classification as a spectroscopy. The same measurement can be conducted in galvanostatic mode, by applying an alternate current while registering the resulting voltage. The output data are expressed in form of impedance (Z), which can be described as the equivalent of the resistance in a direct current circuit, i.e.: a physical quantity describing the opposition of a system to an alternate current. Being a complex number, the impedance can be both expressed in the Cartesian form, with a real (Z') and an imaginary part (Z''), or in the Eulerian form, as a modulus ($|Z|$) and a phase (φ):

$$Z = Z' + iZ'' = |Z| * e^{-i\varphi}$$

where $i = \sqrt{-1}$. Data are then plotted as real against imaginary part of the impedance (Nyquist plot), or as impedance modulus and phase against frequency (Bode plots) (Figure 29). The latter is particularly employed for Cultural Heritage applications, because from that information on the corrosion resistance of the sample can be easily extracted as the low frequency limit of the impedance modulus [270].

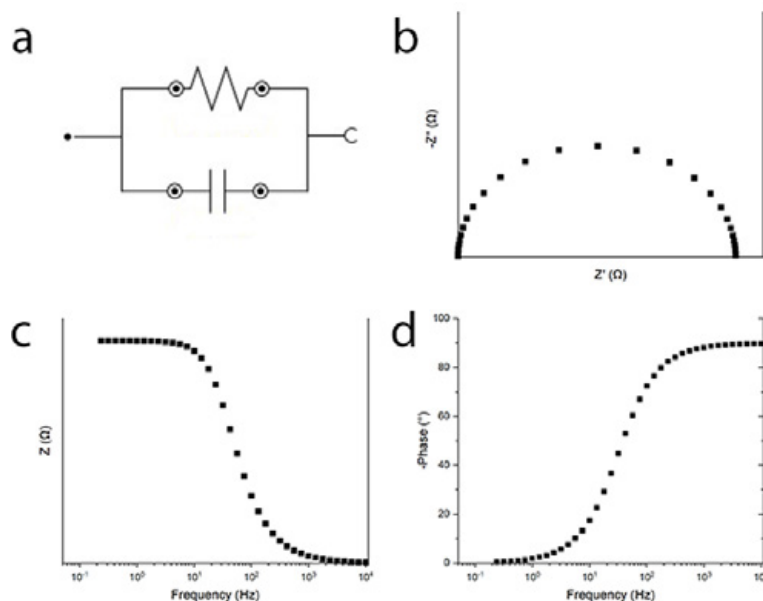


Figure 29 Example of an (RC) circuit (a) and related Nyquist (b) and Bode (c,d) plots.

An EIS instrument requires a potentiostat (equipped with a frequency module analyser) and an electrochemical cell, usually in a three-electrode configuration, comprising a working electrode (WE), a counter electrode (CE) and a reference electrode (RE), all immersed in an electrolyte solution. The WE, in the simplest EIS assembly, is the sample under analysis, which must be in direct electrical contact with the potentiostat (Figure 30).

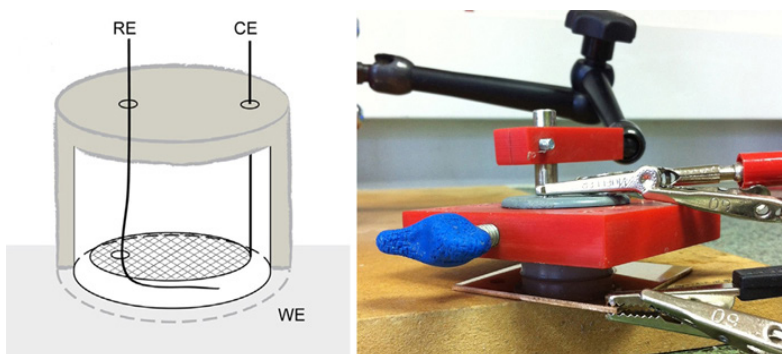


Figure 30 Example of an EIS setup. (left) Scheme and (right) at work. Electrical contact with the sample/WE is commonly granted by pressing a metallic tip on its surface or by direct clamping, as visible in this case in the bottom right corner. Reprinted from [273], with permission from Elsevier.

EIS is a very powerful technique that proved to be able to support conservators in individually identifying objects that require intervention, in evaluating the effect of a treatment [270,274–276], in choosing the most adequate coating [277,278] and in knowing when a coating has to be reapplied [176]. In the past, the research on EIS applied to Cultural heritage object has mainly focused on trying to adapt

the instrumentation to its *in-situ* use. When applying EIS to objects such as statues, it is often necessary to take measurements on non-horizontal surfaces. This can be problematic, due to the presence of liquid electrolyte.

The first attempts to overcome this issue were, for instance, using a cloth soaked with the electrolyte clamped in between the working (the sample) and the counter electrodes [235,269,279,280]. Similar attempts were made using a porous membrane [281], a foam [282] or a polyurethane disk [283] as interface layer. A more efficient solution has been found in the use of solid electrodes, and specifically jellified electrodes. The idea was first exploited by means of electrocardiogram (ECG) gels and other hydrogels for medical applications [284–287]. England and Clare, in particular, have proposed the use of hydrogels in a two-cell configuration (TCEIS), where two jellified electrodes are placed on the same side of the sample and the EIS signal is collected between the two [284]. This is a clever solution to avoid the need to make direct electrical contact with the metallic bulk. However, due to its configuration, using the TCEIS configuration can lead to possible signal dispersion through corrosion layers other than the main electrode-*patina*-bulk-*patina*-electrode path. This creates issues in terms of signal output [288]. Significant noise below 10 kHz has also been observed on a coated bronze sculpture [289]. The evolution of the hydrogel-based design has been the so-called agar gel polymer electrolyte cell (G-PE) [270,271,273,290].

Nowadays, the use of jellified electrolytes is diffused for advanced Cultural Heritage applications [291–293]. Agar, in particular, has proven to be a good choice as jellifying agent, thanks to its high conductivity, low interaction with samples, good contact on rough and irregular surfaces, ease to prepare, and low cost [273]. Instead, the actual choice of the electrolyte composition to be jellified is less standardised. The chemical nature and the amounts of salts in the gel significantly alter the response of the sample. This is related to the fact that the electrolytes play the role of the conservation environment in determining the reaction of the sample, which is then probed by EIS [269]. It means that they have to reproduce the aggressive action of the target environment, without causing long-term effect on the sample, thus fulfilling the non-invasiveness requirement of the method. Many electrolytes have been proposed in literature, such as the industry-standard 0.1 M NaCl [120,277,278,294] or dilute Harrison solution [278], both containing chloride ions. For copper finds, these ions must be avoided, due to the risk of triggering bronze disease. Na₂SO₄ solutions have been used in different concentrations [295–297], as it is a widely used general-purpose electrolyte in lab experiments. However, it lacks of representativeness when it comes to resembling a conservation environments. Several electrolytes have been proposed to mimic outdoor exposure through synthetic rain [298–301]. Coming to archaeological artifacts, most of them, after excavation, are kept in an indoor environment, such as museums or storages. An excellent choice for mimic such environments is bottled mineral water [302,303]. It presents many of the desired characteristics: low aggressiveness, while containing most of the chemical

compounds needed, easy to find and use, low cost, and a fairly long list of established works regarding its use [279,281,304–306]. The most prominent missing feature of mineral water is the lack of the organic component, which can embody the role of VOCs, which are widely present in indoor environments. Another aspect to be taken into account is the non-standardised composition of different mineral waters across the world.

At the present stage, EIS application to archaeological copper-based items is limited by a number of factors. The most prominent is the need for wiring the bulk metal to the working electrode. Excepting for the TCEIS set-up (which has its own limitations), all other setups so far proposed make use of direct clamping, or forced contact with a metal tip (often, a screw), to make the electric connection. This is an acceptable approach for huge statues or other big objects, where it is possible to sacrifice a small spot (most likely, in the inner side, when the object is hollow), or where the corrosion *patina* is limited in thickness. In the case of archaeological metals, however, this is not feasible due to thick *patination* covering the entire object and, thinking of coins and other small objects, without of freely accessible inner sides. Two situations can happen at this time: either the clamp/tip reaches the bulk by damaging *patina* and thus the object, or it does not properly make the electric contact with the bulk of the sample generating signal issues. In absence of an approach that allows to bypass this boundary, EIS use on archaeological copper-based artifacts is consequently restricted.

Another significant limitation for the use of EIS on archaeological items is represented by the lack of proper data interpretation [269,270]. A rough indication about the corrosion rate can be extracted from the low-frequency limit of the impedance modulus. However, the full unravelling of EIS data is difficult to achieve, as they contain many information and require significant modelling assumptions and interpretation. The task gets exponentially worse as the sample grows in complexity, and archaeological items can clearly be classified as highly complex. There are still uncertainties on how to correctly model the impedance behaviour of such samples. One reason for that is the limited amount of EIS data available on real archaeological items, which does not promote the consolidation of data modelling. This, in turn, can be in part imputed to the inability of acquiring good quality data in a totally non-invasive manner. Moreover, the current data available can be distorted due to bad wiring of the sample bulk.

From that, it is evident how beneficial would be for the conservation of archaeological metals, the development of a new EIS setup specifically devoted to this kind of samples.

I.4.2.2.1 Four-electrodes EIS

EIS on metallic samples is often performed in a three-electrode configuration (Figure 31 a). In this case, the bulk of the sample is directly wired, acting as WE. The EIS measure in this case characterise what happens between the bulk of the sample and the external CE. A less common configuration sees the use of four electrode, with an additional external reference used on the WE side, called Sense electrode or Working Sense (WS) (Figure 31 b). In this configuration, WE and CE control the flow of the current in the system, while RE and WS register the variation of the potential. One peculiar characteristics of this configuration is that the registered OCP should always be 0 V, because it is the same of having two identical electrodes in the same electrolyte solution [307].

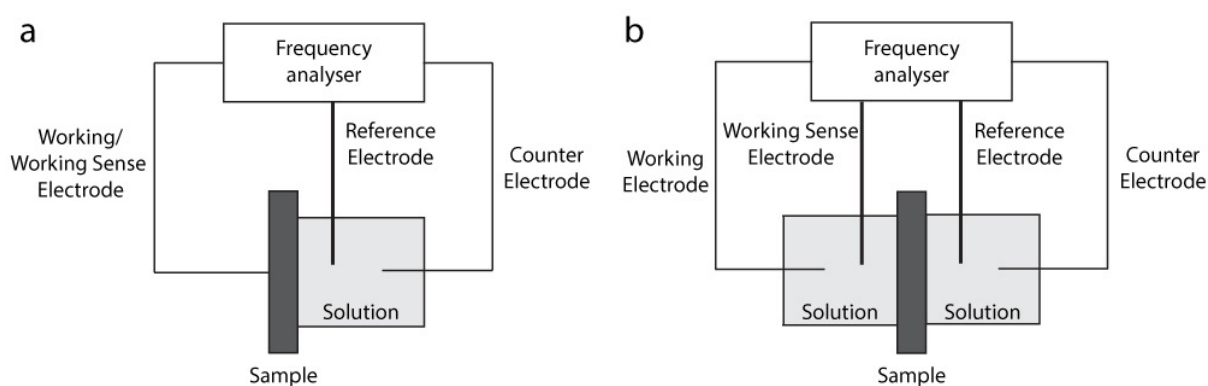


Figure 31 a) Three electrodes and b) Four-electrodes EIS configurations.

Four-electrodes configuration (also called four-probe) is used to analyse processes occurring within the electrolyte. It is commonly applied to the characterisation of insulating objects like membranes, and it is especially popular for the study of fuel cells [308]. It allows for the investigation of electrolytes and films disregarding the influence of working electrode and counter electrode impedances [309]. Currently, no applications of four-electrodes setups for EIS have been previously reported in literature on Cultural Heritage object.

I.5 Description of the experimental work

The critical assessment of the current practise and recent literature reported here revealed several key points that call for new research, methods, technology and materials, inspiring all over the work carried out during the present PhD project. Narrowing down the focus on the latter, the present thesis reports about five experimental sections covering, to different degrees, three macro-topics: archaeometry, diagnostics and conservation. In doing so, multiple advanced analytical techniques are tested, evaluated and optimised for their use on archaeological copper-based objects, namely: μ XCT, FIB-SEM, LA-ICP-MS, SPEM and EIS.

The first experimental section reports about the application of μ XCT to the identification of as-excavated Roman copper-based coins. The primary aim of this research was to face the issues of the identification of large numbers of illegible ancient coins – that retain soil or other debris encrustations or have undergone corrosion - by defining a non-invasive procedure based on μ XCT. In pursuit of this, the study aimed to accomplish the following objectives: to evaluate limitations and challenges associated with invasive and time-consuming cleaning methods typically employed for large coin collections; to assess the potential damage caused by traditional cleaning methods and the subsequent loss of valuable information; to assess the benefits of the μ XCT-based procedure and define its range of applicability within the Roman copper coinage domain.

The second describes a pair of experiments that share the same aim: address the long-standing need for a micro-invasive methodology to investigate corrosion layers and bulk features of archaeological metallic objects. To this end, two technologies are explored: FIB-SEM and LA-ICP-MS. FIB-SEM is a technique that can replace, or at least supplement in notable cases, the use of invasive sampling on ancient metals. The specific scope of the work on FIB-SEM was to bring this potential to light, something that has not been done yet. To this end, much effort has been spent to develop a procedure for the preparation of large and deep FIB-milled trenches on archaeological samples. Multiple tests have been performed to allow the selection of the best working parameters, optimising at the same time machine-time usage and quality of the output. The prepared trenches have been studied via SEM-EDS, in order to demonstrate how, in this way, in-depth information even on bulk features can be extracted from direct observation, with minimal invasiveness overall. The extensive experience in SEM imaging over archaeological samples surface and cross-sections have also brought evidence of the diffused presence of cracks and pores over and within corrosion layers. Early investigation how to address this conservation issue are reported in Appendix A.

On the other hand, the application of LA-ICP-MS to corrosion studies appears challenging but also highly promising in terms of its potential to investigate corrosion features in 1D (depth profiling, line scan), 2D (mapping) and 3D (stack of maps), with a minimal invasiveness. However, these potentialities are totally unexplored as of today. To fill this void, during this PhD project a series of case studies have been conducted which cover all the different possible approaches (1D, 2D, 3D) on different kind of items. The general aim of this part of the work is to put LA-ICP-MS to trial, in order to confirm its potentialities or disclose its limitations.

After this, the experimental focus has moved to SPEM, which share with the previous techniques a vast amount of unexploited potential. The efforts devolved to it have led to the identification of a form of corrosion that has never been observed before on an archaeological item, nor a heritage object: metallic silver whiskering. Using SEM-EDS, FIB trenching, lab-based XPS and SPEM itself, whiskers have been deeply characterised, their origin investigated and discussed, and even a potential diagnostic feature highlighted. SPEM limitations have also been investigated, and to overcome them a potential synergy between SPEM and laser ablation, as sample preparation technique, has been investigated.

The application of the LA-SPEM strategy, other than opening new ways to approach to SPEM, served also as support for the development of new EIS setups, specifically designed for archaeological metals. Nowadays, there is no real alternative to direct bulk wiring when making an EIS measurement on ancient metals. This limits EIS applications to archaeological metals. The aim of this part of the work was to overcome this limitation by tailored design and testing of two setups, the first based on the concept of four-electrode cell, and the second exploiting LA as sample preparation technique coupled with an ad-hoc designed carbon-brush electrode. The setups are first compared between them. After, the four-electrode one is further validated on a number of archaeological artifacts. By addressing the absence of an EIS setup, the final goal of this work was to widen even more the adoption of EIS in the conservation field, making possible to establish in future a large EIS dataset from which start facing the problem of EIS modelling and data interpretation. Another, fundamental scope of the newly developed EIS setup was to serve as an analytical platform for the development of a new protective treatment, making possible to directly compare data coming from archaeological metals and aged samples, as well as the same samples before and after the application of a treatment.

The subsequent building block for such platform was defining an aging protocol to properly replicate the conservation state of an archaeological copper-based artifact, something that has not been addressed from the literature yet. To this end, two different strategies have been tested in parallel, aimed at granting reproducibility, accuracy and speed of the mock-up production: first, an electrochemical-based method, previously reported in literature for the replica of *patinas* from urban environment [261], has been adapted to the scope; as second, an accelerated burial protocol has been devised, which involved

burying a specific number of samples in soil added with mixture of natural and chemical compounds. At designated intervals, solutions were introduced to expedite the aging process. This innovative method not only offers efficiency but also holds implications for authentication studies, particularly considering its origin in a counterfeiter's manual. The results are thoroughly characterised by OM, SEM-EDS, and μ Raman.

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Chapter II Experimental

II.1 Roman copper-based coins

A total of 18 Roman copper-based coins have been analysed throughout this thesis. 12 of them have been investigated through μ XCT, and their description is reported in the related paragraphs for consistency.

The remaining 6 are reported in Table 2 and Table 3. All these coins were recovered in the vicinity of ancient Aquileia (Italy) during archaeological fieldwalking surveys in 2011-2012. They have undergone cleaning by hand of restorers following their finding to remove soil debris, and have been stored since then in laboratory conditions. Additional details relevant for the specific analysis and description of extra samples are reported in the related paragraphs.

Coin ID	Obverse	Reverse	Coin details
579666			<i>Sestertius, Gordianus</i> 243-244 AD, Rome ø max 27 mm, 18.5 g
579676			<i>Denarius, Aurelianus</i> 270-275 AD, Rome ø max 19 mm, 2.1 g
579679			<i>Sestertius, Marcus Aurelius</i> 161-162 AD, Rome ø max 31 mm, 24 g

Table 2 Details of coins 579666, 579676 and 579679. Images are not to scale. They are reproduced upon permission of the Ministry of Culture, Regional Directorate of Museums of Friuli Venezia Giulia. Any further reproduction of such images, duplication by any means, as well as downloading and subsequent manipulation, is strictly prohibited.

Coin ID	Obverse	Reverse	Coin details
579692			<i>Antoninianus, Claudius Gothicus</i> 270-273 AD, Rome ø max 17 mm, 1.5g
582405			<i>Follis, Licinius</i> 315 AD, Siscia ø max 21 mm, 3.6 g
587202			<i>Antoninianus, Claudius Gothicus</i> 268-270 AD, Siscia ø max 16 mm, 2.2g

Table 3 Details of coins 579692, 582405 and 587202. Images are not to scale. They are reproduced upon permission of the Ministry of Culture, Regional Directorate of Museums of Friuli Venezia Giulia. Any further reproduction of such images, duplication by any means, as well as downloading and subsequent manipulation, is strictly prohibited.

II.2 μ XCT for coin identification

II.2.1 Description of the coins scanned

The analysis was conducted on a set of 12 Roman copper-based coins, which had been recovered in the vicinity of ancient Aquileia (Italy) during archaeological fieldwalking surveys. A visual inspection of coins in their as-found conditions revealed compromised and poor conservation states, with surfaces bearing greenish malachite-like *patinas*, typical green-red *patinas* associated with the presence of malachite and cuprite, encrustations with vivid blue or orange shades, and powdery deposits of dirt, as well as thick crusts of soil and accumulated matter. Complete documentation of the coins in their pristine conditions is available in par. III.1.1, along the results from μ XCT scans and traditional cleaning.

II.2.2 μ XCT setup and acquisition parameters

The μ XCT analysis was conducted using a custom-made system assembled by the hosting research group in Università di Bologna (Lab Imaging a raggi X). The system, shown in Figure 32, is composed by a rotating stage, a Hamamatsu L12161-07 75W microfocus X-ray tube with a spot size of 20 μm and a Varian PAX SCAN 2520D flat-panel detector with 1536 horizontal and 1920 vertical pixels, each measuring 127x127 μm^2 , resulting in a total effective area of 19.5 x 24.3 cm^2 . The voltage applied was 150 kV, the maximum for this system, with a current ranging between 140 and 180 μA . To minimise Beam Hardening (BH) effects, different filters (1 mm Al, 0.1 mm Cu, 0.25 mm Pb plus 0.1 mm Cu) were applied to the incident beam. For each scan, approximately 1 hour was required to capture 900 radiographies over 360° in step mode, with each radiography obtained as a mean over 4 repeated acquisitions taken at the same angular position, at a rate ranging from 5 to 3 frames per second. To achieve a voxel of 40 μm side, a magnification of x3.18 was used during the scans.

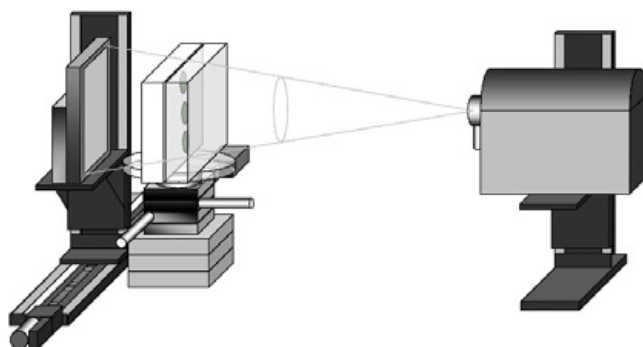


Figure 32 Graphical scheme of the μ XCT setup used. From right to left: the HAMAMATSU X-ray source, the sample holder for the coins, placed on a rotating stage and held in vertical alignment by two blocks of polystyrene, and the VARIAN flat-panel detector

The choice of the number of radiographic projections and of the level of magnification were based on a time-optimisation criterion. The number of projections should at least equal the number of pixels in the horizontal direction, in order not to decrease resolution in regions far from the center of rotation [1,2]. Due to their size and to the $\times 3.18$ magnification adopted, the coins occupied at most ca. half of the horizontal pixels of the detector. On these bases, the number of 900 projections (slightly more than the number of horizontal pixels of the detector occupied by coins) was considered as an optimal compromise. While the μ XCT system used would have allowed a further increase in the level of magnification, in fact, it would have determined an increase in the number of projections required and in the final data size, negatively affecting the total acquisition and elaboration time.

Each μ XCT scan involved 2 to 3 coins, kept still in vertical alignment by two blocks of polystyrene. The total number of coins that could be scanned per time was determined by the combination of detector effective area, level of magnification and coins size. The vertical alignment was chosen in order to avoid the overlapping of multiple coins along the beam direction, which would cause an increase of the path length of X-rays inside metallic bulk and thus an excess of beam absorption and enhanced beam hardening effects, overall worsening the quality of XCT data.

The CT reconstruction was carried out using the Feldkamp algorithm for cone beam CT [3], which is based on filtered-back projection (FBP) [1]. The PARREC (PARallel REConstruction) software was utilised for this purpose. [4–6]. The volume reconstruction of a single scan, which included 2-3 coins, was done simultaneously with the scanning process on a separate computer and was completed in less than an hour.

II.2.3 μ XCT data analysis

Full-scan datacubes have been first reconstructed from μ XCT scans and then corrected for beam hardening (BH). BH is a physical phenomenon that occurs in X-ray imaging when the X-ray tube emits a multi-energy beam. When X-rays of different energies pass through an object, particularly for high-density materials and when thickness is significant, low-energy photons are more easily absorbed than high-energy photons, causing an increase in the average energy of the beam. This effect is known as ‘beam hardening’. For a polychromatic X-Ray beam, the attenuation values deviate from a pure logarithmic function of the absorber’s thickness (Lambert-Beer law). As a result of this phenomenon, with filtered back-projection algorithms, the reconstructed slices will have CT values gradually decreasing from the edges toward the center even in the case of an object with uniform density, resulting in a ‘cupping artifact’ [2]. Furthermore, the tomographic images lose contrast and some object details are not clearly visible.

BH is a well-known phenomenon in computed tomography and is generally corrected by means of a calibration procedure which requires the creation of an *ad hoc* phantom for each type of experiment/material [7–9] or by post-processing correction [10]. The second approach has been followed in this work. Furthermore, to physically limit the phenomenon, filters have been applied in front of the X-ray tube window as described in the previous paragraph.

BH-corrected data subsequently underwent only basic post-processing steps using open-source software ImageJ [11] and 3DSlicer [12]. First, each datacube (including the scans of 2-3 coins) has been split into one datacube per coin. Second, slight angular corrections have been applied to each coin-datacube (using the ‘Reslice’ and ‘Rotate’ commands in ImageJ). When the obverse and the reverse side of a coin showed two different angular orientations, the operation has been conducted twice, generating two distinct datacubes, one per face.

The complete extraction of information for coins identification has been performed from the so-processed datacubes by dynamically navigating through slices (i.e. CT sections). This procedure has been complemented with the generation of images through the application of basic math operations (average, median, standard deviation, sum, maximum or minimum intensity) to neighbour slices, using the ‘Z project’ command in ImageJ, helpful in emphasising specific details.

In the case of coin A4, a low-pass filter has been applied through the ImageJ command ‘bandpass filter’, setting the filtering range from 0 to 5 pixels.

3D renderings have been performed with the support of 3D Slicer software. Volume renderings have been created using the processed datacubes as a whole. For achieving the images reported in the present work, a combination of thresholding and contrast management (through the ‘Shift’ command), virtual slicing (through the ‘ROI’ command) and lighting management (through the ‘Light’ Module) has been used.

The identification of coins was conducted using the processed data, with an archaeologist specialised in numismatics referencing up-to-date catalogues and repositories [13–16].

II.2.4 Traditional cleaning of the coins

The coins were cleaned by a professional conservator who followed a standard workflow for manual, basic cleaning, using simple tools such as a scalpel, dental probes, pins, and synthetic brushes instead of more sophisticated laboratory equipment. Ethanol and acetone were used as softening agents to remove soil crusts, but no chelating agents were used due to the poor conditions of the coins. The entire process was carried out under a magnifying lens to ensure accuracy of the cleaning intervention, and it took approximately one working day to clean each coin.

II.2.5 XRF elemental analysis

The XRF analysis was conducted on the cleaned coins using a Bruker Crono instrument, which included an Rh-target 10W X-ray tube, a 1 mm collimator, and an XFlash® detector. The instrument operated at 50 kV and 200 μ A, with a total acquisition time of 60 seconds. To account for local inhomogeneity, measurements were taken in triplicate for both sides of each coin by varying the position. The spectral elaboration and quantification were performed using Bruker ESPRIT® (v2.2) software, while statistical analysis was carried out using RStudio 1.4 [17].

II.3 FIB-SEM and LA-ICP-MS for corrosion studies

II.3.1 Description of the samples

FIB milling tests were performed on a group of ancient Roman copper-based coins. Specific FIB-SEM investigations were conducted on coins identified by the IDs No. 579676, 579692, 582405, 587202 and coin D. Further details on these coins are available in parr. II.1 and II.2.

LA-ICP-MS investigations were performed on the obverse side of two other coins (Figure 33). The first is an unidentified ancient copper-based coin of archaeological origin (presumably, a late Roman coin). It is characterised by a well-developed yellowish silicate patina, which is commonly defined as “desert patina”. The second is a counterfeit coin mimicking an ancient Greek electrum (a gold-silver alloy) coin of the Agathocles period (50 λίτραί, 317-289 BC, Syracuse). This coin has been conferred to the Center for Cultural Heritage Technology - Istituto Italiano di Tecnologia by order of the GIP (*Giudice per le indagini preliminari*) at the Court of Turin the day 28.07.2023, in the context of the p.p. 38880/17 RGNR mod. 44. Its nature as a fake has been defined on the basis of numismatic evaluation and only a partial archaeometric analysis, based on XRF data.

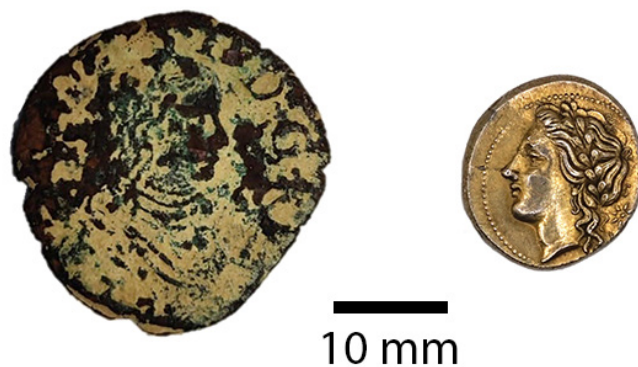


Figure 33 (left) "Desert patina" coin and (right) Electrum coin (photo by Michela De Bernardin).

II.3.2 FIB working parameters

A FEI Helios Nanolab 650 FESEM/FIB Dual Beam was used in this work. It consists of a 30 kV monochromated Schottky FESEM column (Elstar™) and a 30 kV Ga⁺ Focused Ion Beam (Tomahawk™) placed at 52° one from each other. All objects studied in the FIB system were secured

to the stage by means of a PELCO SEMClip™ stub, equipped with three metallic clips (Figure 34). For FIB operation, the objects were tilted 52° from horizontal, assuming a flat surface, to align the surface normal to the ion beam (i.e., milling perpendicular to the surface).

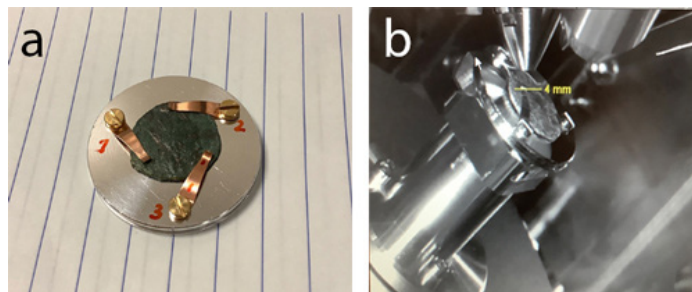


Figure 34 a) Example of sample mounting on the FIB-SEM stub with the clip system b) Sample as mounted in the FIB-SEM chamber.

Cross-sectioning (i.e. trench opening, or trenching) was performed at 30 kV and 21 nA. Attempts to perform trenching at higher currents (47 nA) were also performed. The instrument utilised a multiscan cross-sectioning methodology to create trenches with a staircase geometry, with the wall on the deepest side of the trench representing the cross-section to be analysed later. This kind of geometry was adopted in order to maximise the view on the cross-section, while reducing the quantity of material ablated and thus minimising both operative time and invasivity.

Before performing the trenching, a thin layer (ca. 1 μm) of Pt was deposited on the cross-section side of the future trench using a gas-injection-system (GIS) needle, to reduce the milling artifacts due to uneven sample surface. After the opening of the trench, the wall of the cross-section was further FIB-milled at lower currents (2.5 to 0.77 nA), to reduce milling artifacts like redeposited or melted material and implanted Ga^+ ions, so that the cross-section wall showed the actual features of the inside of the sample.

The overall aesthetic damage of the trenches obtained was not detectable to naked eye.

II.3.3 SEM-EDS analysis of FIB trenches

The SEM-EDS data reported in this work were acquired with three different systems. The first was the FEI Helios Nanolab 650 Dual Beam used for FIB cross-sectioning, which was equipped with an X-Max™ EDS Detector (Oxford Instruments). The second was a JEOL JSM-6490LA, equipped with an

embedded JEOL EDS. The third was a Zeiss GeminiSEM 560, equipped with a X-MaxTM 80mm² EDS (Oxford Instruments). Live time for EDS maps varied from few minutes to one hour. SEM images were taken using secondary electron (SE) or backscattered electron (BSE) at an accelerating voltage between 1 and 30 kV.

The system and acquisition parameters used for each image are specified in the caption of the relevant figure. Data were elaborated with AZtec® (4.4) software, using the TruMap function to deconvolve overlapping contributions from different elements. Carbon has not been considered for quantification due to low reliability of its signal.

II.3.4 μ XRF mapping

A Bruker M4 Tornado, equipped with a microfocus Rh-target X-ray tube, was used to obtain elemental distribution information over the sample. Acquisitions were made at 50 kV, 200 mA and 200 ms/pixel. Data were elaborated using PyMCA 5.8.0 software.

II.3.5 LA-ICP-MS

The LA-ICP-MS instrument used in this work consists of an Analyte Excite ArF excimer 193 nm laser (Teledyne CETAC Photon Machines) coupled to an iCAP-RQ quadrupole ICP-MS (Thermo Scientific). The laser ablation device is equipped with a HelEx II two-volume ablation cell mounted on a high-precision x-y stage. The samples were placed on a standard LA holder and fixed in-place with double-sided tape.

Drilling test: a drilling test was performed on the desert patina coin with the aim to correlate the number of shot with the depth and geometry of ablation. For this reason, different drillings were made with increasing number of shot counts: 10, 20, 40, 80, 100, 150, 200, 300, 500, 600. A circle spot size of 110 μ m, fluence of 6 J/cm², and repetition rate of 10 Hz were used. Detailed operating parameters are reported in Table 4.

Laser	
Laser type	ArF excimer 193 nm
He gas flow cell	0.25 L/min
He gas flow cup	0.25 L/min
Fluence	6.0 J/cm ²
Spot size	110 µm circle
Repetition rate	10 Hz
Ablation mode	Drilling
Shot count	10, 20, 40, 80, 100, 150, 200, 300, 500, 600

Table 4 LA operating parameters for the drilling test on the desert patina coin.

Depth profiling on desert patina coin: using the desert patina coin, a depth profiling analysis was optimized as method to study the corrosion patina of archaeological coins and investigate its process of formation. The parameters of analysis were adjusted considering the results obtained from the drilling test. In particular, the repetition rate was decreased from 10 Hz to 2Hz. These modifications were adopted to increase the time available to the ICP-MS for better separating two different peaks coming from subsequent ablation shots. The use of a standard transfer line allowed to achieve a large wash-out time (WOT, ≈ 100 ms) and monitor a greater number of elements.

Since for the drilling test some redeposition of ablated materials was observed at the edge of craters, a fluence of 4 J/cm² was tested together with 6 J/cm², modifying the shot count accordingly (from 600 with 6 J/cm², to 1000 with 4 J/cm²) to reach approximately the same depth inside the sample. A spot size of 110 µm was used. This choice takes into account three main factors: first, the smaller the spot, the higher the risk to observe tapering effects on the drill shape with the increase of shots count; second, the smaller the crater, more the ablated material struggles to escape and be conveyed to the ICP; third, grain size in the bulk alloy can be of tens of µm, and having a spot size of comparable dimension can hinder the representativeness of the analysis.

Detailed operating parameters are reported in Table 5. Elements were chosen as representative of the composition of corrosion layer and bulk, after preliminary assays. Final data were averaged with a 9-points moving average.

Laser		ICP-MS	
Laser type	ArF excimer 193 nm	RF power	1550 W
He gas flow cell	0.25 L/min	Cooling gas flow	14 L/min
He gas flow cup	0.25 L/min	Auxiliary gas flow	0.8 L/min
Transfer line	Standard	Ar makeup gas flow	0.8 L/min
Fluence	6.0 and 4.0 J/cm ²	Monitored isotopes	²⁸ Si, ⁴³ Ca, ⁵⁷ Fe, ⁶³ Cu, ¹⁰⁷ Ag, ¹¹⁸ Sn, ²⁰⁸ Pb
Spot size	110 µm circle	Dwell time	14 ms for each isotope
Washout time	≈100 ms		
Ablation mode	Drilling		
Repetition rate	2 Hz		
Shot count	600, 1000		

Table 5 LA-ICP-MS operating parameters for the depth profiling on the desert patina coin.

Depth profiling on counterfeit electrum coin: the drilling method optimized using the desert patina coin was used as method for authentication purposes. A false Greek electrum coin was analyzing using the following parameters: fluence 4.0 J/cm², repetition rate 2 Hz, shot count 400, and 110 µm circle spot size. Detailed operating parameters are reported in Table 6. Final data were averaged with a 5-points moving average.

Laser		ICP-MS	
Laser type	ArF excimer 193 nm	RF power	1550 W
He gas flow cell	0.25 L/min	Cooling gas flow	14 L/min
He gas flow cup	0.25 L/min	Auxiliary gas flow	0.8 L/min
Transfer line	Standard	Ar makeup gas flow	0.8 L/min
Fluence	4.0 J/cm ²	Monitored isotopes	⁶³ Cu, ¹⁰⁷ Ag, ¹⁹⁷ Au
Spot size	110 µm circle	Dwell time	20 ms for each isotope
Washout time	≈100 ms		
Repetition rate	2 Hz		
Ablation mode	Drilling		
Shot count	400		

Table 6 LA-ICP-MS operating parameters for the depth profiling on Greek gold coin.

2D/3D Imaging: maps were obtained using a monodirectional area scan mode with a 20 µm square spot size, a laser fluence of 6 J/cm², and fixed dosage of 7 over a total area of 1.9 x 1.3 mm². In this

case, the fluence was selected considering the limited amount of subsequent acquirable 2D maps in a reasonable time, in order to optimise the amount of material ablated per map. A rapid aerosol transfer line (ARIS, Teledyne CETAC Technologies) was used to transport the ablated materials from the surface of the sample to the ICP-MS. The addition of ARIS enables achieving a faster washout time (WOT), typically in the range of 20 ms, specifically designed for high-speed imaging. The WOT for imaging was calculated on a CuSn5Zn5Pb5-C (CC491K) reference alloy, because archaeological metallic *patinas* are characterised by a heterogeneous and unknown surface composition, resulting into larger but unsystematic WOT [18]. Once calculated the WOT and preselected the dosage and the spot size, the laser repetition rate (Hz) was fixed to $1000 \times \text{dosage} / \text{washout time}$, while the resulting scan speed equalled $[(\text{spot size}) / (\text{washout time} / 1000)]$. A repetition rate of 280 Hz corresponding to 800 $\mu\text{m/s}$ of scanning speed was adopted. In addition, the selection of a higher dosage enabled the generation of each pixel based on the multiple – partially overlapping – laser pulses that improve the signal-to-noise ratio and the image quality, especially when a smaller spot size is used and multi elements are required. Such a fast laser frequency required fast aerosol transport (achieved using the ARIS), but also accurate synchronization with the ICP-MS acquisition method. The use of a quadrupole (sequential) detector forced us to select a small group of analytes/isotopes to be monitored within a total sweep time equivalent to the WOT. The elements of interest were selected based on preliminary line scanning of the surface near the region of interest (ROI). Based on the preliminary data, the individual dwell time of selected elements were adjusted to be inversely proportional to their expected signal intensity (concentration). Six isotopes were recorded per image: ^{29}Si , ^{57}Fe , ^{65}Cu , ^{107}Ag , ^{118}Sn , ^{208}Pb . Detailed operating parameters are reported in Table 7.

Laser		ICP-MS	
Laser type	ArF excimer 193 nm	RF power	1550 W
He gas flow cell	0.25 L/min	Cooling gas flow	14 L/min
He gas flow cup	0.25 L/min	Auxiliary gas flow	0.8 L/min
Transfer line	ARIS	Ar makeup gas flow	0.8 L/min
Fluence	6.0 J/cm ²	Monitored isotopes	^{29}Si , ^{57}Fe , ^{65}Cu , ^{107}Ag , ^{118}Sn , ^{208}Pb
Spot size	20 μm square	Total sweep time (duty cycle)	20 ms (60 %)
Washout time	25 ms		
Ablation mode	Fixed dosage (7)		
Repetition rate	280 Hz		
Scanning mode	Monodirectional raster		

Table 7 Operating parameters of the LA-ICP-MS 2D and 3D imaging of corroded coin

Three-dimensional elemental maps were obtained by repeated ablation of the same region of interest (ROI) in the same operating conditions. Each layer map was acquired and saved individually as a .csv file, and then stacked during the processing phase. This enabled to consistently monitor both the elemental composition of a single ablated layer and the 3D volume distribution of elements. The data elaboration steps (including background subtraction, drift correction, and image reconstruction) were performed using the software HDIP (Teledyne Photon Machines, Bozeman, MT, USA). Further image post-processing steps were executed in a MatLab environment.

II.3.6 Optical Profilometry

A KLA Zeta-20 Optical Profilometer was used to contextually achieve a high-resolution all-in-focus image and a Profilometric analysis of the sample surface. A 10x optics and a z-resolution of 1.5 μm were used for the imaging of drillings and of the ablated area for the 3D mapping, while a 20x optics and a z-resolution of 0.5 μm were used for the higher resolution detail of the border of the ablated area. Data were elaborated with the Zeta3D software. A high-pass filter was used to remove spike artifacts due to light reflection on the sample surface.

II.3.7 Cross-section preparation and SEM-EDS investigation of electrum coin

The counterfeit electrum coin was manually cut with a jewellery saw, embedded in a polyester resin (PRESI 2S) and then mechanically polished with SiC abrasive papers from P240 to P2200, finished with diamond paste up to 1 μm and rinsed with Milli-Q water and ethanol.

The so-prepared cross-section was then analysed using a Zeiss EVO® MA 25. The cross-section was fixed on a stub with a conductive tap and metallised with graphite (ca. 200 nm thickness) prior to the analysis. Element analysis was performed with an X-MAX™ 80 mm² EDS probe (Oxford Instrument). An accelerating voltage of 25 kV and a current between 400 - 800 pA were used.

II.4 SPEM and Silver whiskering

II.4.1 Description of archaeological coin samples

SPEM investigations were conducted on the obverse side of two ancient Roman coins (ID no. 582405 and 587202). Further details on these coins are available in parr. II.1. XRF analysis allows to classify both coins as a quaternary Cu-Pb-Sn-Ag alloy.

II.4.2 Design and preparation of the laser-ablated micro-digs

In the ESCAMICROSCOPY beamline setup at ELETTRA Sincrotrone Trieste, the primary X-ray beam is perpendicular to the sample surface, and the photoelectron analyser has a 30° take-off angle. The geometry of the digs and the ablation process were specifically designed for allowing the signal generated from points within the dig to reach the analyser (Figure 35).

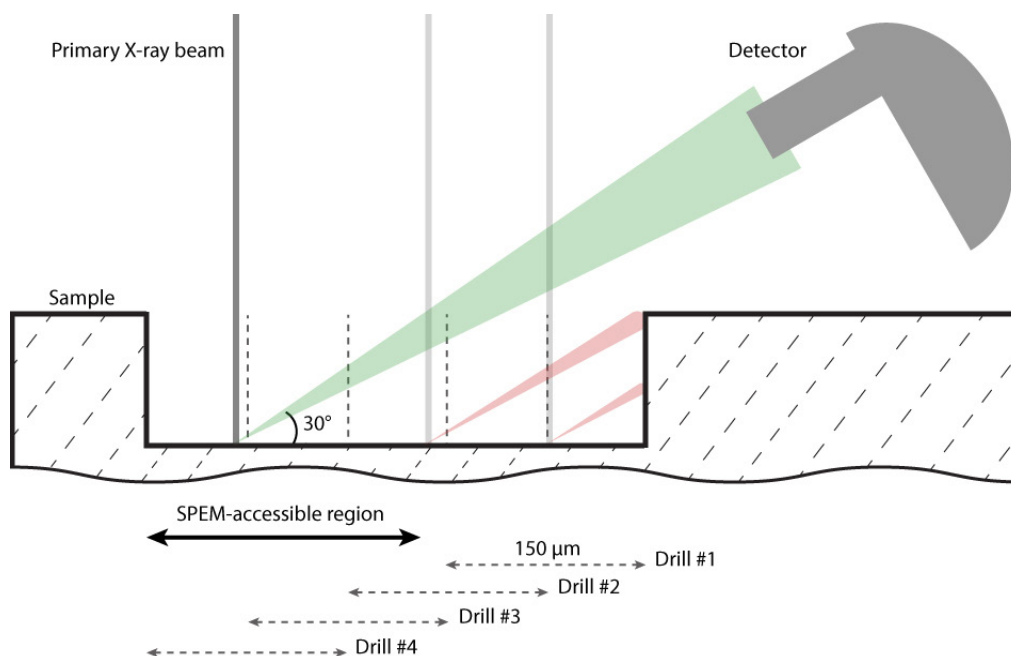


Figure 35 Scheme of the SPEM experiment and of micro-digs design.

In order to produce each dig with a specific geometry and aspect ratio, four individual drillings, each of 700 pulses at 4.0 J/cm^2 energy, with a repetition rate of 10 Hz and a $150 \text{ }\mu\text{m}$ square laser spot, have been sequentially ablated with an overlapping of the 50% using an Analyte Excite ArF excimer 193 nm laser (Teledyne CETAC Photon Machines). Two digs have been ablated in opposite direction, in order to cover both possible relative orientations between the detector and the sample. Immediately after the ablation has been concluded, the coin has been dismounted from the holder and placed inside a desiccator under Ar atmosphere and sealed for the transportation to the synchrotron. There, the opening of the desiccator and the mounting of the sample in the SPEM chamber have been performed in inert Ar atmosphere. These precautions have been taken in order to limit the oxidation of eventual metallic Cu exposed.

II.4.3 Preparation of laser-ablated reference pellets

Pellets have been prepared by mechanically pressing pure chemicals powder with a pelletiser. The pure chemical compounds used were Copper (I) oxide (Cu_2O , abcr, AB 115070), Copper (II) oxide (CuO , abcr, AB 202960), Copper (II) sulphate pentahydrate ($\text{CuSO}_4 \cdot (\text{H}_2\text{O})_5$, Supelco, 1.027900250), and Copper(II) carbonate dihydroxide ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$, abcr, AB 207486).

Pellets were ablated using the same laser used for microdigs, with a fluence of 4.0 J/cm^2 , scan speed of $583.3 \text{ }\mu\text{m/s}$ and a $35 \text{ }\mu\text{m}$ square laser spot, in order to ablate an area of ca. $3 \times 3 \text{ mm}^2$.

II.4.4 Scanning PhotoElectron Microscopy (SPEM)

SPEM measurements were performed at the ESCAMICROSCOPY beamline of the ELETTRA synchrotron, in Trieste (Italy). A primary SR-X-ray beam of 1080.1 eV was used. The X-ray beam can be focused down to 180 nm, but was employed in a defocused manner, to achieve a spot size of about $5 \text{ }\mu\text{m}$. This was done in order to facilitate the individuation of Cu^0 -rich spots inside microdigs and mitigate the charging effect. The experimental station was equipped with a SPECS PHOIBOS 100 Hemispherical Electron Analyzer placed at 30° respect to the sample surface, having a wide angle set of electrostatic lenses and a 48-channel electron detector. The spectra are recorded with an overall energy resolution of 0.2 eV for C, and 0.37 eV for F and S, and with a pass energy of 20 or 40 eV. Binding energies are calibrated using the Au $4f_{7/2}$ at 84.0 eV peak.

SPEM maps are taken by scanning the surface, each pixel containing a low-definition XPS spectrum taken with a pass energy of 40 eV. SPEM maps are strongly affected by the morphology of the surface. In order to subtract morphological effects, maps are normalised over the background selecting a range of energies as “peak”, and then dividing this range over a second one defined as “background”. On maps showing variable charging behaviour, the two maps per element are taken as follows: first, as ‘peak’ is taken a higher range of energies, and it is divided on a “background” at the low-end of the energy windows; second, the opposite is done. This is done because charging causes the shift of XPS energy towards lower energy.

II.4.5 Lab-based XPS

XPS was carried out through a Kratos Axis Ultra^{DLD} spectrometer (Kratos Analytical Ltd.) equipped with a monochromated Al X-ray source ($h\nu = 1486.6$ eV) operated at 20 mA and 15 kV. Reference samples were stuck on the sample holder using carbon tape to maximize electrical contact, while archaeological samples were mounted using the same metallic clamps as for FIB and SEM stub mounting.

Wide survey scans were collected at a photoelectron pass energy of 160 eV and energy step of 1 eV, while high-resolution spectra were collected at a photoelectron pass energy of 20 eV and an energy step of 0.1 eV. A take-off angle of 0° with respect to sample's normal direction was used for all analyses. Differential electrical charging effects were neutralized on all samples with a charge neutralizer. The standard spot size was $300 \times 700 \mu\text{m}^2$, while smaller spot sizes were obtained by means of pinholes. The calibrated spectra have been referenced to the adventitious carbon 1s peak at 284.8 eV. The spectra were analyzed with the CasaXPS software (Casa Software Ltd., version 2.3.24) [19], and the residual background was eliminated by the Shirley method.

The charge neutralization system used consists of a filament and an electrode plate, named charge balance electrode, mounted at the bottom of the electrostatic input lens system. During utilization, a current passing through the neutralizer filament causes electrons to be thermo-ionically emitted [20]. These electrons are forced out of the filament by a negative bias applied to the charge balance electrode and are subsequently focused on the sample surface by the magnetic field generated by the “magnetic immersion lens” positioned below the sample, as described in Figure 36.

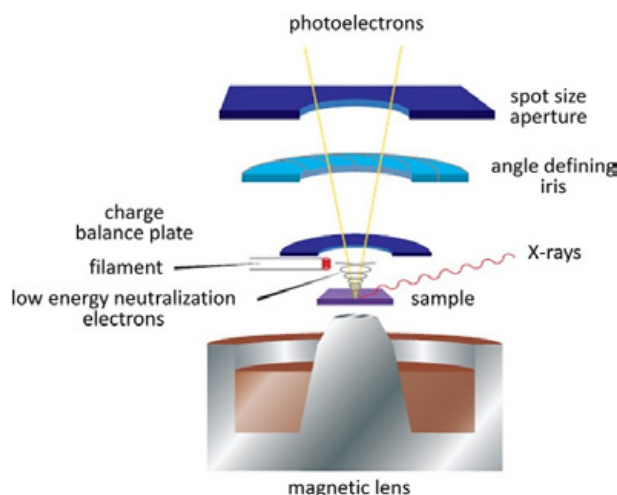


Figure 36 Representation of the charge neutraliser assembly, together with the magnetic and electrostatic lenses system of the Kratos AXIS Ultra^{DLD} spectrometer. Figure reproduced from reference [20].

The AXIS Ultra^{DLD} charge neutralizer has three parameters that can be used to optimize charge neutralization: filament current (around 2 A), filament bias voltage (1–2 V), and charge balance voltage (1–5 V). The filament current is proportional to the number of electrons available for charge neutralization, while the voltage applied to the filament provides the electrons with the initial energy to leave the filament and overcome the space charge region. Above a threshold value, this parameter only slightly affects the number of electrons available for neutralization. Lastly, the charge balance voltage gives a negative potential that is dynamically maintained between the charge balance electrode and the sample surface by the neutralization electrons. The surface potential consequently shifts in response to the charge balance voltage and sets the energy position for the best spectrum [20]. Normally, the charge balance is the only parameter that needs to be modified to improve charge neutralization.

The optimization procedure is conducted on the adventitious C 1s region varying the charge balance voltage by 0.1–0.2 eV at a time inside the permitted range (1–5 V). The aim is to maximize the peak intensity and, at the same time, to minimize the peak width (FWHM, *Full-Width-at-Half-Maximum*). The shift is in principle proportional to the charge balance voltage. A plateau condition usually exists over a range of about 1–2 eV above the charge balance optimum value, in which the best peak shape and FWHM are substantially preserved and there is only a rigid shift in peak position proportional to the charge balance voltage. Instead, such neutralization conditions do not work effectively below the charge balance optimum value (sub+-compensation of surface charging), causing unpredictable peak shapes and FWHM.

II.4.6 Other characterisation techniques

FIB-SEM investigation: FIB cross-sections and SEM-EDS analyses were performed with the FEI and ZEISS system described in parr. II.3.2 and II.3.3. Acquisition parameters are specified in captions. Data were elaborated with AZtec® (4.4) software.

Optical Profilometry: Profilometric analysis was conducted with a KLA Zeta-20 Optical Profilometer equipped with a 50x optics. Data were elaborated with the Zeta3D software. A high-pass filter was used to remove spike artifacts due to light reflection on the sample surface.

μXRF mapping: A Bruker M4 Tornado, equipped with a microfocus Rh-target X-ray tube, was used to obtain elemental distribution information on the sample. Acquisitions were made at 50 kV, 200 mA and 200 ms/pixel, over an area of ca. 12x12 mm². Data were elaborated using PyMCA 5.8.0 software.

II.5 Electrochemical Impedance Spectroscopy

II.5.1 Description of archaeological coin samples

Four ancient Roman coins investigated by EIS. They are identified by ID no. 579666, 579679, 587202 (see par. II.1) and ID No. A3 (after cleaning, see par. II.2). The chemical composition of the coins was previously assessed by XRF analysis. The older sestertius (579679) was found to be made of a ternary Cu-Zn-Sn alloy, with low amount of Zn, while the more recent one (579666) was made of a quaternary Cu-Pb-Sn-Zn alloy, with high content of Pb and a lower amount of Zn. This variation in the alloy composition can be well predicted, as explained in par. I.1. XRF analysis allows to classify both coins 587202 and A3 as a quaternary Cu-Pb-Sn-Ag alloy, as expected from their coin type (for coin A3, see section III.1).

II.5.2 Design of the EIS setups

Two new cell designs were tested used in this work and had, as their basic unit, a half-cell made by a hollow Teflon cylinder, filled with a jellified electrolyte in which two Pt electrodes (99.95%, 0.5mm $\varnothing$, Thermo Scientific Chemicals) were immersed (Figure 37) The gel-sample interface was of 19.6 mm². A gasket was included between the gel and sample surface in order to avoid mechanical friction between TEFLON and the surface of the sample.

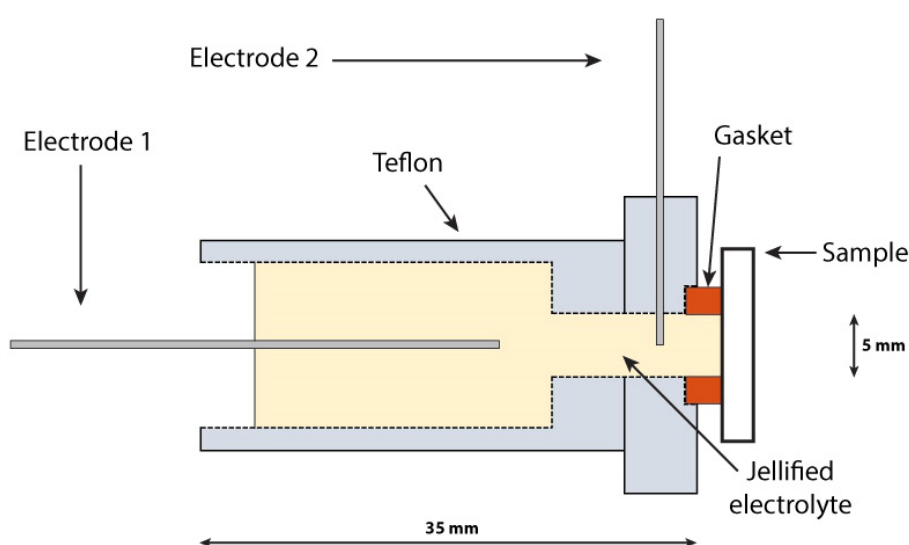


Figure 37 Gel half-cell design. Both electrodes are made of Pt.

The first cell tested, called Carbon-brush setup (CB setup, Figure 38), was assembled in the classical three-electrode configuration. It comprises a Pt wire as counter electrode (CE) and a Pt wire as pseudo-reference (RE) electrode, both immersed in the gel. This part of the cell is made by a semi-cell of the type in Figure 37. The working electrode (WE) is represented by the investigated sample, which is pressed against the jellified interface to ensure the closure of the electrical circuit. The peculiarity of the CB setup is the way in which the metallic bulk of the sample was wired. On one side of the sample, a micro-dig of 100 μm diameter was produced within the patina layer by laser ablation. The depth of the hole was such that the naked copper surface was reached, as verified by SPEM (see section III.3). The electrical contact with the exposed bulk metal was obtained using a bundle of graphite micro-fibres soldered to a copper wire, sealed in a borosilicate glass capillary. The complete scheme of the CB setup and an applicative example are shown in Figure 38.

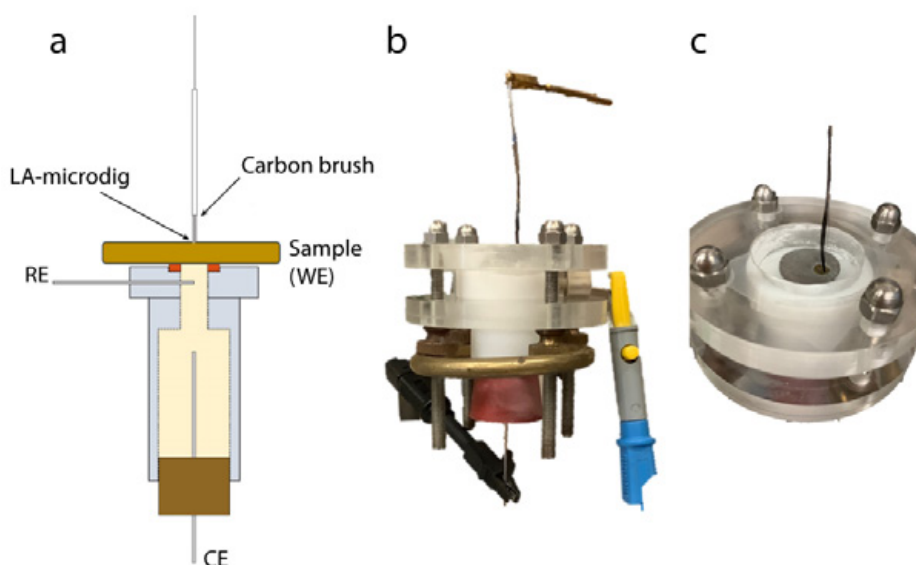


Figure 38 Carbon-brush setup: a) scheme, b) side view, c) top view.

For the experiments shown herein, the same LA-microdigs prepared on coin 587202 for the SPEM were used. Such dings were oversized in order to allow the in-depth SPEM investigation. It must be considered that the 100 μm -diameter dig is practically invisible to the naked eye.

The second cell was based on a four-electrode setup (4E), typically used for membrane impedance study [21]. The 4E setup was realised by placing the sample between two gel half-cells (Figure 39). In this configuration, in one half-cell, the two Pt electrodes played the role of CE and reference electrode (RE) while, in the other half-cell, the two Pt electrodes acted as WE and working sense (WS) electrodes.

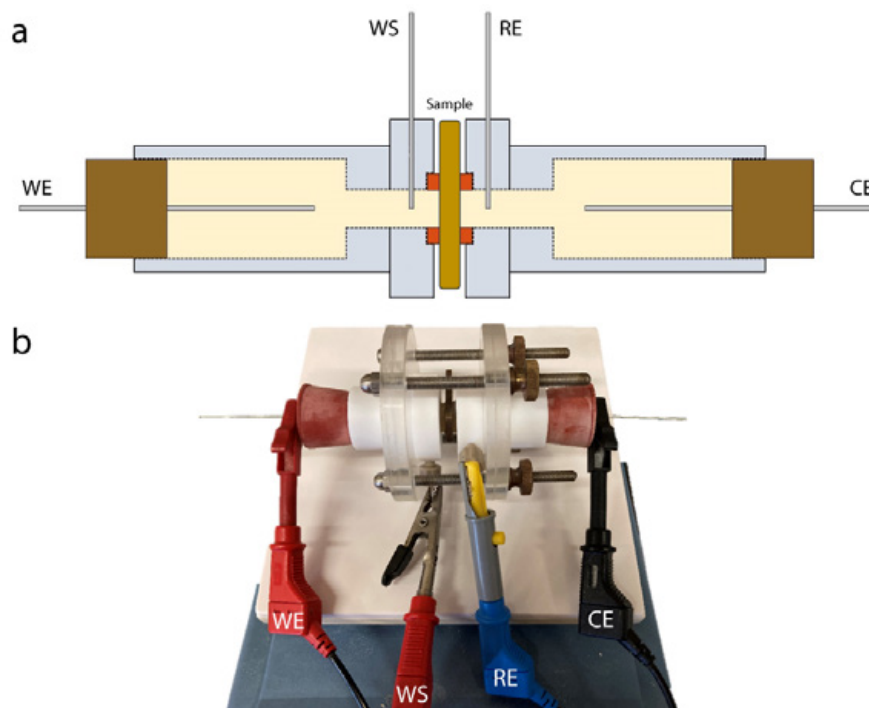


Figure 39 4E setup: a) scheme, b) at work.

For the standard approach is concerned, the direct electrical contact between sample and instrument was realised by pressing a Cu sheet against the sample, and clamping it with a crocodile. This avoided mm-sized signs over the sample surface as direct clamping or tip-pressing would do.

II.5.3 Electrolyte and gel preparation

The base electrolyte solution adopted was designed to fulfil the following conditions: (1) mimic, as much as possible, the indoor environment conditions to which copper-based archaeological alloys are usually subjected after excavation. This is needed because the impedance response of a sample strictly depends on the environment in which it is immersed, so, in order to achieve useful information, conditions comparable to the real conservation environment must be replicated. (2) Guarantee enough conductivity. (3) Be mild enough not to cause long-term alteration on objects. These criteria were met using bottled mineral water (Levissima®, conductivity 130 $\mu\text{S}/\text{cm}$), added with 80 mg/L of sodium formate (Sigma Aldrich, 456020) to simulate the VOCs component of indoor air pollutants [22,23]. The resulting composition is reported in composition shown in Table 8 and final pH was 7.6.

SO_4^{2-}	NO_3^-	NO_2^-	HCO_3^-	HCOO^-	F^-	Na^+	Mg^{2+}	K^+	Ca^{2+}	SiO_2
19.9	1.2	< 0.002	55.8	53.1	0.2	28.9	1.6	1.5	22.2	5.8

Table 8 Composition of the liquid electrolyte (formate addition included), expressed in mg/L.

The gel was prepared by adding agar powder (Thermo Scientific, H26724) to the electrolyte solution. The mixture was heated up to 70°C for few minutes. As the mixture started to jellify, it was casted into the Teflon cell with the two Pt electrodes already in it. Gel was allowed to rest at least one hour before putting it in contact with the sample, to let it cool and consolidate. For the initial comparison between the CB and 4E setups, an agar concentration of 3% was used, as reported in literature [24]. In further measurements, the preparation was optimised to a 3.5% in agar content, in order to enhance the mechanical performance of the gel (i.e. viscosity when put contact with the sample and velocity of preparation).

II.5.4 EIS acquisition parameters

EIS experiments were carried out with a Multi Autolab M204 equipped with a FRA32M modulus for the electrochemical impedance spectroscopy, applying a logarithmic sweeping frequency of five steps per decade, from 10 kHz to 10 mHz. Impedance measurements were performed at the open circuit potential (E_{OCP}), applying a sinusoidal signal of 10 mV rms. Data analysis was conducted with the Nova 2.1 software.

II.6 Reproduction of archaeological *patinas*

II.6.1 Metallic substrates and chemicals

Two metallic round bars produced via continuous casting were used as metallic substrates for the accelerated aging, one made of a CuSn5Zn5Pb5-C / CC491K (B555) alloy (B555, from here on) of 37 mm diameter, and the other of a CuSn7Zn4Pb7-C / CC493K alloy (B774) of 26 mm diameter (Musola Metalli Srl). Both were quaternary bronzes, with alloying composition in the range of the one used in ancient Roman coinage. The bars were cut in planchets of 2-3 mm thickness, and then further cut in 2 (B774) or 3 (B555) slices of similar area. Final substrates were mechanically polished before use, using SiC abrasive papers from P240 to P1200, and rinsed with Milli-Q water and ethanol.

Copper (I) oxide (Cu_2O , abcr, AB 115070) and Copper (II) carbonate dihydroxide ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$, abcr, AB 207486) were used as pure powders, along with oxalic acid dihydrate ($\text{C}_2\text{H}_2\text{O}_4 \cdot (\text{H}_2\text{O})_2$, Sigma Aldrich, 33506). Other chemicals used were sodium sulfate (Na_2SO_4 , Sigma Aldrich, 238597), sodium nitrate (NaNO_3 , Merck, 221341), sodium bicarbonate (NaHCO_3 , Sigma Aldrich, S5761), urea (NH_2CONH_2 , Flortis) and sodium chloride (NaCl , Sigma Aldrich, 71376).

II.6.2 Electrochemical aging

B555 samples were electrochemically aged individually. Before aging, they were partially covered with an insulating varnish (generic nail varnish), leaving only a small portion of the non-immersed half exposed in order to allow the electrical contact with the WE. The other half of the sample was immersed in an aerated solution consisting of 0.2 g/L Na_2SO_4 , 0.2 g/L NaNO_3 + 0.2 g/L NaHCO_3 , neutralised to pH 7.0 by addition of HNO_3 0.3 M and kept at 30° C [25]. A Pt mesh was used as CE, placed in a separated cell filled with the same electrolyte and connected to the WE through a salt bridge. A saturated Ag|AgCl electrode was used as RE. After a stable open circuit potential (OCP) was reached, the sample was first subjected to a potential of -0.20 V, then it was left 48 h at 0.14 V, and a further 48 h at 0.12 V. Potential values are expressed with E_{OCP} as zero reference.

Electrochemically aged samples were named after their alloy composition (B555), followed by the letters “EL” (for “electrochemical”).

II.6.3 Counterfeiter's aging

The counterfeiter's aging (CF) replicated a method published by a prison guard in a book in which he gathered the information received by a famous forger in prison [26]. The method consisted in several steps (**Figure 40**): (1) first, the metal samples were placed on hot coals for few hours; (2) then, they were placed inside an all-purpose soil (COMPO, pH 7.8 as declared by the manufacturer) with an underlayer of expanded clay, in plastic box with small apertures at the bottom to avoid stagnation of liquids. The soil-metal system was first watered with a universal fertiliser (ORVITAL S.P.A., containing 7% of Ammonium phosphate dibasic ($(\text{NH}_4)_2\text{HPO}_4$) and 3% of Ammonium phosphate monobasic ($(\text{NH}_4)\text{H}_2\text{PO}_4$)), and then covered with fresh smashed tomatoes. (3) The system was placed outside in place sheltered from rain and direct light, and periodically watered with a simplified synthetic urine solution, made by 2% w/V NH_2CONH_2 and 1.2% w/V NaCl in water.

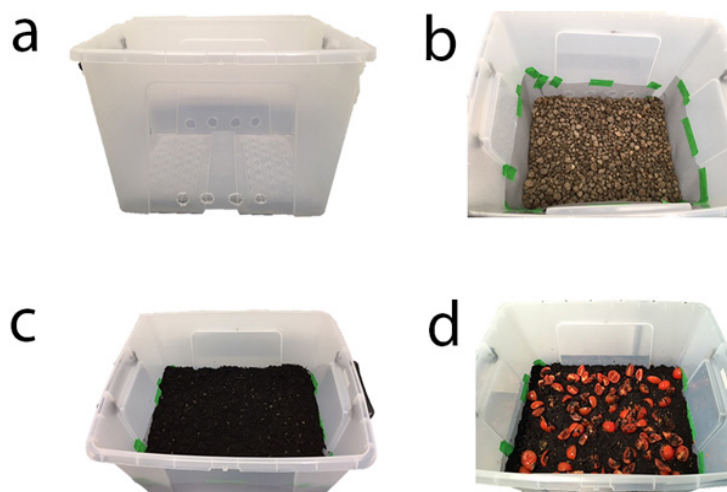


Figure 40 Subsequent steps for the setting of the CF aging system. a) Box with small apertures. b) Underlayer of expanded clay. c) All-purpose soil layer, in which coins are inserted and then watered with universal fertiliser. d) Top covering with mashed tomatoes.

Group of samples were extracted from the aging system at different times, two-to-three samples per alloy type each time. Once extracted, they were carefully cleaned from the soil in excess mimicking the action of a conservator, by using ethanol as softening agent. After this, they were left dry and then stored in vacuum.

Samples were named after its alloy composition (B555 or B774), followed by the letters “CF” (for “counterfeiter”) and a sequential numbering from 1 to 4, indicating the sequence of samples extraction from the aging system, which was as follows: 16 days (CF1), 45 days (CF2), 120 days (CF3), 150 days

(CF4). Samples marked as “CF0” indicates samples that were only left on hot coals for few hours and were not aged further.

II.6.4 Cross-section preparation

Aged samples were manually cut with a jewellery saw and embedded in a polyester resin (PRESI 2S). Embedded samples were mechanically polished with SiC abrasive papers from P240 to P2200, finished with diamond paste up to 1 μm and rinsed with Milli-Q water and ethanol.

II.6.5 Characterisation techniques

Micro-Raman Spectroscopy: Raman spectra were collected using a Thermo Fisher DXR™3 Raman Microscope (Thermo Fisher Scientific) equipped with a 10x, 50x and 100x optics, reaching a spatial resolution of 1 μm and a confocal depth of 2 μm . The acquisition of Raman modes was made by employing as excitation source a 532 nm laser (power between 0.2 mW and 2 mW) in continuous wave mode. All the spectra were collected in the spectral range 3550-78 cm^{-1} . Acquisition time and accumulations were optimised for each sample (varied between 0.5 and 2 seconds of acquisition time, with 50 to 200 accumulations). The spectra analysis was performed operating with OMNIC Software supplied by the instrument manufacturer, and they were automatically corrected for fluorescence by the software using a polynomial curve fitting. Reference spectra were taken on KBr pellets of pure compounds on the same instrument and with similar acquisition parameters.

Optical Microscopy: Optical investigations were performed with two systems: the optical microscope included in the micro-Raman instrument, equipped with 10x, 50x and 100x objectives, plus a Zeiss Axioplan Optical Microscope, equipped with 5x, 20x and 50x objectives.

SEM-EDS: SEM investigations on cross-sections were performed employing a Zeiss EVO® MA 25, equipped with a backscattered electron detector. Cross-sections were fixed on a stub with a conductive tap and sputtered with graphite (ca. 200 nm thickness) prior to the analysis. Element analysis was performed with an X-MAX 80 mm² EDS probe (Oxford Instrument). An accelerating voltage of 25 kV and a current between 400 - 800 pA were used. EDS maps were acquired for a total time of ca. 30 min, while spot analyses for 180 s.

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Chapter III Results and Discussion

III.1 μ XCT for the Non-Invasive and Time-efficient Identification of Roman Copper-based Coins

In the work reported in this section, X-ray Computed Micro-Tomography (μ XCT) was utilised as a non-destructive and non-invasive method to recover the original surface features and reveal the characteristics of encrusted, illegible Roman copper-based coins before any mechanical cleaning process is performed. The 11 coins analysed were retrieved from the topsoil during an archaeological survey in the countryside of the ancient city of Aquileia, Italy, and were severely degraded, covered with accumulated matter and pronounced soil deposits developed over centuries of burial. After being scanned, they were cleaned using traditional mechanical methods by hand of a conservator and the results compared by a numismatist with the digital cleaning achieved via μ XCT. One additional coin (coin D), which was mechanically cleaned prior to this study, was scanned by μ XCT once cleaned. XRF was further used to confirm coins attribution and reveal the influence of different alloy composition on the applicability of the μ XCT method, as well as on the corrosion process of the coins.

III.1.1 Results of coins identification via μ XCT vs traditional cleaning

The 12 coins analysed via μ XCT were classified into different groups based on the level of identification achieved. Group A (Figure 41) includes five coins that were fully identified, while Group B (Figure 44) comprises five coins that were partially identified. One coin was illegible and placed in Group C (Figure 45), while Group D (Figure 46) consists of one coin that was cleaned before undergoing μ XCT scanning. Metrological data of coins before and after mechanical cleaning are reported in Table 9. For each coin, a numismatic interpretation based on the tomographic data is provided, along with a comparison of the results obtained through traditional cleaning methods.

Sample	ID Numbers	Before cleaning		After cleaning		
		Diameter <i>mm</i>	Weight <i>g</i>	Diameter <i>mm</i>	Weight <i>g</i>	Thickness <i>mm</i>
A1	20.S239-2.2549	29.2	7.9	28.8	6.4	2.5
A2	20.S239-2.2565	22.6	3.5	22.9	2.9	3.5
A3	20.S239-2.2568	19.9	2.6	19.5	2.0	2.1
A4	20.S239-2.2569	16.2	1.4	16.4	1.3	1.6
A5	20.S239-2.140602	19.3	1.9	19.3	1.7	2.5
B1	20.S239-2.2496	20.6	2.0	20.6	1.8	1.7
B2	20.S239-2.2556	15.1	2.7	15.0	2.4	2.3
B3	20.S239-2.2560	25.8	8.8	26.3	8.3	3.0
B4	20.S239-2.140524	17.3	1.6	17.3	1.6	1.3
B5	20.S239-2.2501	27.7	8.7	25.9	7.5	3.8
C	20.S239-2.2555	31.4	28.4	31.9	27.9	5.0
D	582411	-	-	15.0	1.6	1.6

Table 9 Metrology of coins before and after their cleaning. Coin D was cleaned prior to the present study. Diameter and thickness are intended as maximum value of multiple taken with a digital calliper and are expressed in millimetres. Weight has been measured with a precision balance and is expressed in grams. Tolerances are ± 0.5 mm and ± 0.1 g, respectively.

III.1.1.1 Group A - Complete identification

Five coins were successfully identified using μ XCT. Reconstructed volumes and 3D rendering techniques based on tomographic data allowed for the determination not only of the numismatic type, but also of the specific coin issue through comparison with reference coins from online repositories. Figure 41 displays images of the coins as they were retrieved from the archaeological site and compares the results obtained from traditional cleaning and μ XCT, along with the reference images used for identification. It is evident that the μ XCT data provided a much higher level of detail of the original surface that was still preserved beneath or within the corrosion layers, thereby facilitating coin identification.

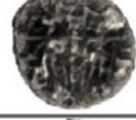
Sample		As-retrieved	Cleaned	XCT-based rendering	Reference
A1	obv				
	rev				
A2	obv				
	rev				
A3	obv				
	rev				
A4	obv				
	rev				
A5	obv				
	rev				

Figure 41 Group A: five coins completely identified using μ XCT. Images of coins correspond to: as retrieved from the excavation site, after cleaning, after 3D rendering based on tomographic reconstructions, and reference images from online repository (with the permission of wildwinds.com [1]). Obverse (obv in figure) and reverse (rev) sides are provided for each coin. Images are not to scale. Full reference data are provided in Table 10. Reproduced from [2]. Images of coins as retrieved and after cleaning are reproduced upon permission of the Ministry of Culture, General Directorate of Archaeology, Fine Arts and Landscape of Friuli Venezia Giulia. Any further reproduction of such images, duplication by any means, as well as downloading and subsequent manipulation, is strictly prohibited.

In the case of coin A1, the analysis revealed the well-preserved profile of *Maximianus Herculius* under layers of accumulated matter and corrosion. The coin has been identified as a proper *follis* issued by the Imperial mint of *Ticinum* (modern Pavia, in Italy) in 300-303 CE or in 304-305 CE. The obverse side

shows the laureate head of the emperor facing right, while the reverse side depicts *dea Moneta* (goddess of Mint) standing, facing left, holding scales with the right hand and *cornucopiae* on the left arm. Results obtained after the cleaning process are consistent with those from the μ XCT analysis only for the obverse side of the coin, displaying the recognisable profile of *Maximianus* with some letters. On the reverse side, however, no traces of the female figure or of the legend found in the tomographic reconstruction can be discerned after cleaning.

Sample	Reference data		Full numismatic legend	Photo with the permission of:
A1	Maximianus <i>Follis</i> (AE1) RIC VI 45b/47b Ticinum (300-303/304-305 CE)	<i>obv</i> <i>rev</i>	IMP C MA[XIMIANV]S PF AVG [SACRA MONET AVG]G ET CAES[S NOSTER]; exergue T ² [T]	wildwinds.com https://www.wildwinds.com/coins/r ic/maximianus/ ticinum RIC_045b .1.jpg
A2	Valerianus I <i>Antoninianus</i> RIC V.1 253 Milan (257-259 CE)	<i>obv</i> <i>rev</i>	IMP VALERIANVS P AVG SAL[VS A]VGG	wildwinds.com ex TimeLine Originals, June 2009 https://www.wildwinds.com/coins/r ic/valerian I/RIC_0253.jpg
A3	Crispus Caesar <i>Nummus</i> (AE3) RIC VII 132 Arles (317 CE)	<i>obv</i> <i>rev</i>	CR[ISPVS NOB CAES] [PRINCIPIA-IVV]ENTVTIS; exergue [QARL]; across the field [R]-S	wildwinds.com ex cng.fr, July 2001 https://www.wildwinds.com/coins/r ic/crispus/ arles RIC_132.jpg
A4	Constans I <i>Nummus</i> (AE3) RIC VIII 88A Siscia (337-341 CE)	<i>obv</i> <i>rev</i>	CO[NSTAN-S PF AVG] GLOR-IA-[EXERC-ITVS]; exergue ASIS [?]	wildwinds.com ex ArtCoinsRoma, July 2012 http://www.wildwinds.com/coins/r ic/constans/ siscia RIC_viii_088.jp g
A4 (O mark)	Constans I <i>Nummus</i> (AE3) RIC VIII 77 Siscia (346- 348 CE)	<i>obv</i> <i>rev</i>	CO[NSTAN-S MAX AVG] GLOR-IA-[EXERC-ITVS]; exergue ASIS [?]	wildwinds.com August 2008 https://www.wildwinds.com/coins/r ic/constans/ siscia RIC_viii_077.jp g
A5	Severus Alexander <i>Denarius</i> RIC IV.1 92 Rome (229 CE)	<i>obv</i> <i>rev</i>	IMP SEV ALE-XAND AVG [PM TRP V]-III-C-OS III [PP]	wildwinds.com ex TimeLine Originals, July 2009 https://www.wildwinds.com/coins/r ic/severus_alexander/RIC_0092.jpg

Table 10 Data of references used for coin identification in Figure 41, and related acknowledgments. Square brackets in legend description contain characters that are expected for the respective numismatic type, but not readable on the coin. Reproduced from [2].

Coin A2 presented a thick layer of dirt and corrosion on both sides, with a portion on the upper part presumably already detached when it was found on site. Nonetheless, μ XCT supported the identification of the coin as an *antoninianus* issued by Valerian I (257-259 CE, mint of *Mediolanum*). On the obverse, the radiate, draped bust of the emperor Valerian I facing right can be observed, while, on the reverse side, *dea Salus* (goddess of Health) appears draped, standing facing right and feeding a serpent held in her arms. The cleaned coin, on the other hand, is scarcely legible on the obverse side, as only traces of a radiate head can be seen. On the reverse side, *Salus* figure can be discerned. Therefore, the coin is only partially readable after cleaning.

The tomographic reconstruction performed on coin A3 revealed the head of *Caesar Crispus*, son of emperor Constantine I, on the obverse side. The coin is identifiable as a small bronze (AE3, *nummus*) issued by the mint of Arles (317 CE) bearing the laureate, draped, and cuirassed bust of the young Caesar facing right on the obverse. On the reverse, the god Mars is standing on the right in military dress, with a coat across the left shoulder, leaning on the shield, and holding a vertical spear, reversed. After mechanical cleaning, the legibility of the coin is still minimal due to its degraded conservation conditions, which further led to a small portion of the *patina* being detached on the obverse. Two letters ('C R', i.e., the beginning of the name *Crispus*) and a detail of the laurel crown were revealed via μ XCT in the area affected by the detachment, while after cleaning only a faint mark of the latter was visible. On the reverse, instead, only Mars' spear is distinguishable.

Coin A4 is identified after the μ XCT analysis as a small bronze (AE3, *nummus*) of Constans I issued between 337 and 341 CE in *Siscia* (modern Sisak, Croatia). It displays the bust of the emperor with a rosette diadem, draped, and cuirassed facing right on the obverse. On the reverse, two soldiers holding spears and shields flank a standard, with the Chi-Rho on the banner. In particular, the mark on the banner was initially identified as an O mark. After the application of a band-pass filter, the Chi-Rho mark became clearly visible (Figure 42), allowing a shift in the dating of the object from 346-348 CE back to a decade earlier. After the cleaning process, the coin shows the faint profile of an emperor with a rosette diadem: the letters 'CON' are visible as well as scarce traces of 'TA' (i.e. the remnants of the name *Constans*). On the reverse, the corrosion makes almost every detail of the struck surface indiscernible. Only the relief of the two soldiers is still recognisable.

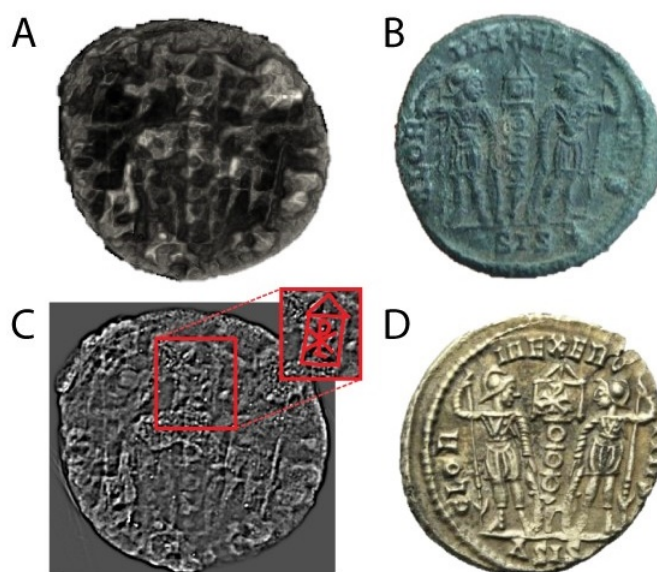


Figure 42 Coin A4: (A) 3D rendering and (B) related identification based on unfiltered μ XCT data. (C) Reconstructed slice after the application of a low-pass filter, with the 'Chi-Rho' mark highlighted in red. (D) Final identification. Reproduced from [2].

Despite the apparently poor condition of coin A5, μ XCT revealed the fine profile of emperor Severus Alexander. The coin can be identified as a *denarius* issued by the young ruler in 229 CE in Rome. On the obverse, it shows the laureate head of the emperor facing right. On the reverse, there is the god Mars helmeted, walking left, holding an olive branch in the right hand, and a spear and shield in the left. Coin A5 is the only one that proved to be almost as identifiable after the traditional cleaning. Figure 43 portrays the obverse side of coin A5, and compares the results achieved by μ XCT and cleaning. It is evident that the level of details of the lettering is finer and more precise on the XCT-based rendering. Furthermore, during the physical cleaning, a small portion of the legend was detached, revealing a silvered but flat surface in the area where the letters 'XA' and part of the letter 'N' (i.e. the remnants of the name *Alexander*) were visible in the 3D rendering, which thus got lost during cleaning.

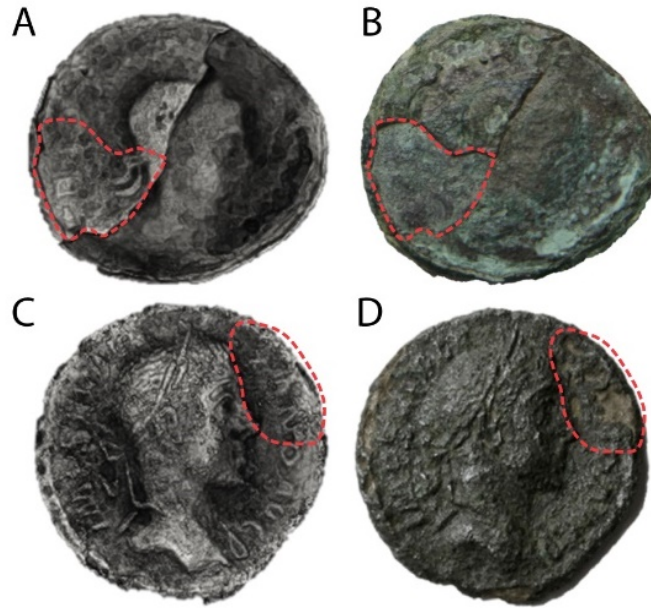


Figure 43 Comparison of the μ XCT-based 3D rendering and photo after traditional cleaning for the obverse side of coins A3 (A: 3D rendering; B: photo) and A5 (C: 3D rendering; D: photo). The flakes fallen off during cleaning phase are highlighted in red. Reproduced from [2]. Images (B) and (D) are reproduced upon permission of the Ministry of Culture, General Directorate of Archeology, Fine Arts and Landscape of Friuli Venezia Giulia. Any further reproduction of such images, duplication by any means, as well as downloading and subsequent manipulation, is strictly prohibited.

III.1.1.2 Group B - Partial identification

Figure 44 summarises the results of the five coins where μ XCT has successfully retrieved all surviving details of the original surface, but it was not sufficient for a complete identification of the coins. μ XCT allowed to distinguish between the obverse and reverse sides, revealing faint traces of the head profiles of issuing emperors, two radiate (B1, B2), two laureate (B3, B4), and one not discernible (B5). In three instances, glimpses of a standing figure on the reverse were visible, two male (B2, B3) and one female (B1). The reverse of B4 remained illegible. On the reverse of coin B5, an 'S' mark is visible, oddly appearing as a hollow cavity. Overall, the metrology and the partial details provided by μ XCT allowed for hypothetical identification as two small bronze denominations (AE3) possibly from the 4th century (B2, B4), an *antoninianus* possibly from the mid-3rd century (B1), and two Imperial *asses* (B3 and B5), the first of which might be attributed to a Flavian emperor based on the profile emerged with the μ XCT. All coins in Group B displayed features after cleaning that are comparable to the ones observed on the virtually restored ones.

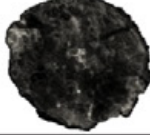
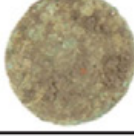
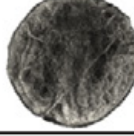
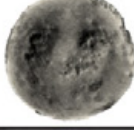
Sample		As-retrieved	XCT-based rendering	Cleaned
B1	obv			
	rev			
B2	obv			
	rev			
B3	obv			
	rev			
B4	obv			
	rev			
B5	obv			
	rev			

Figure 44 Group of five coins partially identified using μ XCT. Images display (from left to right, for each single row): coin as retrieved from the excavation site, 3D rendering based on tomographic reconstructions, coin after cleaning. 'obv' and 'rev' stand for obverse and reverse side. Images are not drawn to scale. Images of coins as retrieved and after cleaning are reproduced upon permission of the Ministry of Culture, General Directorate of Archaeology, Fine Arts and Landscape of Friuli Venezia Giulia. Any further reproduction of such images, duplication by any means, as well as downloading and subsequent manipulation, is strictly prohibited.

III.1.1.3 Group C and D

Coin C, tentatively identified as a Republican *as* according to numismatic evaluation, showed no visible signs of the original surface under μ XCT (Figure 45) due to severe beam hardening effects. Nevertheless, the coin showed a completely worn surface after the cleaning process, most likely due to severe corrosion.

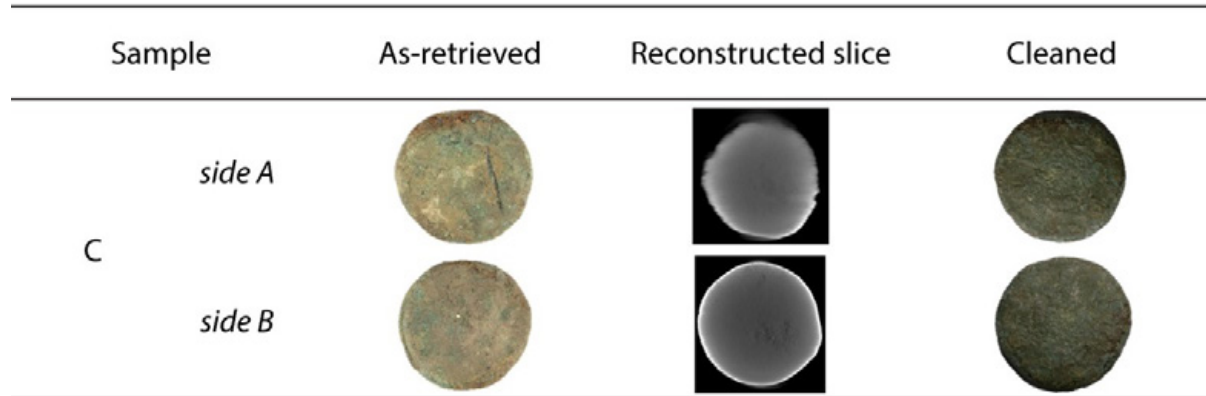


Figure 45 Coin C, completely illegible under μ XCT. Images display (from left to right, for each single row): coin as retrieved from the archaeological site, a representative slice from the tomographic reconstruction, coin after cleaning. Side A and side B indicate the two faces of the coin, since the conservation conditions did not allow to recognise obverse and reverse. Images of the coin as retrieved and after cleaning are reproduced upon permission of the Ministry of Culture, General Directorate of Archaeology, Fine Arts and Landscape of Friuli Venezia Giulia. Any further reproduction of such images, duplication by any means, as well as downloading and subsequent manipulation, is strictly prohibited.

Unlike the other coins analysed in this work, Coin D has been subjected to a physical cleaning prior to μ XCT scanning, without any success in retrieving useful information for its identification. The tomographic reconstruction revealed the presence of the letters ‘S C’ (Figure 46 and Figure 47) presumably standing for ‘*Senatus Consultum*’, interpreted as a hint to the authority acknowledged to the Roman Senate over the minting of copper-based coinage. This mark was commonly present on the reverse side of copper-alloy coins until the period of *Diocletianus* (ca. 294 CE) [3,4].

To conclude, there has been no case of mis-identification between virtual and mechanical cleaning.

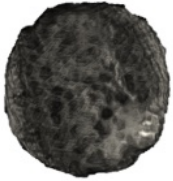
Sample		As-retrieved	XCT-based rendering
D	obv		
	rev		

Figure 46 Single coin cleaned before tomographic analysis and revealing an ‘S C’ write on a side. (left) Optical photograph and (right) 3D rendering based on μ XCT data. ‘obv’ and ‘rev’ stand for obverse and reverse side. Images are not to drawn scale. Images of the coin as retrieved are reproduced upon permission of the Ministry of Culture, Regional Directorate of Museums of Friuli Venezia Giulia. Any further reproduction of such images, duplication by any means, as well as downloading and subsequent manipulation, is strictly prohibited.

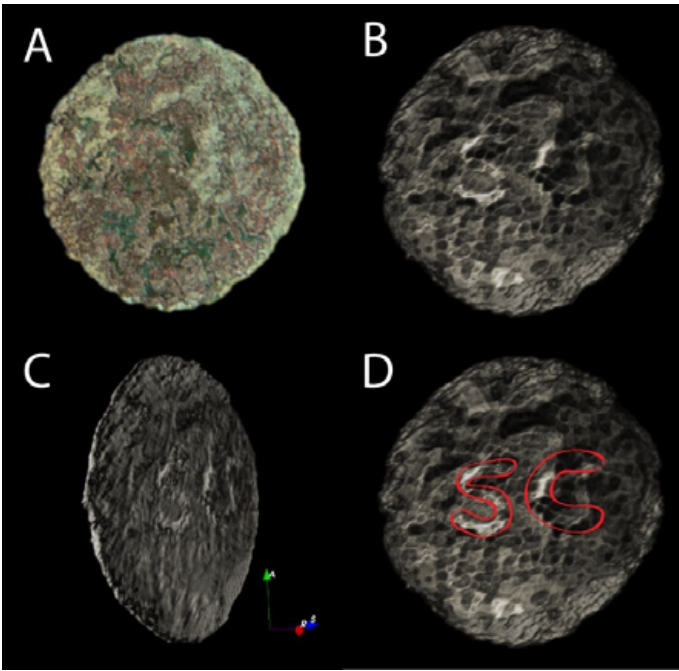


Figure 47 (A) Coin D. (B) Single slice from the tomographic reconstruction. (C) 3D rendering based on tomographic data (D) ‘S C’ mark highlighted in red on top of (B). Reproduced from [2]. Image (A) is reproduced upon permission of the Ministry of Culture, Regional Directorate of Museums of Friuli Venezia Giulia. Any further reproduction of such images, duplication by any means, as well as downloading and subsequent manipulation, is strictly prohibited.

III.1.2 Verification of coins denomination using XRF

The XRF analysis was performed after the mechanical cleaning to confirm the identification of the coins in terms of typology. While XRF is commonly used to estimate the elemental composition of materials, the presence of thick alteration layers and accumulated matter on corroded ancient coins makes it challenging to achieve precise quantification of the bulk composition [5]. Therefore, in this context, the XRF data have been treated as semi-quantitative information regarding the constituent material of the coins. Complete results are provided in Table 11. As expected, Cu was found to be the primary component in all the coins, with a content varying from 46 to 97 mass percentage (wt.%). The significant presence of common alloying agents for Roman copper coins, such as Ag, Sn, and Pb, was attested in most coins. Zn, on the other hand, was found only in coin B2 as a trace element. Contamination from soil elements (Mg, Al, Si, Mn, P) was observed in all the analysed coins [6]. A small amount of Cl was detected only on coin A3, locally reaching 1.7 wt.%. The surface of this coin after cleaning presents a powdery pale green corrosion product diffused on both sides, but more concentrated in some areas, suggesting an ongoing bronze disease process [7].

# Sample	Al	Si	P	S	Cl	Ca	Ti	Mn	Ni	Fe	Cu	Zn	Ag	Sn	Pb	Sum
A1	1.65 ± 0.09	0.10 ± 0.07	0.24 ± 0.08	0.8 ± 0.2	-	2.6 ± 0.9	0.13 ± 0.01	0.05 ± 0.03	0.02 ± 0.01	1.5 ± 0.2	62.6 ± 4.2	-	6.4 ± 1.1	12.2 ± 1.7	11.8 ± 2.1	100.10
A2	2.4 ± 0.2	1.3 ± 0.4	0.01 ± 0.01	0.29 ± 0.08	-	5.0 ± 2.4	0.22 ± 0.08	Trace	0.02 ± 0.01	0.49 ± 0.05	58.2 ± 12.4	-	31.8 ± 12.1	-	0.37 ± 0.06	100.10
A3	1.4 ± 0.2	0.6 ± 0.2	Trace	0.26 ± 0.08	0.5 ± 0.3	1.9 ± 1.0	0.14 ± 0.01	Trace	0.04 ± 0.01	0.28 ± 0.04	61.5 ± 6.8	-	2.4 ± 0.9	12.1 ± 1.9	19.0 ± 7.1	100.11
A4	1.4 ± 0.2	0.5 ± 0.3	Trace	-	-	0.8 ± 0.2	0.13 ± 0.01	-	0.06 ± 0.02	0.34 ± 0.08	56.1 ± 7.2	-	2.0 ± 0.5	12.6 ± 2.0	26.2 ± 5.4	100.13
A5	3.0 ± 0.2	0.5 ± 0.1	0.05 ± 0.03	1.7 ± 0.2	-	0.7 ± 0.2	0.12 ± 0.01	-	0.03 ± 0.01	0.14 ± 0.04	46.1 ± 3.4	-	47.5 ± 3.1	-	0.26 ± 0.08	100.10
B1	1.49 ± 0.09	0.36 ± 0.09	0.16 ± 0.03	-	-	1.0 ± 0.2	0.12 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	1.5 ± 0.2	66.1 ± 2.6	-	5.3 ± 0.9	18.6 ± 1.9	5.4 ± 0.9	100.10
B2	1.0 ± 0.1	0.33 ± 0.1	0.7 ± 0.2	0.09 ± 0.02	-	0.96 ± 0.09	0.10 ± 0.01	0.01 ± 0.01	0.03 ± 0.01	0.9 ± 0.2	61.2 ± 2.0	0.07 ± 0.02	0.15 ± 0.01	25.6 ± 1.7	9.0 ± 0.4	100.14
B3	2.10 ± 0.05	0.30 ± 0.06	0.05 ± 0.01	0.09 ± 0.01	-	0.5 ± 0.2	0.10 ± 0.01	0.02 ± 0.01	Trace	0.23 ± 0.05	96.6 ± 0.2	-	-	-	-	99.97
B4	1.63 ± 0.05	0.02 ± 0.02	0.10 ± 0.02	-	-	0.53 ± 0.03	0.12 ± 0.01	0.01 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	69.3 ± 0.8	-	-	-	28.2 ± 0.8	100.02
B5	1.93 ± 0.08	0.8 ± 0.4	0.15 ± 0.06	1.5 ± 0.6	-	0.4 ± 0.1	0.11 ± 0.01	Trace	Trace	0.16 ± 0.04	95.0 ± 1.1	-	-	-	-	100.04
C	1.5 ± 0.1	0.9 ± 0.2	-	0.11 ± 0.03	-	1.6 ± 0.3	0.18 ± 0.01	Trace	0.02 ± 0.01	2.4 ± 0.6	67.0 ± 4.1	-	-	18.4 ± 1.3	7.9 ± 2.7	100.02
D	2.4 ± 0.1	2.1 ± 0.4	0.10 ± 0.01	-	-	1.2 ± 0.2	0.15 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	1.2 ± 0.2	92.8 ± 0.9	-	-	-	-	99.97

Table 11 Semi-quantitative results from XRF analysis, in mass percentage (wt%). Each measurement has been conducted in triplicate on each side of coins, at different spots. The results shown are the mean of the six measurements, normalised to 100%. The error is estimated as the standard deviation of the mean. For all the coins, Al, Si, Ca, Ti, Ni and Fe were detected and considered as soil contamination or part of corrosion compound. The same applies to traces of Mn, P and Cl occasionally found. Elements marked as 'Traces' are visible in the XRF spectrum, but with values lower than 0.01.

The XRF data confirm the identification of coin types as indicated by tomographic reconstructions and numismatic evaluation. As expected from their presumed numismatic type, coins A2 (*antoninianus*) and A5 (*denarius*) show a high proportion of silver in the alloy [8,9], whereas coins A3, A4 (two *nummi*), and A1 (a *follis*) only contain minimal amounts of silver, but significant amounts of tin and lead [3,9–14]. The lower amount of Ag for coin B1 suggests that it could belong to a late *antoninianus* [8], which is consistent with the numismatist's evaluation. The presence of lead and tin in coin C supports its identification as a Republican *as* [15,16]. The binary Cu-Pb and ternary Cu-Sn-Pb (with traces of Ag) alloys of coins B4 and B2, respectively, are compatible with 4th-century *nummi* from different periods [3,8,10–12], while the lack of alloying agents in coins B3 and B5 is typical of Imperial *asses* [9,17]. Coin D appears to be made of pure copper, which, together with the 'S C' mark and the metrology, suggests its identification as a fraction of the *as* of the Imperial era. The absence of zinc, traditionally linked to *sestertii*, further supports the proposed interpretation of the coin types.

III.1.3 Beam hardening and BH correction

Beam hardening has been observed in all the tomographic reconstructions. In our case, beam hardening prevented the retrieval of any kind of information from the core of the objects. Despite this, the outer surface of the coin was always visible in the tomographic reconstructions, except for the case of coin C (Figure 45). The presence of beam hardening possibly indicates that the coins have residual metallic bulk within.

After the application of the BH correction, the contrast increases, highlighting, thus, the lettering along with other details. Figure 48 reports an example of the effects of the BH correction on the dataset. In order to quantitatively evaluate these effects, the contrast at the two opposite sides of the emperor head (in two distinct ROIs marked in red and yellow, respectively) has been calculated before and after the application of BH correction, using the following expression:

$$C = \frac{L2 - L1}{L2 + L1}$$

where L1 and L2 are the intensity values at the selected points along the intensity profiles shown in Figure 48b. An image contrast increment (i.e. clearer distinction of features) of 15% (red ROI) and 20% (yellow ROI) can be observed.

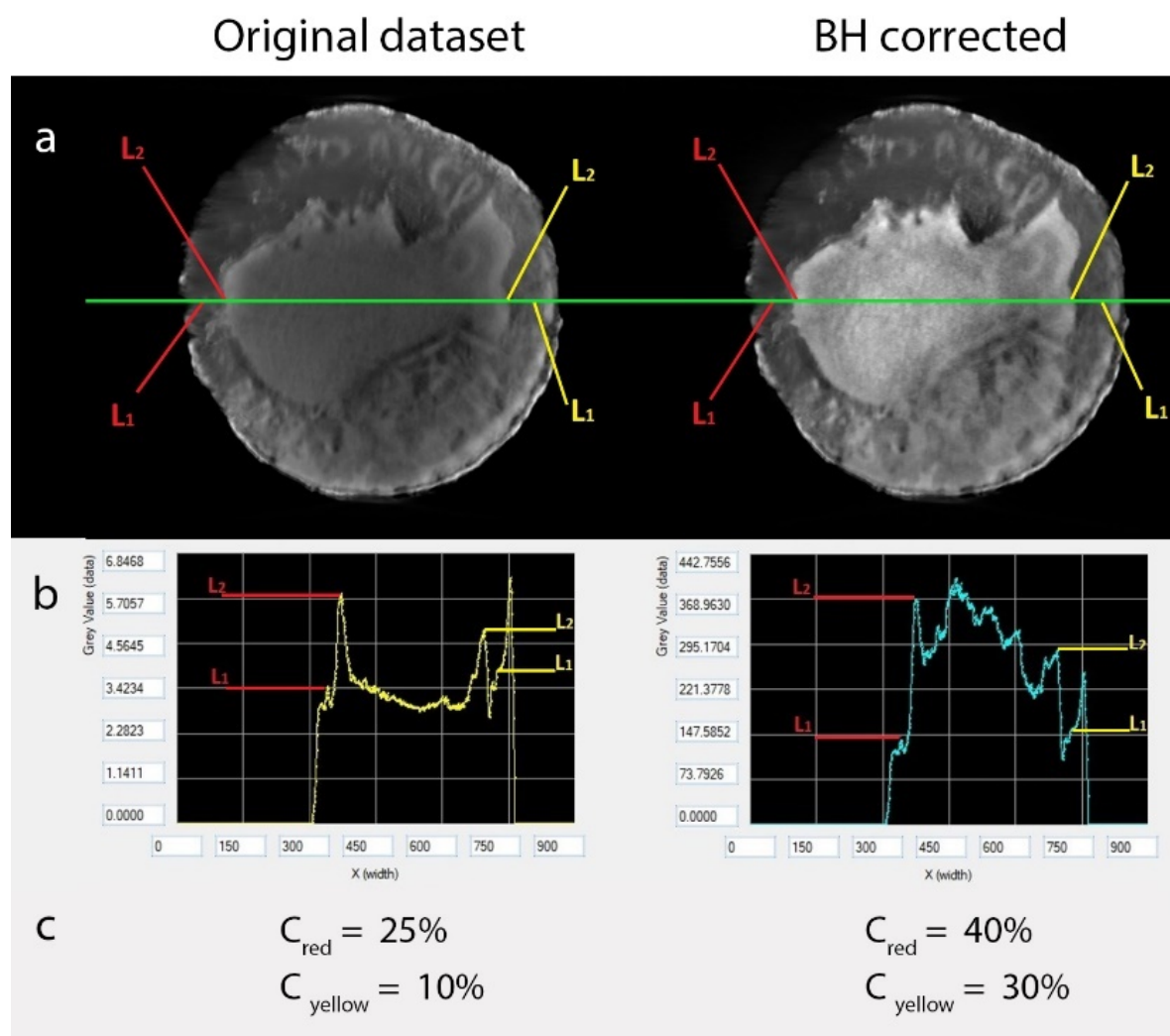


Figure 48 Example of the effects of BH correction on coin A5 (obverse). a) Two corresponding slices from the original dataset (left) and from the BH corrected one (right) are reported. The green line indicates localization where the intensity profiles (shown in b)) are taken. L1 and L2 markers of corresponding colors (red and yellow) indicate, in both slices and intensity profiles, the same pixels, which have been used for the calculation of the contrast reported in c). Specifically, C_{red} has been calculated using the red L1/L2 marker, C_{yellow} has been calculated using the yellow L1/L2 markers.

III.1.4 Notes on image processing

It is important to notice that the complete extraction of any surviving detail from the original surface of the coins was already achieved after the basic steps listed in par. II.2.3 (i.e.: datacube splitting, small angular corrections, dynamic navigation through slices, basic math operations to neighbour slices), as can be observed from the comparison between 3D renderings and physically cleaned coins in Figure 41 and Figure 44. In particular, the application of small angular corrections proved to be significantly helpful in enhancing features extraction, by allowing to align the coin faces perpendicularly to the slicing direction (Figure 49).

In the case of coin A4 (Figure 42), a low-pass filter has been further used in order to remove higher frequency features, correlated to noise and corrosion, and enhance the reading of the mark on the banner. The latter represents the only case in which an elaboration step, additional to angular correction and basic math operations, was needed. Further elaborations, such as image filtering, have been attempted on all coins, but they did not led to the discovery of any further information. For such reason, all the images reported in the manuscript come from unfiltered data (excepting Figure 42 C).

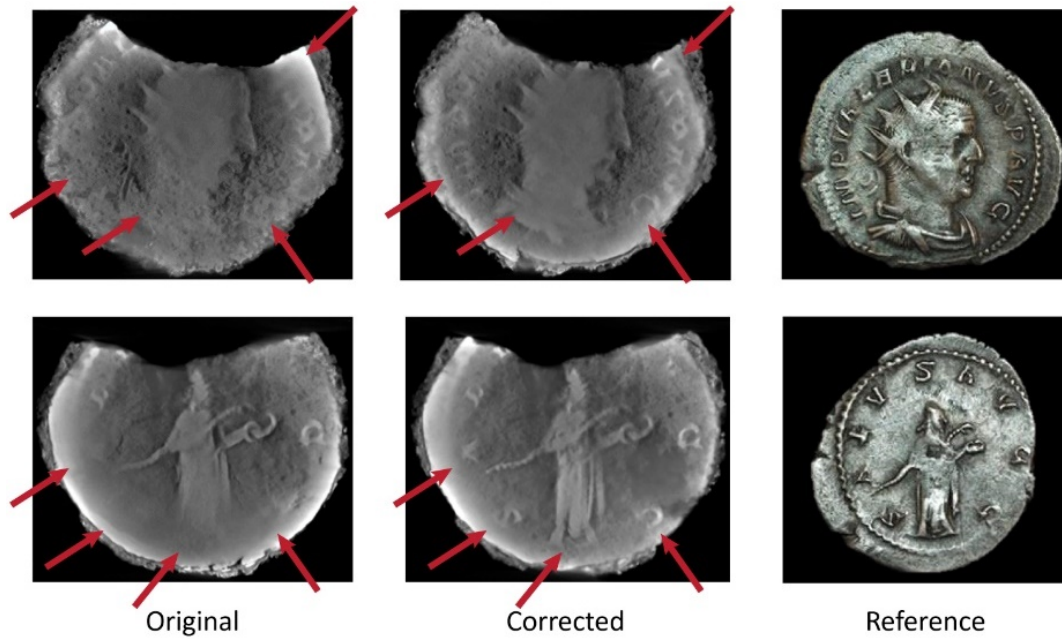


Figure 49 Example of a slice from the tomographic reconstruction of coin A2 to highlight the effect of angular correction on its readability: original (left), after correction (middle), and reference image (right). Obverse (top) and reverse (bottom) are both provided. Red arrows indicate major changes following angular correction.

3D renderings, instead, have been mostly employed for communication purposes. In fact, only 3D renderings allowed for the display of all the details of a coin side and thus for summarising the results obtained in a single, static image. However, 3D renderings may also support the extraction of information, in particular thanks to the dynamic lighting capabilities, and they also open the way to a plethora of further applications, from virtual cleaning to digital twinning.

Lastly, it must be noted that, even if a minimum in the intensity histogram of datacubes could be observed, segmentation by global thresholding from such distribution provided only limited results. Figure 50 shows the cross-sectional views of coin A3 as example, with all other coins showing a similar behaviour. This entails that a complete separation between bulk and corrosion feature could not be done by automatic analysis.

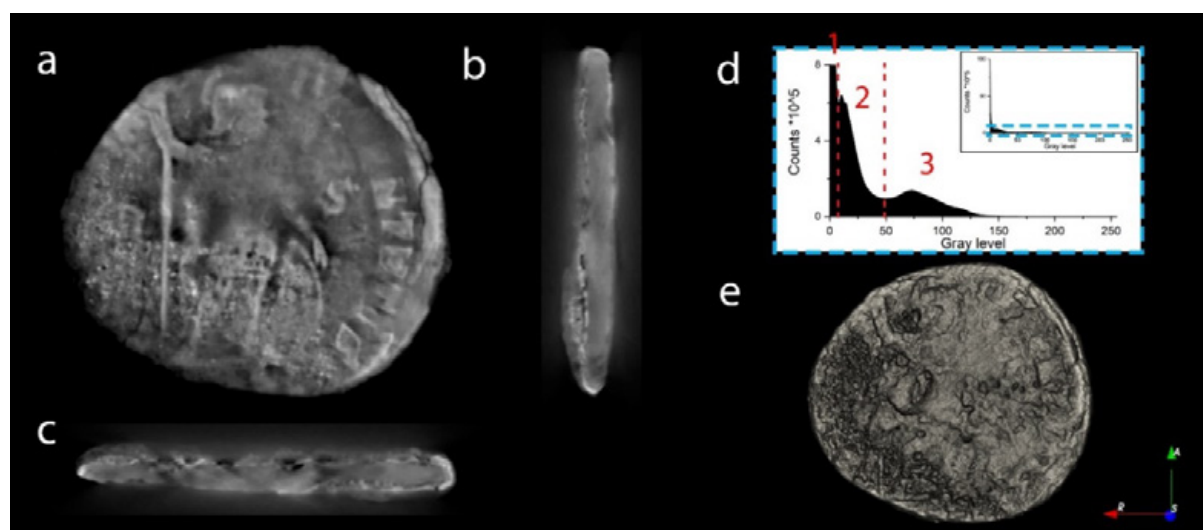


Figure 50 a) Slice from the reverse side of coin A3. b) and c) cross-sectional views of the coin. d) Intensity histogram of the full datacube. Onset: full-scale histogram. Main figure: zoom on the lower zone. Region marked with '1' is linked to noise. e) 3D volume rendering after segmentation by global thresholding at the minimum between regions '2' and '3' in the histogram d), considering only the pixels above this threshold.

III.1.5 Discussion

III.1.5.1 Effect of Pb content

Despite the reports on the detrimental effects of Pb on the identification process [18], in this work it appears that its sole presence, in amounts compatible with Roman coinage, does not represent a limiting factor. In fact, all coins of Group A have been identified despite the presence of Pb up to 26 wt.%. It should be noted that XRF on corroded coins tends to overestimate Pb content [5] due to high self-absorption effects given by this element, and literature data for coins similar to A1 report a range of values from 1 to 10 wt.% [14]. However, when a high content of Pb is coupled with increased coin thickness, the readability appears to be hindered. This is the case with coin C, for which the tomographic reconstruction showed a low level of readability due to high absorption effects and consequent low counting of transmitted photons, which also limited the a posteriori correction of beam hardening. Coin C is an alleged Republican *as*, i.e., a class of coins that usually presents a high thickness (5 mm) and a significant Pb content [15–17]. On the other hand, coins that exhibit only a high thickness with no significant Pb content (Imperial *asses*, coins B3 and B5) have been reconstructed via μ XCT without issues. It is important to note that 3rd-century *nummi* and late *antoniniani* fall well within the range of applicability of μ XCT. This is particularly important to note since the majority of large hoards of ancient Roman copper-based coins are comprised of *nummi* and *antoniniani* [19,20].

It is clear that the readability of a coin is affected only when a high absorbing element such as Pb is present along with a significant object thickness. However, the effects of high absorbing coins can be mitigated by using high-energy X-ray sources that increase the number of transmitted photons [21]. Although we successfully applied our identification method to the most common Roman copper-based coin typologies using a standard 150 kV setup, the use of dedicated high-energy systems can broaden the applicability of the method to include all remaining typologies. μ XCT setups with high-energy source are available both commercially as lab-based instruments [22], and in specific synchrotron beamlines (such as the ESRF) [23]. Although synchrotron-based μ XCT represents a less accessible option, it can boast a high level of resolution, potentially addressing the requirements of individual challenging cases.

III.1.5.2 Effect of Ag content

A correlation between the material of the coins and the conditions of their original surface can be observed. The coins that have silver in their composition appear to be in a better state of preservation. This may seem obvious for Ag-rich coins, such as coins A2 and A5. However, for the other three coins of group A, we can hypothesise that their preservation is due to the mechanism of Type I *patinas* in copper-tin alloys, as defined by Robbiola et al. (1998). This process involves the formation of a semi-protective inner layer consisting of tin compounds, which effectively controls the ongoing corrosion of objects over extended periods. As a result, it facilitates the enhanced preservation of surface details. In copper-tin alloys, this mechanism typically does not occur in aggressive environments, like the lagoon, due to the fast initial dissolution rate of copper. Silver, on the other hand, can play a similar role to tin but form stable compounds even in aggressive environments. The formation of a layer of silver compounds, such as Ag_2O or AgCl , can mediate the ion flux inward and outward [57,58], slowing down the overall corrosion process and resulting in better preserved surface morphologies of copper-based silver-containing coins. Additionally, silver may be more concentrated near the original surface due to selective dissolution of copper [24], or due to artificial surface enrichment typical for these class of coins [25–29]. Thanks to its natural resistance to corrosion, a local enrichment of silver may enhance its effect on the preservation of the original surface morphology. This may also facilitate the identification of the coins due to the higher contrast that silver provides under X-ray irradiation.

III.1.5.3 Corrosion patinas under μ XCT

The analysis of the tomographic data, supported by 3D renderings and post-cleaning documentation, suggests that the information necessary for coin identification is often stored within the corrosion *patina*, rather than on the surface of the residual bulk metal. For example, the observed side of coin B5

exhibits a corrosion *patina* with a thickness similar to that of the residual bulk. Within that *patina*, some details can be discerned, while the bulk metal only exhibits a completely worn surface.

This phenomenon may be due to X-ray absorption contrast arising from a concentration step in metal ions at a certain position within the *patina* [30]. This position may correspond to the interface between the secondary *patina*, formed by the re-deposition of outward-diffusing metal ions mixed with soil compounds, and the primary *patina*, constituted by in-place oxidised metal atoms and inward-diffusing anions from the environments. The topology of this interface, which barely corresponds in position to the original surface of the coin, may hold memory of the latter and thus reveal the stored information under X-ray tomography, as also suggested by Scott and Bertholon [31,32].

The tomographic analysis of coin D does not provide a clear indication of whether the information necessary for identification is preserved within the *patina* or on top of the residual bulk. In the latter case, the original metallic surface may not have been completely disrupted by the corrosion process and could be covered by a layer of secondary corrosion products that appears as a surface smooth enough to flatten the details of the original surface (such as the 'S C' mark) and compact enough to resist removal during the cleaning process. Similar observations have been previously reported as a deviation from the Type I *patina* [24]. Without any visible signs of residual original surface details, the cleaning of the coin was stopped to prevent any risk to its structural integrity. However, the use of μ XCT allowed us to retrieve the hidden information easily and without any risk.

It is important to note that some corrosion *patinas* of copper objects are brittle, poorly adherent, and can be easily removed under mechanical stress. Invasive manipulation of copper coins can pose significant risks to their structural integrity. This was demonstrated in the case of coins A3 and A5, where the removal of corrosion flakes resulted in the loss of lettering details and poor legibility (as shown in Figure 43). However, the use of tomographic data acquired before cleaning allowed us to retrieve and digitally preserve this information.

The effectiveness of μ XCT in identifying coins is further highlighted in cases where traditional cleaning methods leads to the inevitable loss of information due to the presence of *bronze disease*. The topological information stored within the affected zones may be lost due to invasive cleaning and resulting mechanical stress. Bronze disease by-products, mainly hydroxychlorides, are decoherent and can be easily removed during cleaning, as seen in the case of coin A3. After cleaning, the coin shows a pale green vacancy where a well-defined figure of a soldier was previously visible in the μ XCT scan of the reverse side (Figure 51). Furthermore, the application of μ XCT allows to postpone of the exposure of active compounds to environmental oxygen and moisture, thereby delaying the eventual re-activation

of the autocatalytic decaying process. This provides an opportunity for off-site stabilisation treatment to be undertaken immediately after cleaning, thus preserving the integrity of the coin.



Figure 51 Reverse side of coin A3 (A) before cleaning, (B) virtually cleaned with μ XCT and (C) after traditional cleaning. The loss of most of the figure of a soldier after the invasive mechanical cleaning is evident. Reproduced from [2]. Images of the coin as retrieved and after cleaning are reproduced upon permission of the Ministry of Culture, General Directorate of Archaeology, Fine Arts and Landscape of Friuli Venezia Giulia. Any further reproduction of such images, duplication by any means, as well as downloading and subsequent manipulation, is strictly prohibited.

III.1.6 Summary

This study showcases the effectiveness of μ XCT in archaeological practice and numismatic research for the rapid and non-invasive identification of unprocessed copper-based Roman coins, eliminating the need for manual cleaning. The results demonstrate that μ XCT can retrieve as much information from corroded coins as mechanical cleaning, while surpassing traditional cleaning methods in terms of identifying the numismatic type of the coins and improving time-efficiency.

The findings indicate that μ XCT is applicable for the digital restoration and identification of common types of copper-based Roman coins, including *nummi*, *antoniniani*, *denarii*, *folles*, and Imperial *asses*. Furthermore, the research highlights the risks associated with mechanical cleaning, such as the removal of information-bearing *patina* and corrosion by-products, emphasising the importance of a non-invasive identification process prior to any invasive intervention. A correlation between the presence of small amounts of silver, identified by XRF, and the better state of conservation of copper coins has also been observed and explained in terms of corrosion mechanisms.

The proposed method offers numerous advantages in the study and management of ancient coins. It only requires minimal post-processing, that can be performed with open source software. By scanning collections of uncleaned coins, it significantly reduces the time required for their identification,

addressing the long-standing challenge of large-scale coin analysis. It reduces the need for mechanical cleaning, reducing the risk of irreversible damage and loss of information. Even in cases where cleaning is necessary, the approach minimises potential damage by providing digital preservation of information and guiding conservators in the practice of the micro-excavation of coins. Additionally, the use of μ XCT enables 3D digitisation of the coins, creating virtual replicas that can be included in online repositories and used for scientific dissemination.

The findings of this study reveal that μ XCT surpasses traditional cleaning methods and indicate that the technique should be actively integrated into archaeological and numismatic practice, positively improving the management and preservation protocols of numismatic collections. Overall, μ XCT scanning is a powerful tool that has the potential to facilitate and promote the study and preservation of coins, with broader implications for archaeological practices and beyond.

III.2 FIB-SEM and LA-ICP-MS as novel techniques for corrosion studies

Two micro-invasive techniques, rarely used on metallic heritage, were investigated as potential alternative to invasive sampling in archaeometric and diagnostic study of archaeological copper-based artifacts: FIB-SEM and LA-ICP-MS.

First, an optimised protocol for FIB-deep trenching was developed. Various technical aspects regarding the preparation and the subsequent EDS analysis of deep FIB-cross sections, as well as the complementary use of μ XRF mapping, were investigated. Finally, the application of the developed protocol to an archaeological copper-based coin is reported as proof of concept.

On the other side, 1D elemental depth profiles and 2D/3D elemental maps were obtained by LA-ICP-MS on an ancient Roman coin and a counterfeited ancient Greek electrum coin. The scope in this case was to highlight the potential and limitations of LA-ICP-MS applied to metallic heritage, representing a starting point for future research on the topic.

III.2.1 FIB-SEM: stretching the technological limit to a new level

III.2.1.1 Trench area selection by μ XRF mapping

μ XRF mapping has been used in two different ways to select ROIs where to prepare FIB-milled cross-sections (FIB-CS, or CS). In the first case, a search for superficial enrichment of Ag has been carried out by investigating the ratio between Ag L and K lines. In fact, the information associated with the less energetic X-rays of the L-lines come from a depth of just few μm inside the sample, whereas K-line X-rays come from a much greater depth, in the order of tens of μm . Consequently, if the Ag L/K ratio diverges from the theoretical one for a sample with a uniform distribution of Ag along its thickness, it reveals the presence of a localised enrichment or depletion of this element towards the sample surface [33]. The same principle can be applied to other elements for which two distinct lines are available in the spectrum, even two lines of the same group ($K\alpha$ vs $K\beta$, etc.), even though in this case the difference in the depth of the information is smaller, because the energy of the lines is closer.

The working flow in the present case has been to scan multiple coin samples with μ XRF, then to select areas with an Ag L/K ratio significantly higher than the rest of the sample, and finally to check with SEM-EDS the ROI right before performing FIB trenching (Figure 52).

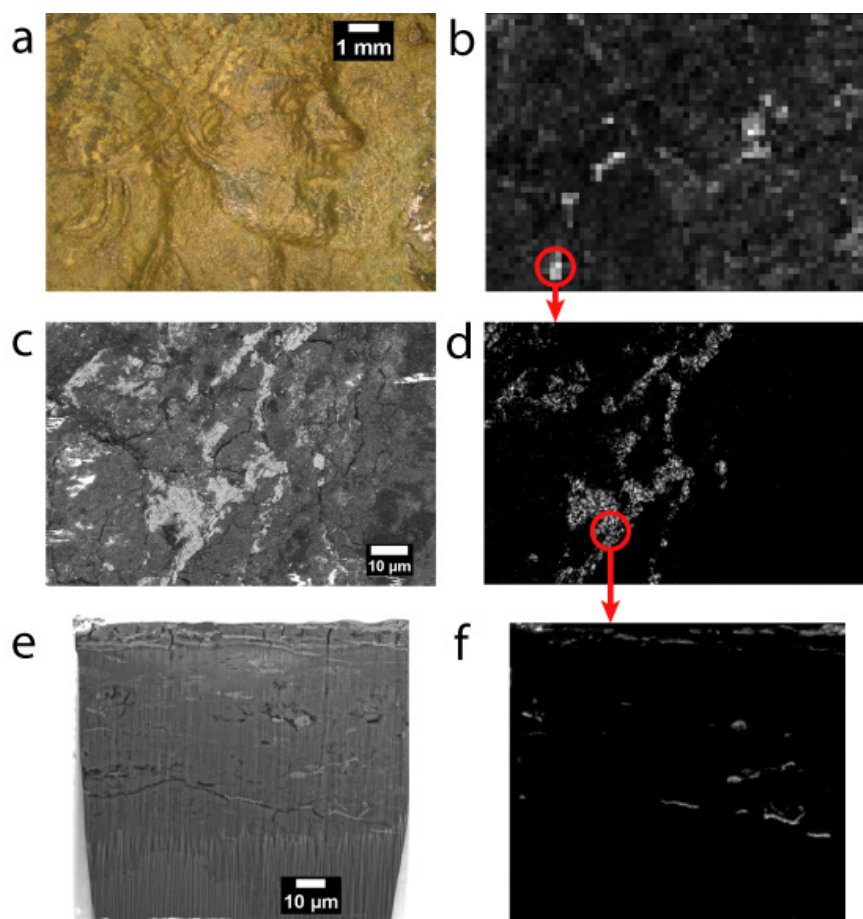


Figure 52 Working flow for the complementary use of μ XRF mapping and FIB cross/sectioning. First, surface enrichment of Ag are detected on (a) coin 587202 using the (b) $Ag\ L/Ag\ K$ map from μ XRF data (b). Following that, (c,d) SEM-EDS is performed to confirm the observation and select the specific place where to perform the (e,f) FIB cross-sectioning. All SEM-EDS data are acquired with the ZEISS system. (d) and (f) are Ag L EDS maps. Red circles marks the proper area selected each time.

The second example of how μ XRF mapping can be used in combination with FIB trenching is the identification of ROIs enriched in soil elements (Si, K, Ca, Al, eventually Fe and Pb if not belonging to the alloy of the sample), which have archaeometric potential as they store information strictly related to the burial environment. As visible in Figure 53, the identification of such areas from XRF data is straightforward.

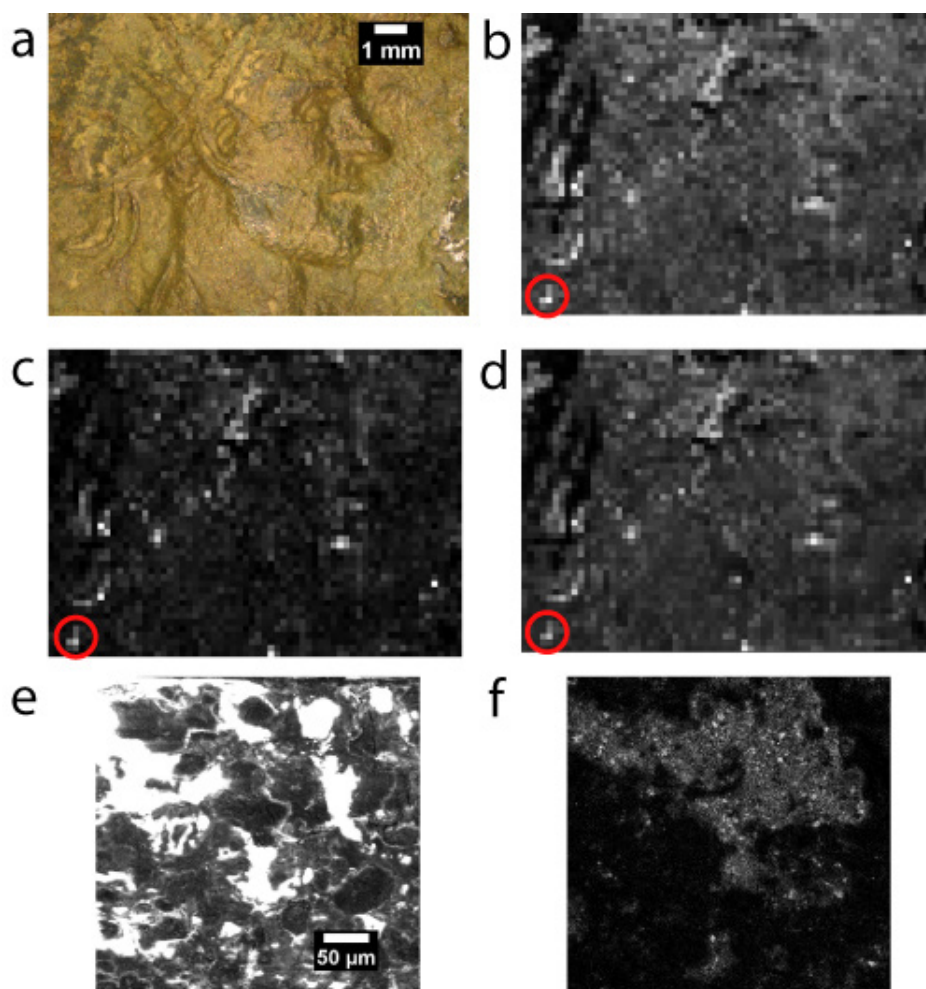


Figure 53 (a) Coin 587202. b,c,d) μ XRF maps of Al K, K K, Si K lines. e,f) SEM and Si K line EDS map of the selected ROI (FEI system). The resulting FIB cross-section is shown in Figure 57. Red circles marks the proper area selected each time.

III.2.1.2 Optimisation of trenching strategy

The development of the trenching strategy has started by replicating FIB-milled CSs of standard size (Figure 54 a). Already in the first attempts, archaeological *patinas* have proven to be milled by FIB with high yield. The instrument has a pre-calibrated milling protocol for silicon substrates, and milling parameters are expressed in terms of actual μm of milled material desired. While the same x and y parameters (defined as the axes in the plane of the sample surface) are reproducible across different samples, the z parameter (the milling depth) is strongly material-dependent. It has been observed that, in the case of archaeological coins covered by thick patinas, trenches milled with a z parameter set below 10 μm achieved an actual milling depth above 150 μm .

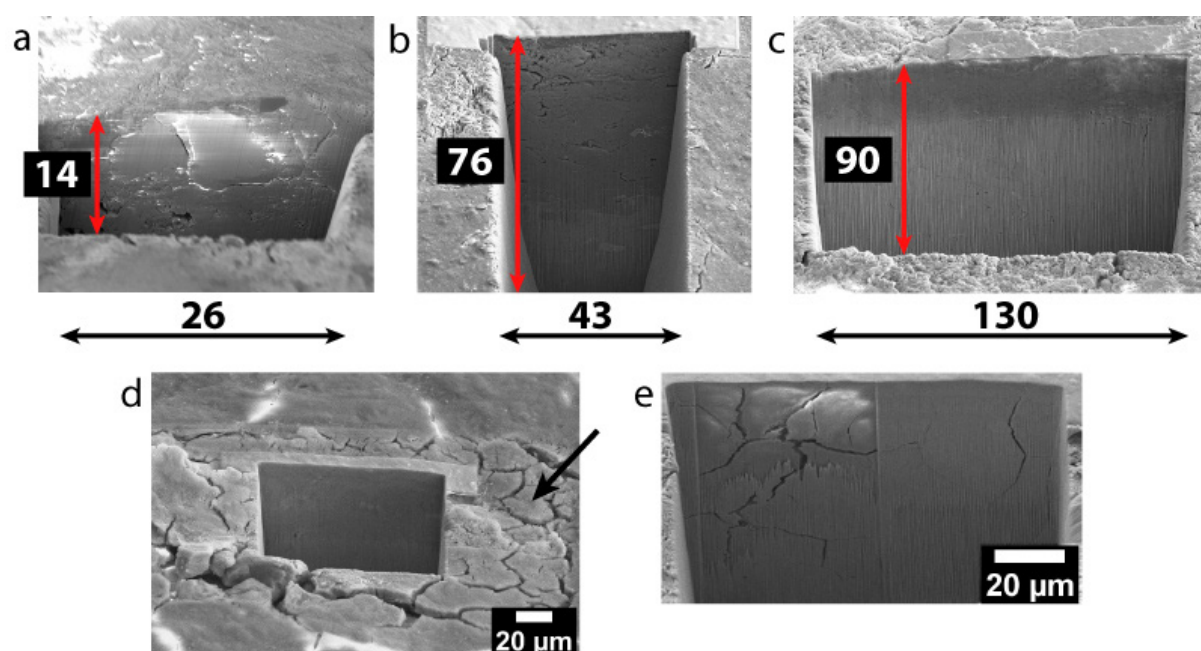


Figure 54 a,b,c) FIB-milled trenches of increasing size on various archaeological copper-based Roman coins. a) coin D, b) 587202, c) 579676, d,e) 579692. Reported length are in μm . Milling depth (in red) is measured taking into account perspective effects. d) FIB-milled trench using a 47 nA current. e) Detail of the CS showed in d). Images a,b,c and d are taken with the FEI system (SEM-SE, 52° , at 2, 10, 15 and 30 kV, respectively). Image e is taken with the JEOL system (SEM-SE, 40° , 10 kV).

Subsequent trenching attempts on various coin samples achieved a gradual increase in the size of the cross-section (CS) wall (Figure 54 a,b,c), while remaining below the threshold of detection with naked eye. Different current settings for the Ga^+ ion gun have been tested. In particular, higher currents allow for faster milling, but also increase the amount of milling artefacts. 21 nA has been selected as the best trade-off between trench quality and milling time. In fact, by increasing the current one step further at 47 nA, ion beam energy has become too high for the kind of material constituting an archaeological *patina*, causing it to fracture upon interaction with the beam even just during FIB-imaging of the surface (Figure 54 d,e). With the 21 nA FIB beam, instead, no beam-induced fracturing has been observed. Moreover, the opening of trenches of up to $130 \times 200 \times 150 \mu\text{m}$ has taken an amount of time that fitted in an overnight session (14-16h). Since the instrument performs this operation autonomously, letting it carry out the trench opening overnight has allowed for a positive optimisation of the machine shifts.

The prominent formation of stalagmite-like milling effects has been observed for deep trenches, with a severity proportional to the milling depth (Figure 55). To reduce the impact of these effects, known in literature as “curtaining effect” [34], on the quality of the CS, a series of subsequent cleaning steps have been performed, slightly moving the focus of the FIB beam from the surface to the inner part of the sample after each milling step. This targeted cleaning strategy allowed for obtaining sufficiently polished CS walls to be analysed by SEM-BSE and EDS. An example is given in Figure 55 c,d,e.

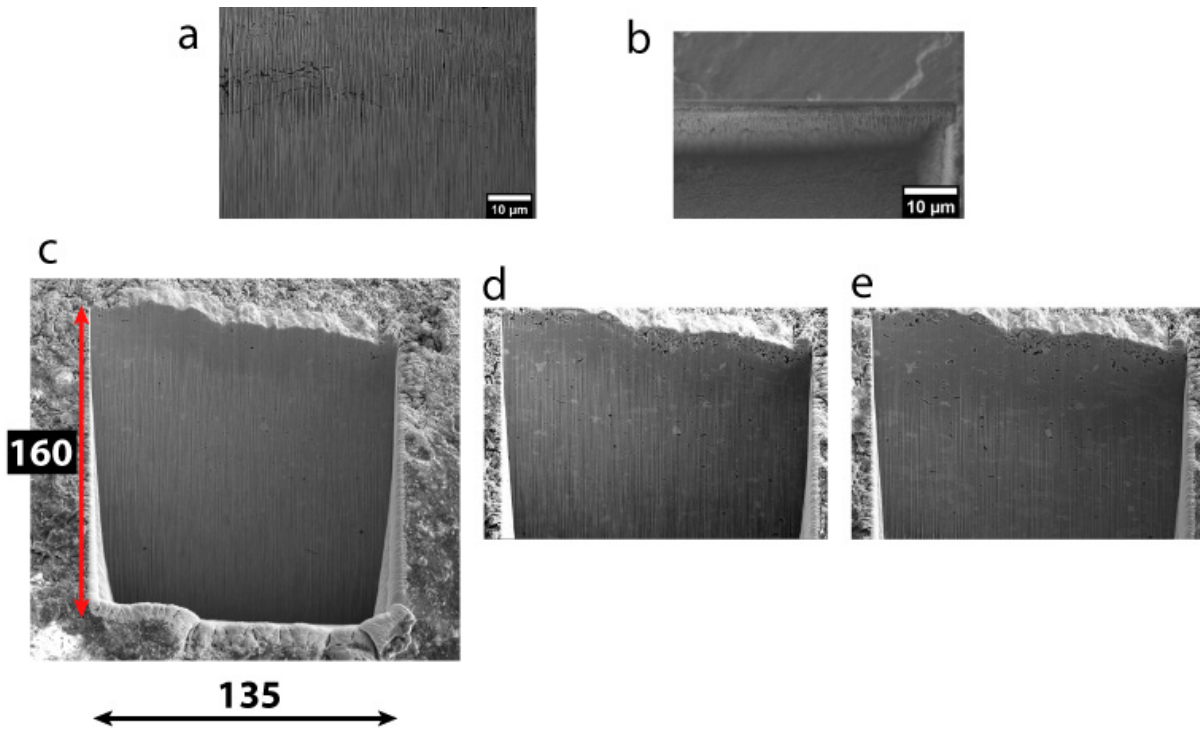


Figure 55 a) SEM-SE image showing a close-up of the curtaining effect on a CS wall on coin 587202. b) FIB image showing a top view of the curtaining effects on coin 579676. c,d,e) SEM-SE images of a trench on coin 582405. c) Trench as-milled., d) after a run of cleanings and e) after a second run of cleanings. All images are taken with the FEI system. SEM-SE images are taken at 52° using a voltage of 5, 10, 10 and 15 kV, respectively. FIB image in (b) is taken at 0° and 30 kV. Reported length are in μm . Milling depth is measured taking into account perspective effects.

Producing trenches in ROIs rich in soil contaminants (like Si, Al and Ca) have proved to be more difficult. For instance, in the case shown in Figure 57 a satisfying result has been achieved only by repeating the trench opening two times and after many cleaning runs. From the EDS map of the cleaned CS, it is evident that a thick layer of silicates was present in this region. A similar, although more extreme behaviour has been observed on a Roman stone mosaic *tessera* (Figure 56).

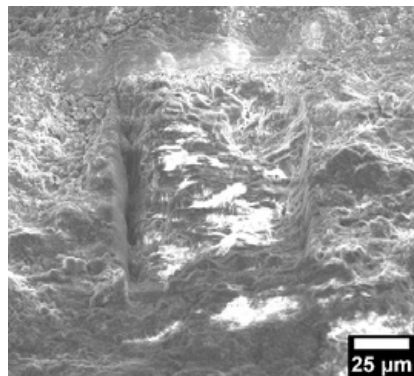


Figure 56 SEM-SE image of an attempt to produce a FIB-CS on a stone mosaic tessera. The milling process is poor and uneven, with only the edges of the milling area barely visible.

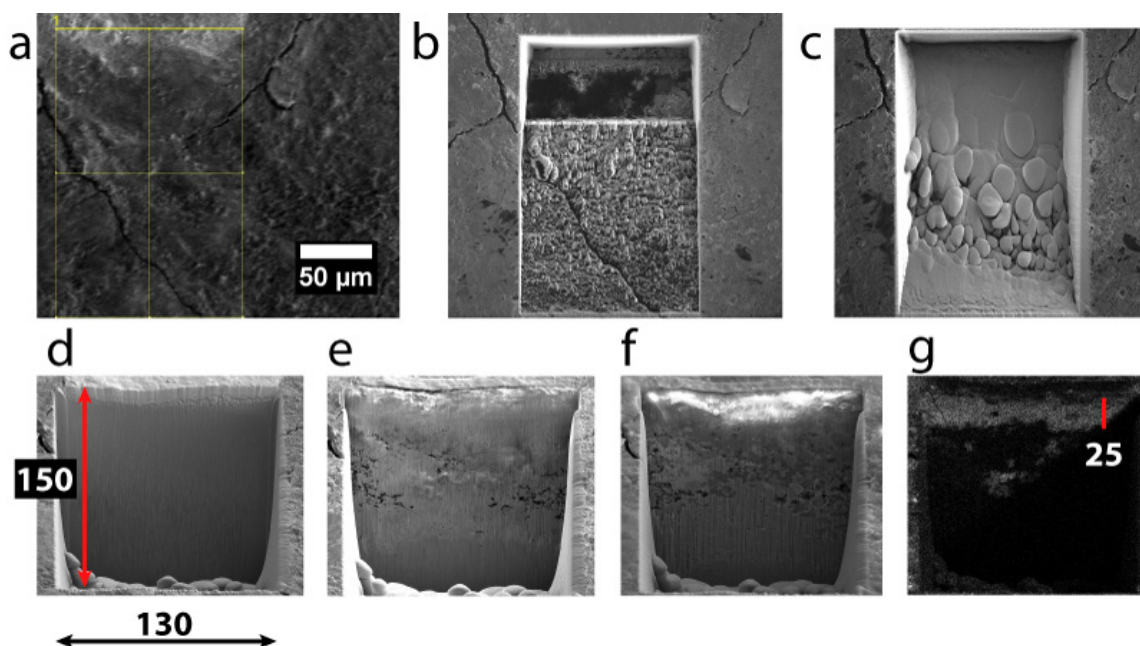


Figure 57 a,b,c) FIB images taken at 0° and 30 kV of the trench area in soil-contaminants rich ROI of coin 582405 (a) before trenching, (b) after the first trenching run and the milling of a rectangle next to the CS wall, and (c) after another trenching run. d,e,f) SEM-SE images of the CS wall (d) after trenching) and (e,f) after various runs of cleaning. SEM images are taken at 52° and at 5, 5 and 30 kV, respectively. g) Si K EDS map, taken at 20 kV. All data are acquired with the FEI system. Reported length are in μm . Milling depth (in red) is measured taking into account perspective effects.

III.2.1.3 EDS investigation of deep trenches

Different accelerating voltage conditions have been investigated for the SEM-EDS analysis of CSs, focusing on the range between 8 and 30 kV (namely, 8, 15, 20, 22 and 30 kV). The lower value, in fact, represents the advisable limit for performing EDS on materials containing Cu, Ag and Sn, given that their L-lines are all conveniently excited at this accelerating voltage. The upper value, instead, was instrument-related, given that above this threshold, the efficiency of the system sharply decreased and the timescale for achieving satisfactory EDS maps gets longer.

As can be observed in Figure 58, increasing the voltage above 15 kV, the effects linked to curtaining effect are progressively disregarded, revealing the actual features of the analysed material. This is evident from both SEM-BSE and EDS data. Data acquired at 8 kV, instead, are more influenced by the surface morphology of the CS. From one side, this emphasises curtaining effects. On the other side, better-defined shapes for grains on the CS surface are retrieved. The biggest variation in the definition of grain features has been observed between 15 and 22 kV. Additionally, spatial resolution for elements with energy lines falling below 4 keV are enhanced when working at 8 kV due to different distribution of electrons energy in the primary beam. From a practical point of view, we are speaking about all the

elemental lines used for the EDS analysis of archaeological copper-based object (i.e. Ag L, Sn L, Pb L/M, and K lines of light elements), except for Cu K, Fe K and, eventually, Zn K, which are not enough stimulated in these conditions. In their place, the respective L lines can be used. Considering all these aspects, an accelerating voltage of 20 kV has been considered as the best trade-off between image quality, signal output and probing depth. When specific features on well-cleaned CS regions had to be investigated in detail, an 8 kV was used instead.

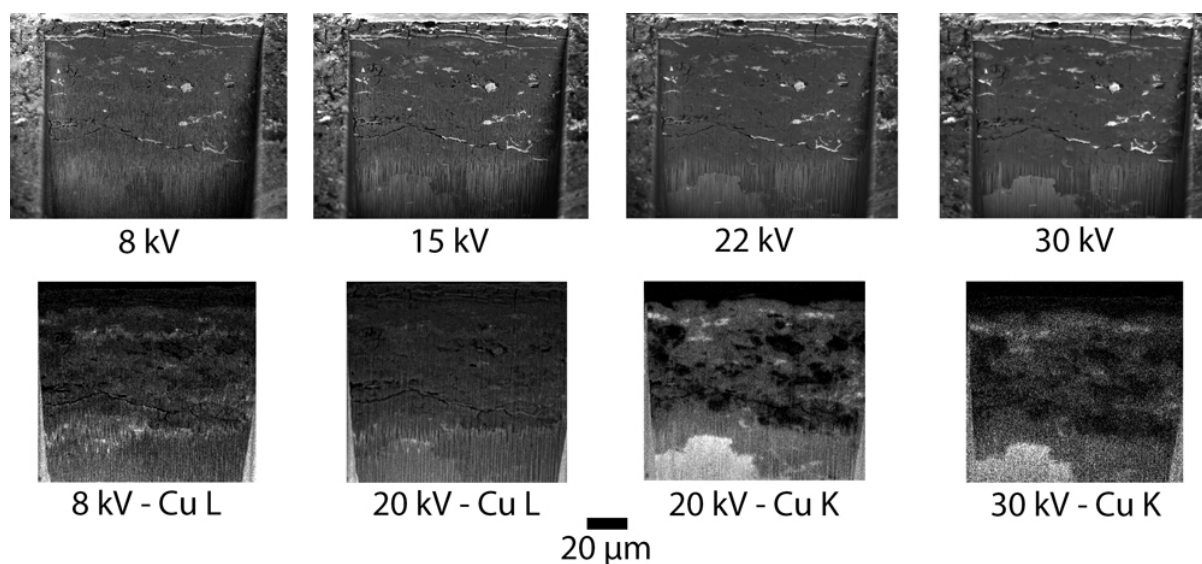


Figure 58 (top row) SEM-BSE of a deep trench on coin 587202, taken at the indicated accelerating voltage. (bottom row) EDS maps of the same trench. All images are taken with the ZEISS system, at 14.7°. The scale is the same for all images.

EDS investigation of FIB deep trenches has required some precautions. In particular, in some cases EDS maps have suffered from shading effect (Figure 59). Given the sharpness and shape of the shading, it appears to be caused by the occlusion of the EDS detector's view by one of the edges of the trench. To prevent this to happen, once the instrument geometry is known, trench must be designed accordingly. In particular, adequate trench opening size should be planned. Moreover, areas with a convex geometry or the presence of reliefs should be avoided.

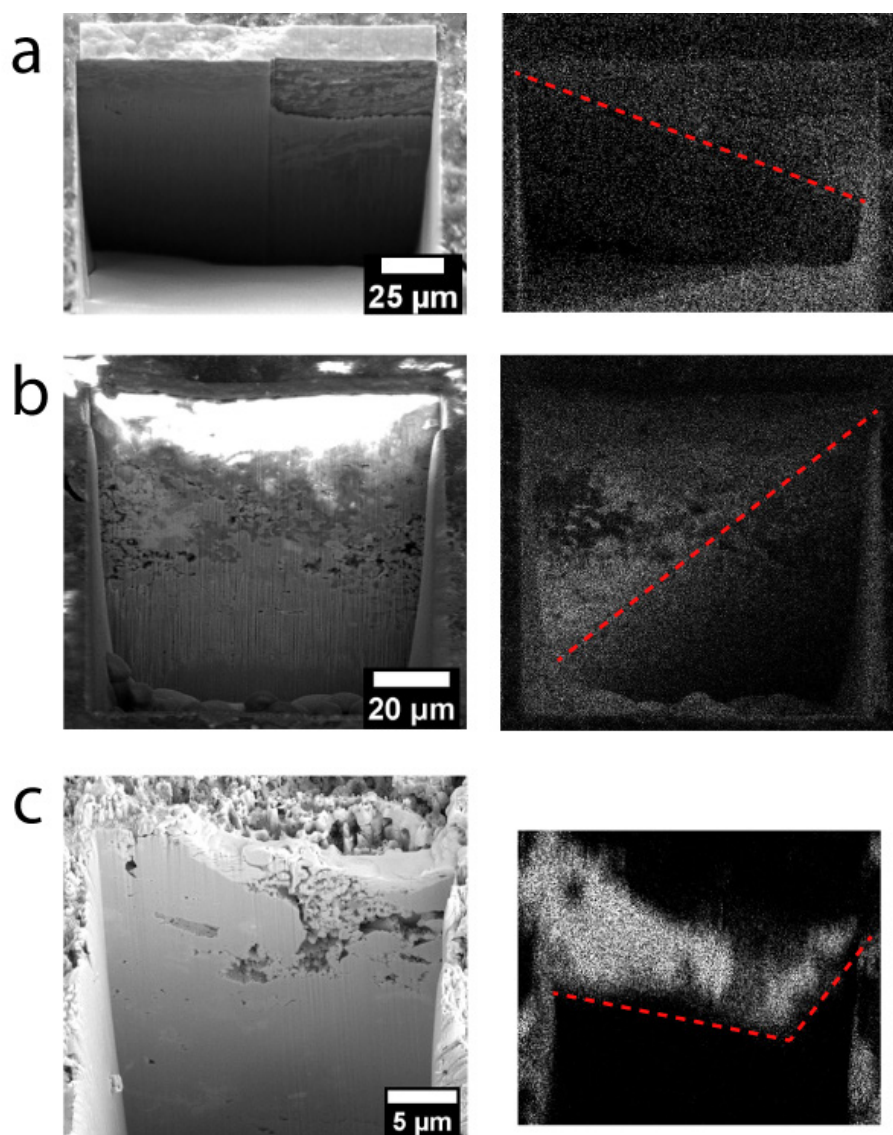


Figure 59 Examples of shading on EDS data due to detector-trench orientation mismatch on three different SEM-EDS systems. Images on the left are SEM-SE micrographs, while on the right Cu K maps are displayed, except for (c) that portrays a Cu L map. a) Shading caused by the left trench edge in the JEOL system. b) In the FEI system, EDS detector is on a specular side of the SEM column in respect to the JEOL system, and also shading is specular than in case (a). c) Shading caused by the front trench margin in the ZEISS system, most likely due to a convex morphology of the local sample surface. Red dashed lines are added for visual guidance.

EDS analyses of FIB deep trenches have in some cases presented a slight drifting effect (see Figure 60). Due to this, all the EDS maps taken with the ZEISS system have been done using the “Autolock” tool for drift correction integrated in the AZtec software, which compensates drifting effects via software at the price of a reduced resolution. No drifting effects have been observed with the drift correction enabled.

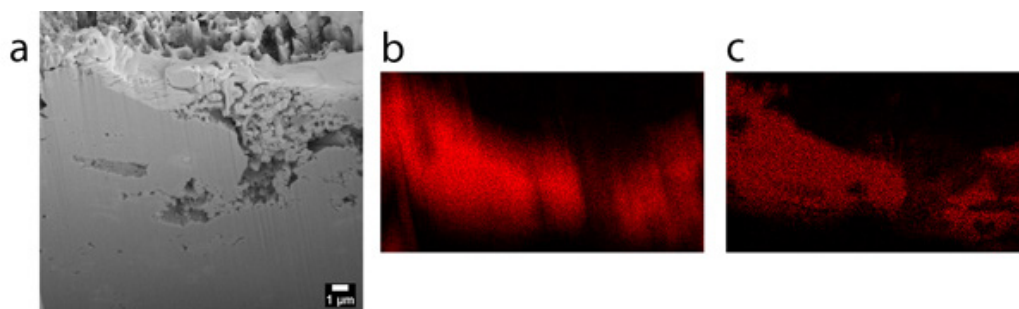


Figure 60 a) SEM-SE image of the upper side of a CS wall on coin 582405. b,c) corresponding Cu L line EDS maps, (b) without and (c) with drift correction. EDS maps are taken at 8 kV. Live time for maps (b) and (c) are comparable (ca. 10 minutes).

III.2.1.4 Case studies on Roman coins

Figure 61 shows a deep trench prepared on coin 582405. The main ROI selection criterion in this case was a significant surface silver enrichment in the area. Ag-related XRF data and further discussion about the origin of this enrichment are discussed in detail in section III.3.1. This ROI has been also selected for the low signals detected for Si and soil-related elements, from the same XRF data.

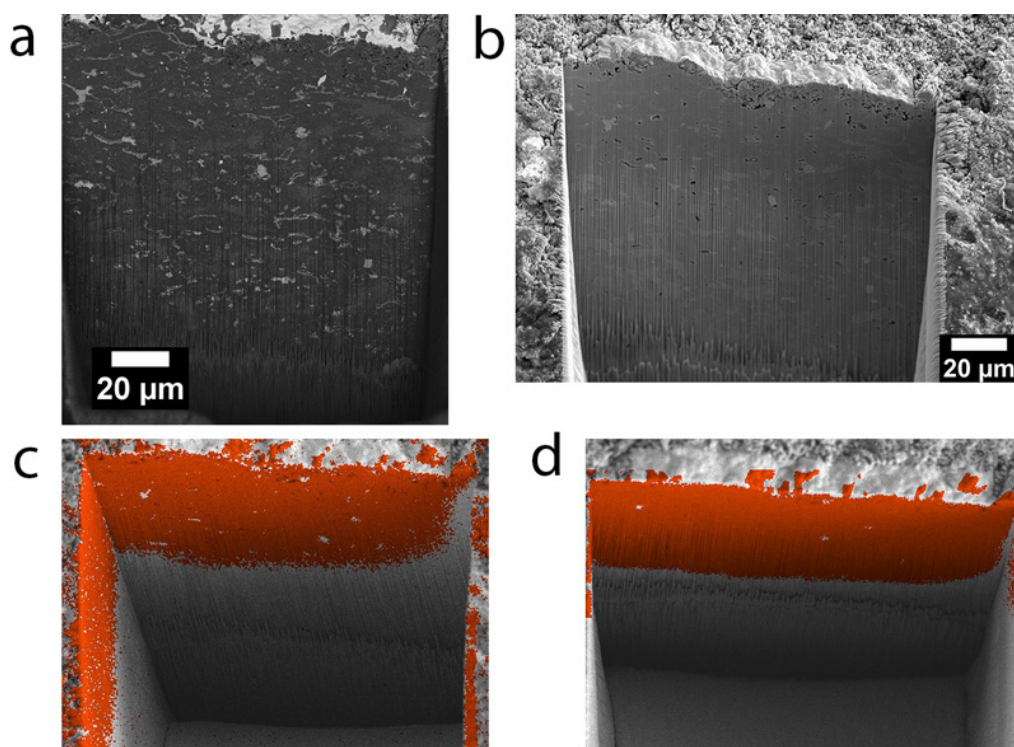


Figure 61 a,b) SEM-BSE and SEM-SE images of the CS prepared from coin 582405, using an X-Y-Z setting of 130-127-10 μm at 21 nA, and 15 cleaning steps at 0.77 nA. c,d) Cu L line maps EDS maps taken at two different tilting angles ($\pm 5^\circ$. Absolute angle values are not available in this configuration). As can be seen, the portion of the CS exposed to the EDS detector grows, from ca. 50 to ca. 120 μm.

This trench gives an example of shaded EDS maps and illustrates how to overcome it and achieve a detailed elemental analysis. The shading was in this case generated by an obstruction of the EDS-detector field-of-view due to the trench edge on the opposite side of the CS wall. For this reason, the sample was slightly tilted to enhance the exposition of the CS towards the EDS detector. This caused an apparent flattening of the CS wall under the SEM and, consequently, on the EDS maps (Figure 61 c,d). Nonetheless, the high resolution of the EDS data has allowed for the reconstruction of a frontal view starting from flattened maps, by projecting the EDS maps on a SEM image taken frontally, during the post-processing phase (Figure 62 a). Such elaboration was facilitated by the presence of clearly identifiable markers, such as well-defined grains and porosity. Since no milling effects-related influence were observed on the EDS data, all acquisitions have been made at an accelerating voltage of 8 kV.

From the low magnification map and the detail of the top-central area (Figure 62), it is visible a decuprification zone along topmost side of the CS, right below the Pt deposited for the trenching process. EDS semi-quantitative data (Table 12, points A and B) reveal an enrichment in Sn, plus minor components from soil (Fe and Si). In particular, soil-related elements are present, in modest quantity, only in this discontinuous layer, which extends no more than 5 μm from the surface. This indicates that the ROI-selection parameter was chosen properly and this region of the surface was not covered by soil residues.

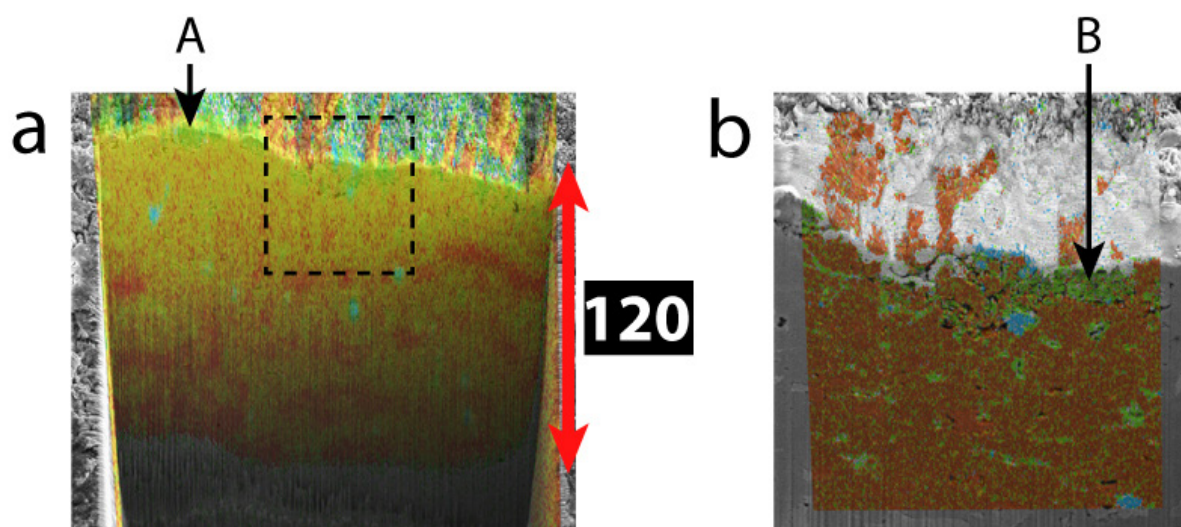


Figure 62 a) Cu L (red), O K (green) and Ag L (light blue) lines EDS map taken at same tilting angle as in Figure 61 d and stretched afterwards to overlap with Figure 61 a. The depth value is expressed in μm and takes into account perspective effects. b) The same map, taken at higher magnification in the area indicated by the black dashed square in (a).

Point	O	Si	S	Cl	Fe	Cu	As	Ag	Sn	Pb	Total
A	51.7				4.5	32.5	1.3		8.1	1.9	100.0
B	61.6	1.4			5.0	16.4	1.6		11.0	3.0	100.0
Γ	32.7					66.4			0.5	0.4	100.0
Δ	32.9					65.8			1.0	0.3	100.0
E	31.9					66.5			1.0	0.6	100.0
Z	21.8		12.4			65.0				0.8	100.0
H	46.5					36.9	2.1		10.0	4.6	100.1
Θ	42.1					44.0			11.5	2.5	100.1
I	50.4					31.4	2.5		10.3	5.5	100.1
K	25.0					26.7		48.3			100.0
Λ	58.1			3.1		20.2			5.2	13.5	100.1
M	3.5					96.5					100.0
N	5.3					93.4			1.3		100.0

Table 12 Semi-quantitative EDS data. Points location is indicated in Figure 62 and Figure 63. Values are expressed in atomic percentage (at.%).

More insights are given by the higher magnification analysis on the left side of the CS (Figure 63). Here, starting from the top, a prevalent matrix of oxidised Cu can be seen below the decuprification zone. This matrix appears to be made of copper oxides (points Γ, Δ, E), with only minimal amount of other alloying elements present. The presence of small amounts of copper and sulphide, probably ascribable to Cu_2S or CuS , is also evidenciated (point Z). Within this matrix, phases rich in Sn are present, in which the ratio between Cu and Sn is close to 31:8 (points H, Θ, I), typical of an intermetallic δ -bronze phase. Along this, there are Pb-enriched and Ag-enriched clusters. Semi-quantitative data suggests that Ag could be in the form of Ag_2O (point K), while PbO and PbCl_2 are the most probable compounds for Pb (point Λ), even though the presence of carbonates could not be assessed in this analysis and thus cannot be excluded.

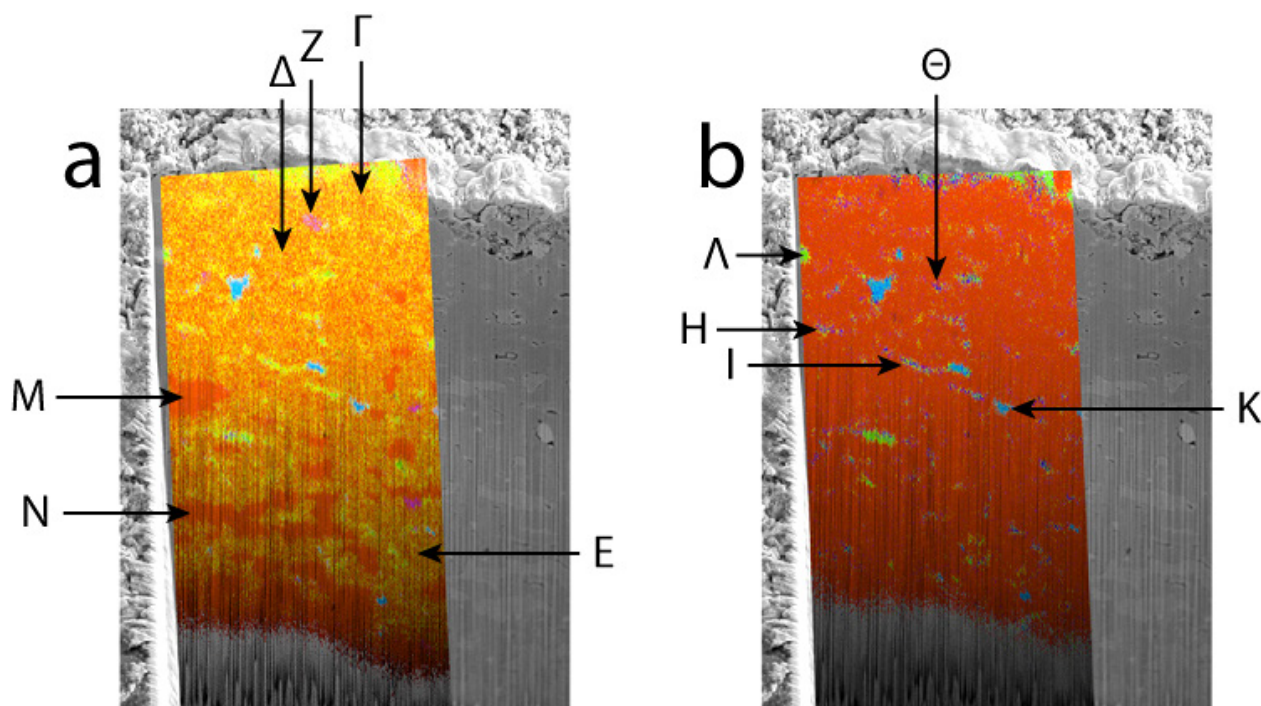


Figure 63 a) Cu L (red), O K (green) and Ag L (light blue) line EDS map of the left region of the CS. Yellow colour is generated by the overlapping of red and green. b) Cu L (red), Pb M (green) Ag L (light blue) and Sn L (purple) EDS map of the left region of the CS.

The situation gradually changes starting from 50 μm below the sample surface. Along the Cu_2O matrix, a new phase apparently made of metallic Cu appears (points M, N). The relative amount of Cu over Cu_2O and the size of Cu grains gradually increase towards the bottom side of the CS, where the metallic component becomes prevalent.

Taking into consideration what has been observed in this analysis and comparing it with XRF data, which hints at a Cu-rich alloy (Figure 64), it is possible to hypothesise that what is shown by the cross-section is a corroded zone showing pseudomorphic replacement (for a detailed explanation of the phenomenon, see par. I.1.3). In this hypothesis, what we are looking at are the hollow features of the bulk alloy, which was prevalently constituted by α -Cu rich dendrites. δ -Sn rich phases, together with clustered Ag and Pb-rich phases, were relatively small and located at the interface between the dendrites.

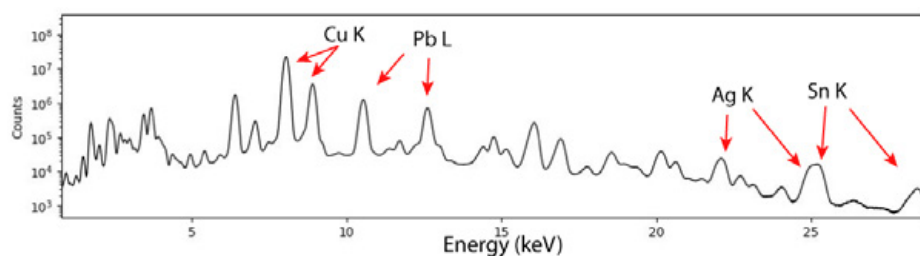


Figure 64 XRF spectrum of coin 582405. Sum spectrum of a large map of ca. 10x10 mm².

Evidently, the corrosion has evolved by first attacking and completely oxidising the δ -phases, while dendrites have been attacked gradually, from the boundary of each α -grain towards their center [31]. A coring of the dendrites (i.e. a higher concentration of Cu in their central part) may have helped the central part of dendrites to longer survive to corrosion, resulting in the presence of metallic Cu islands, which get bigger going toward the bulk of the objects. The elongated shape of dendrites residues and of δ -grains in the direction parallel to the sample surface suggests that the object was mechanically cold-worked [35], which is a highly probable scenario given the nature of the sample.

As a closing remark, it must be underlined that the specific features as depth of corrosion, amount of soil residues and, in part, the distribution of the phases can be quite variable on other points of the same sample. However, the indication achieved on its metallography are general.

III.2.1.5 Occurrence of porosity and cracks on archaeological *patinas*

Corrosion is a process that occurs due to the interplay between environmental and object-related factors. For copper-based archaeological items, the identification of degradation factors strictly linked to the chemistry and microstructure of the *patina*-metal system is not straightforward, apart from chlorinated compounds in the case of bronze disease.

There is one feature that has been regularly encountered in most of the archaeological samples analysed during FIB-SEM analysis campaign, which could undermine the corrosion protection granted by a stable *patina*: the porosity of the *patina* itself. Cracks and pores have been observed on the external *patina* surface (Figure 65 a,b) as often as inside deep *patina* layers, within FIB cross-sections (Figure 65 c) of copper-based roman coins. Even though this is not enough to conclude the presence of open porosity, it is still a matter of concern because porosity can represent an important weak point for otherwise stable *patinas*. Porosity, in fact, allows aggressive agents from the environment to penetrate well inside, eventually reaching and further degrading bulk metal, or more in general creating local

conditions for degradation. This affects also samples with quiescent bronze disease, which could be triggered by the direct contact with water and oxygen. Reduce *patina* porosity and avoid the formation of new cracks would be thus an essential task for a protective treatment to fulfil. On this path, early investigation about the use of an oxalic acid-based treatment have been performed and are reported in Appendix A.

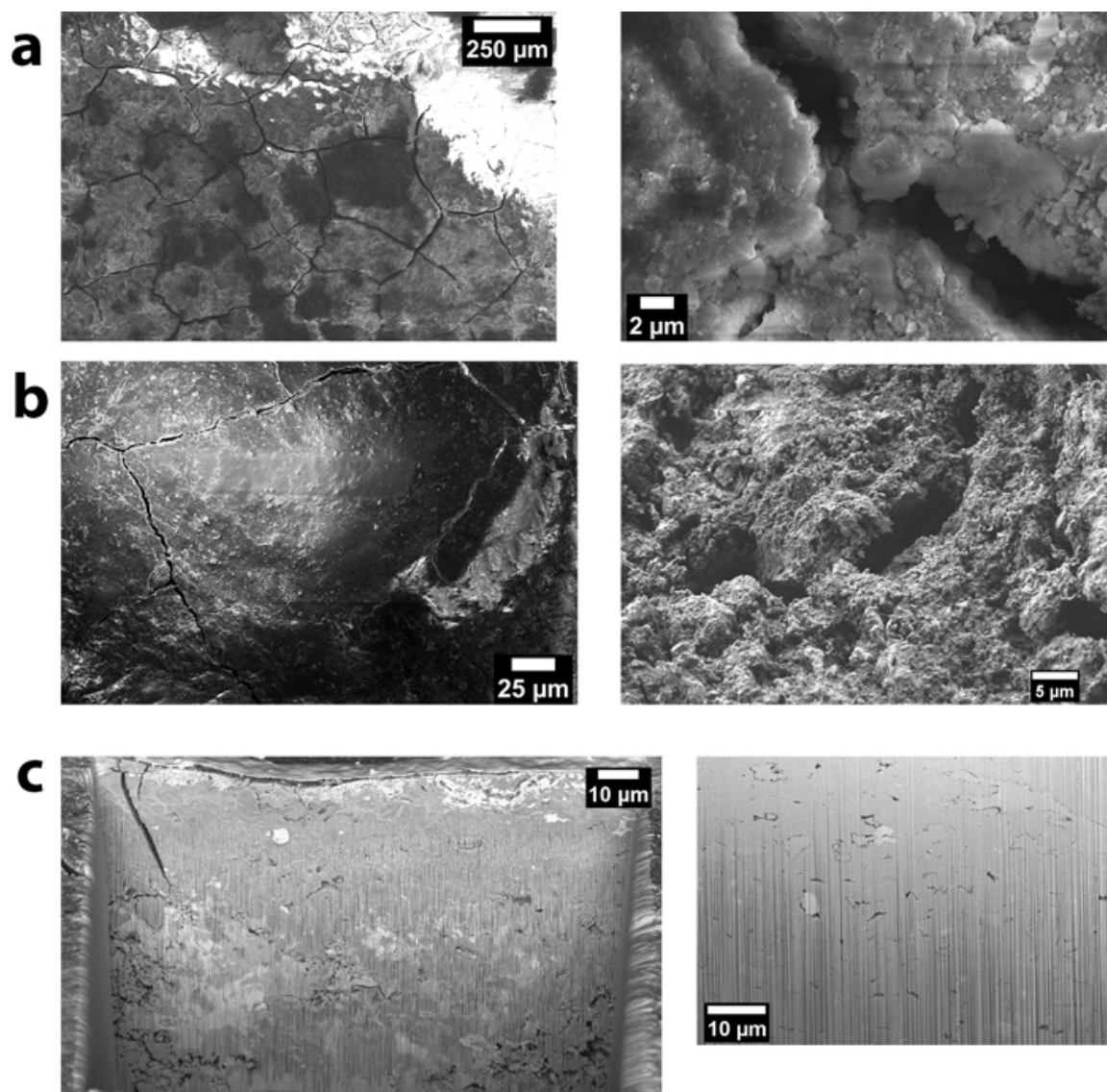


Figure 65 SEM-SE example images of cracks and pores on the surface and inside the archaeological patina of copper-based artifacts found during FIB-SEM investigations. a) surface cracks on coin 579676, 15 kV FEI system. b) surface cracks and pores on coin 582405, 5 kV FEI system (left) and 1 kV ZEISS system (right). c) internal porosity over FIB CS on coin 582405, 8 kV (left) and 2 kV (right) ZEISS system.

III.2.2 Application examples of LA-ICP-MS for Diagnostic and Archaeometry

III.2.2.1 1D – Preliminary drilling test

Preliminary drilling tests have been performed on the “desert *patina*” coin, in order to evaluate the efficiency of the laser ablation process. Ten drills have been laser-ablated all in the same region of the coin surface, in order to mitigate as much as possible the influence of the variability of sample properties across its surface (. Drills have been after observed by optical profilometry. The results shown in Figure 66 tell that a linear correlation between number of laser shots and ablation depth achieved could not be obtained. In particular, the first drill (10 shots) had a too low depth to be determined by optical profilometry. From the second to the fourth drills (20 to 80 shots), a near-linear trend is observed with an ablation efficiency of about 0.4-0.5 μm per shot, trend that deviates towards an apparent logarithmic one at higher number of shots (Figure 66 e). However, a clear definition of a general behaviour is hindered by a strong dispersion of the values observed. Most likely, the non-linearity observed from the fifth to the tenth drill (100 to 600 shots) must be attributed to the high heterogeneity in material composition both on the plane of the surface, and in its depth profile. In fact, *patina* is made of soil contaminants and corrosion products, which have very different behaviour one from the other, and metallic bulk is even more different from these. It is thus expectable the achieved ablation depth to be strongly influenced by changes in *patina* composition, or in the relative thickness of the different layers of which it is composed. The original morphology of the surface, including its roughness, could also have played an important role.

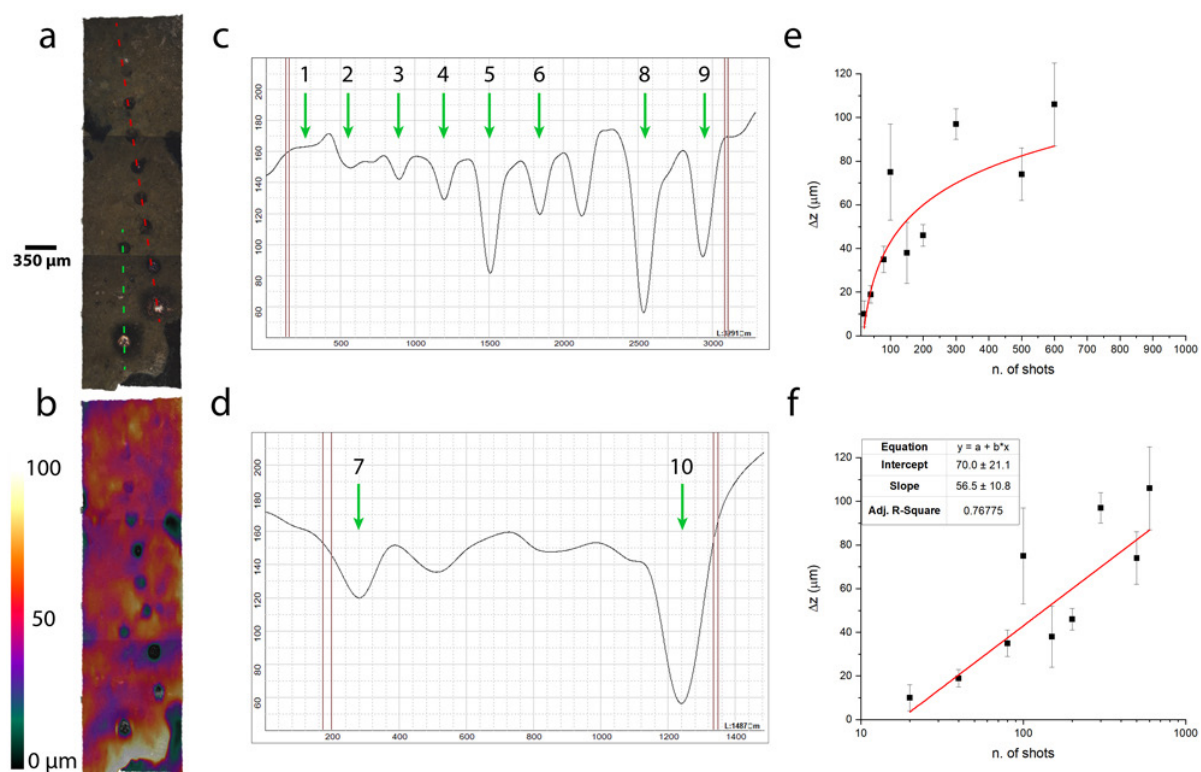


Figure 66 a) Optical micrograph of the ten drillings made by LA-ICP-MS with an increasing number of laser shots. b) False colour map, corresponding to a), indicating altimetry. Black points are low, white are high. c,d) Profilometric cross-sections of the drills. Cross-section lines are shown in a) as a red (for c) and a green (for d) dashed line. e) Ablation depth (Δz) vs number of laser shots. f) Linear-log plot of e), on which linear fitting has been performed. The obtained fitting is also reported in plot e) on a linear scale for the x-axis. All scales are in µm. Drill #7 has been made two times due to a setting error in the first run.

Nonetheless, the shape of the ablated drills appears to be uniform, with limited conicity even after a high number of shots (Figure 67). Around drills made with the highest number of shots, a black halo could be observed. Most likely, it was linked to redeposited material (also visible in the corresponding

profilometric data on the left). The halo disappeared by gentle brushing with a cotton swab soaked with ethanol.

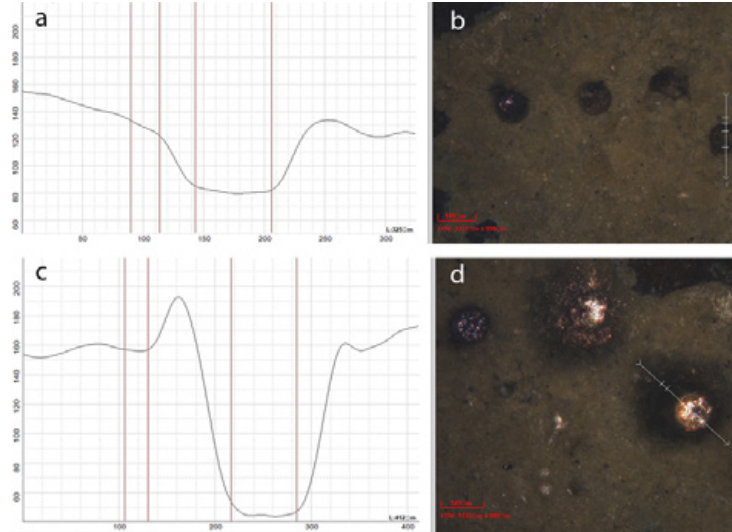


Figure 67 a,c) Profilometric cross-sections of the corresponding drills n. 7 (b) and 10 (d). Red lines in (a,c) marks the points used for quantitative measurements. White lines in (b,d) marks the line along which the profilometric cross-sections in (a,c) where taken. All scales are in μm .

III.2.2.2 1D - Depth profiling for corrosion study

Two elemental depth profiling have been performed in near and similar spots (A and B) on the desert patina coin (Figure 68). The main difference between the two depth-profiles is that the first is done at 6 J/cm^2 of fluence for a total of 600 shots, while the second is done at a lower fluence (4 J/cm^2) but lasted for a longer time (1000 shots).

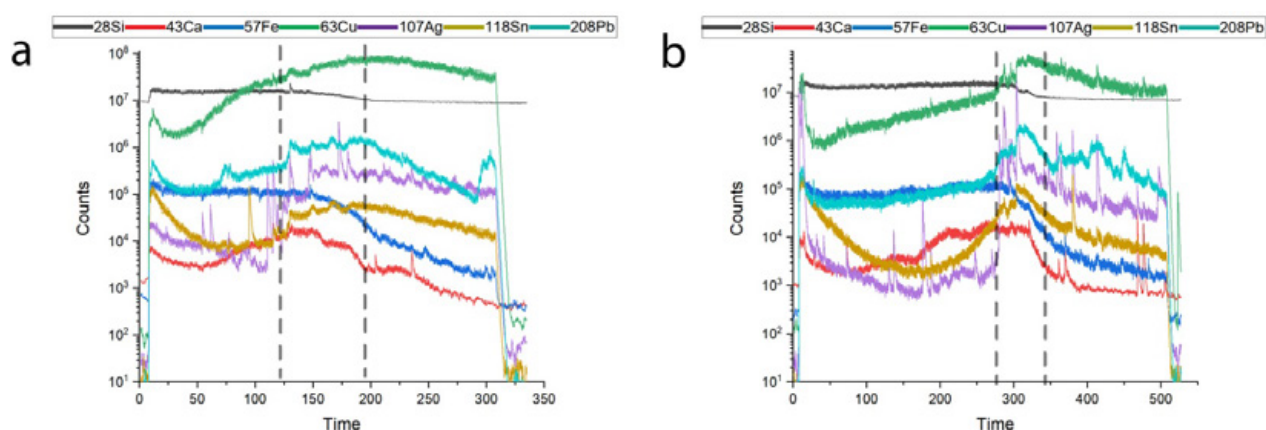


Figure 68 LA-ICP-MS depth profiling taken on two spots on the desert patina coin. a) Spot A and b) spot B. Dashed vertical lines are added for visual guidance on the interfaces positions where significant changes in the signals occur. Elements: ^{28}Si (dark gray), ^{43}Ca (red), ^{57}Fe (blue), ^{63}Cu (green), ^{107}Ag (violet), ^{118}Sn (yellow), ^{208}Pb (light blue).

The depth-profiles have revealed the presence of two main phases, the outer one rich in Si, Fe, and Ca and, below this, one richer in Cu, Pb, Sn and Ag (Figure 69). The interface between the two phases is marked by a decrease in Si signal and by an opposite trend for the Cu signal, together with marked change for Sn, Ag and Pb. After this threshold, Si, Ca and Fe start to gradually decrease, until Si reaches its noise-level. After this second threshold, the ratio between elements is constant unless some spike of concentration, while the total signal gradually decreases due to the reduced ablation efficiency inside deep drills.

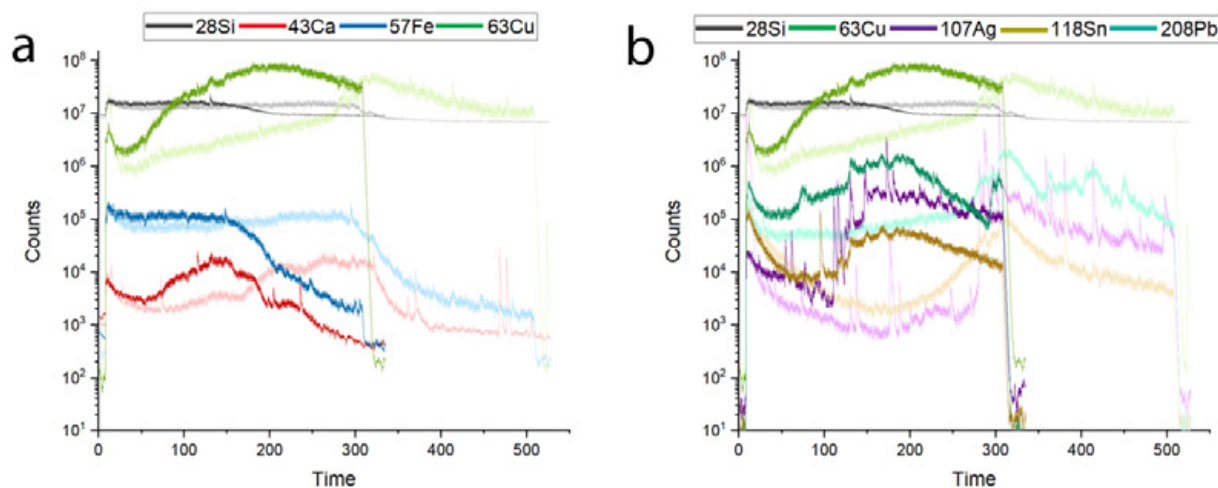


Figure 69 Detail of a) Si, Ca, Fe and Cu, and of b) Si, Cu, Ag, Sn and Pb. Dark colours are from point A, light colours from point B. Elements: ^{28}Si (dark gray), ^{43}Ca (red), ^{57}Fe (blue), ^{63}Cu (green), ^{107}Ag (violet), ^{118}Sn (yellow), ^{208}Pb (light blue).

The outer layer can be recognised as the outer patina layer, mostly composed by soil components. While being characterised by the elements coming from the bulk of the alloy, it is questionable if the last,

deeper phase can be attributed to the metallic bulk alloy, or rather belongs to an internal corroded layer. In fact, LA-ICP-MS in the configuration used cannot monitor elements present in relevant quantity in the air, or that fractionate as anions (N, O, S, Cl to cite few). Without this indication, it is rather difficult to understand if the ablation process has reached the bulk (i.e. spikes in alloying elements signals are due to ablation of the different phases present in the bulk alloy) or else what is being analysed is still an intermediate corroded layer.

The intermediate layer is quite narrow and sees a gradual decrease in soil components, while bulk elements show a sharp increase. Considering the mechanics of ablation, this interphase may be attributed to a transitory situation in which laser have reached a second layer in the center of the ablation spot, while it is still ablating material also from the above layer on the drill walls.

Depth profiles of points A and B show a significant difference in the number of shots needed to reach and surpass the internal interfaces. This difference can be justified by the different fluence used for the two depth profiles, more than with the heterogeneity of the sample. Using the test reported in the previous paragraph as an indicative calibration for depth profile A (given the same fluence used, i.e. 6 J/cm²), an ablation depth of 40-50 µm (ca. 220 shots) and 60-80 µm (ca. 350 shots) is obtained. Inference on the actual ablation efficiency of depth profile B (fluence 4 J/cm²) are hard to make, due to the heterogeneity in patina layers thickness across the sample. However, the difference in the shot count needed to reach the internal interfaces between the two depth-profiles is compatible with a different ablation yield between 6 and 4 J/cm² of laser fluence.

Some considerations can be made on the relative trends of the elements from the bulk alloy (Figure 70). The samples appear to be a copper coin, with limited amount of Pb, Ag, and Sn. In the first soil-rich layer, after a generalised initial spike, Cu and Pb slightly increase, while Sn and Ag gradually decrease until the first threshold. This suggests an enrichment in Cu and Pb in the outer part of the patina, most likely due to their higher tendency to leach from bulk towards the environment during the corrosion process. This is a well-known phenomenon [36], generated by the same mechanism usually leading to tin enrichment (see par. I.1.3) or silver enrichment, when leached ions are not dispersed into the environment due to re-precipitation, or by limited mass transport due to presence of an additional outer layer (made by external compounds like silicates and soil, or by secondary corrosion products previously formed).

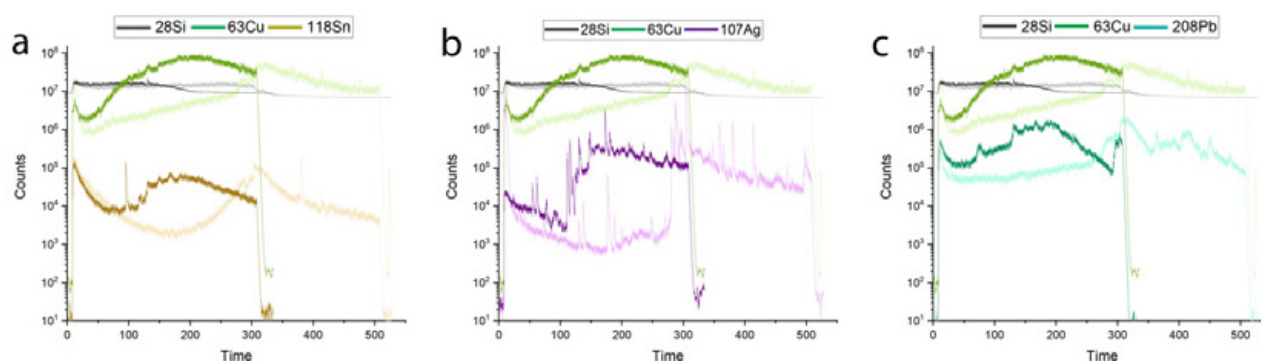


Figure 70 Detail of a) Si, Cu and Sn, b) Si, Cu and Ag, c) Si, Cu, Pb. Dark colours are from point A, light colours from point B. Elements: ^{28}Si (dark gray), ^{63}Cu (green), ^{107}Ag (violet), ^{118}Sn (yellow), ^{208}Pb (light blue).

In the deeper phase, instead, Sn closely follows the trend of Cu, while Ag and Pb presents marked heterogeneities. In particular, Ag seems clustered in small grains, where its concentration is much higher. Pb has a similar behaviour, unless that the size of the grains in which it is enriched appears larger, or at least Pb-rich phases are more clustered. This is in accordance with the metallurgy of ancient copper-based alloys (see par. I.1.2), since Ag and Pb are little to not soluble in Cu phases, tending to form separated enriched phases. In particular, Pb have a strong tendency to cluster even in large grains.

This may represent an indication that the ablation achieved to reach the bulk of the sample, however as evidenced in the FIB-SEM analyses, the inner corrosion phase may well present an elemental distribution that resembles the one of the bulk alloy. Therefore, such observations cannot be considered as a final proof for this achievement, in absence of a longer plateau of stability in the signal recorded or of a complementary analysis.

III.2.2.3 1D - Depth profiling for identification of forgery

In this application, a counterfeited ancient Greek electrum coin has been investigated by LA-ICP-MS depth profiling. A legit coin of this type should be made instead of electrum, which is an Au-Ag alloy with variable ratio between the two alloying components, and possible secondary amount of Cu [37]. From Figure 71, it is evident how the coin is practically of pure Ag, with a limited amount of Cu and Au just as trace element in the bulk. Au as primary component is confined on the very first layers of material, making it just a thin coating. The Au count spike is ca. 3 s wide (Figure 71 a), i.e. ca. 6 shots. Taking into consideration the 5-point moving average, the ablation performance observed in the previous drilling test, and the fact that such test was performed at a higher fluence (6 J/cm^2 , instead of the 4 J/cm^2 used in this case), a thickness of $0.2\text{-}2 \text{ }\mu\text{m}$ can be estimated for the Au layer. SEM-EDS,

performed on a sampled cross-section, later confirmed that the thickness of the Au layer was ca. 0.5 μm , sitting at the top of an Ag bulk metal.

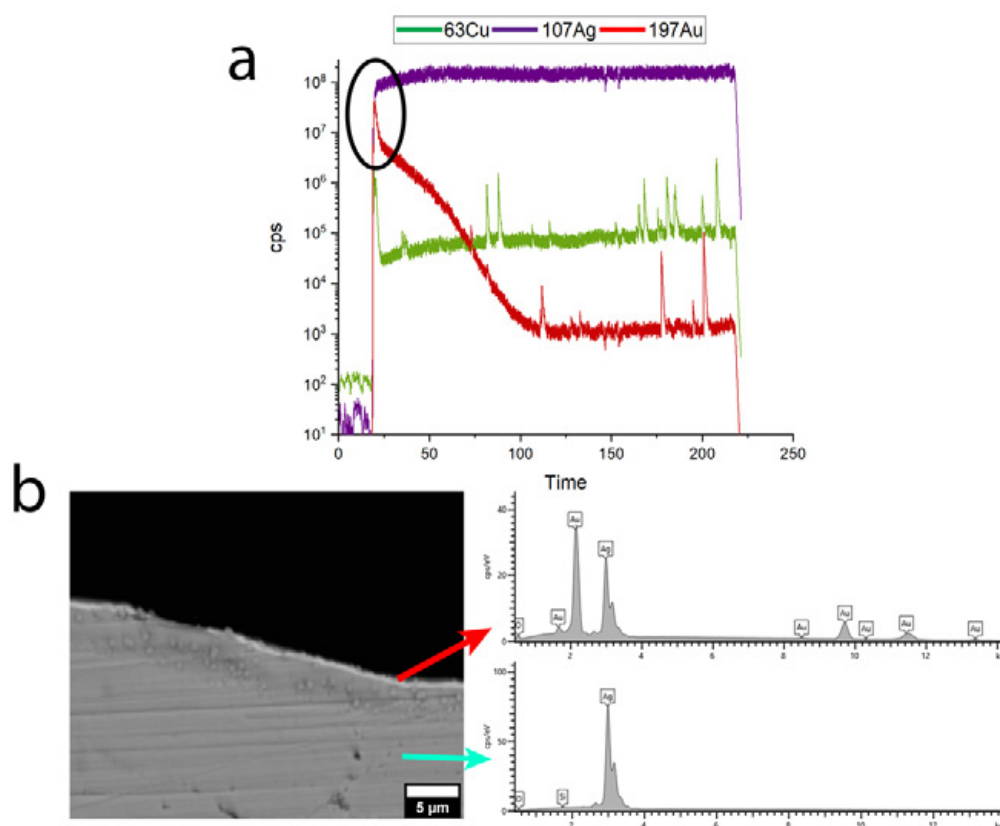


Figure 71 a) LA-ICP-MS depth profiling on a supposed ancient Greek gold coin. The black ellipse marks the gold-enriched layer. b) SEM-SE image of the cross-section of the coin, and EDS spectra corresponding to the points marked with the red and light blue arrows.

III.2.2.4 2D and 3D Mapping

A 3D elemental mapping has been performed on the desert patina coin, by sequentially ablating 9 different layers over the same area (Figure 72). All the elements show a concentration that follow a similar trend, decreasing gradually and uniformly along the ablation run except for Pb, which remains highly concentrated in clustered points. In the rightmost region, there is an evident increase in Sn concentration in the last ablation run. From the comparison of the situation before and after the ablation (Figure 73), it appears that the newly exposed Sn-rich regions match with metallic-like areas on the surface. It can thus be argued that, after 9 ablation layers, the laser was starting to attain the outermost metallic alloy material, approximately reaching the interphase between the internal and external phases observed in depth profiling mode.

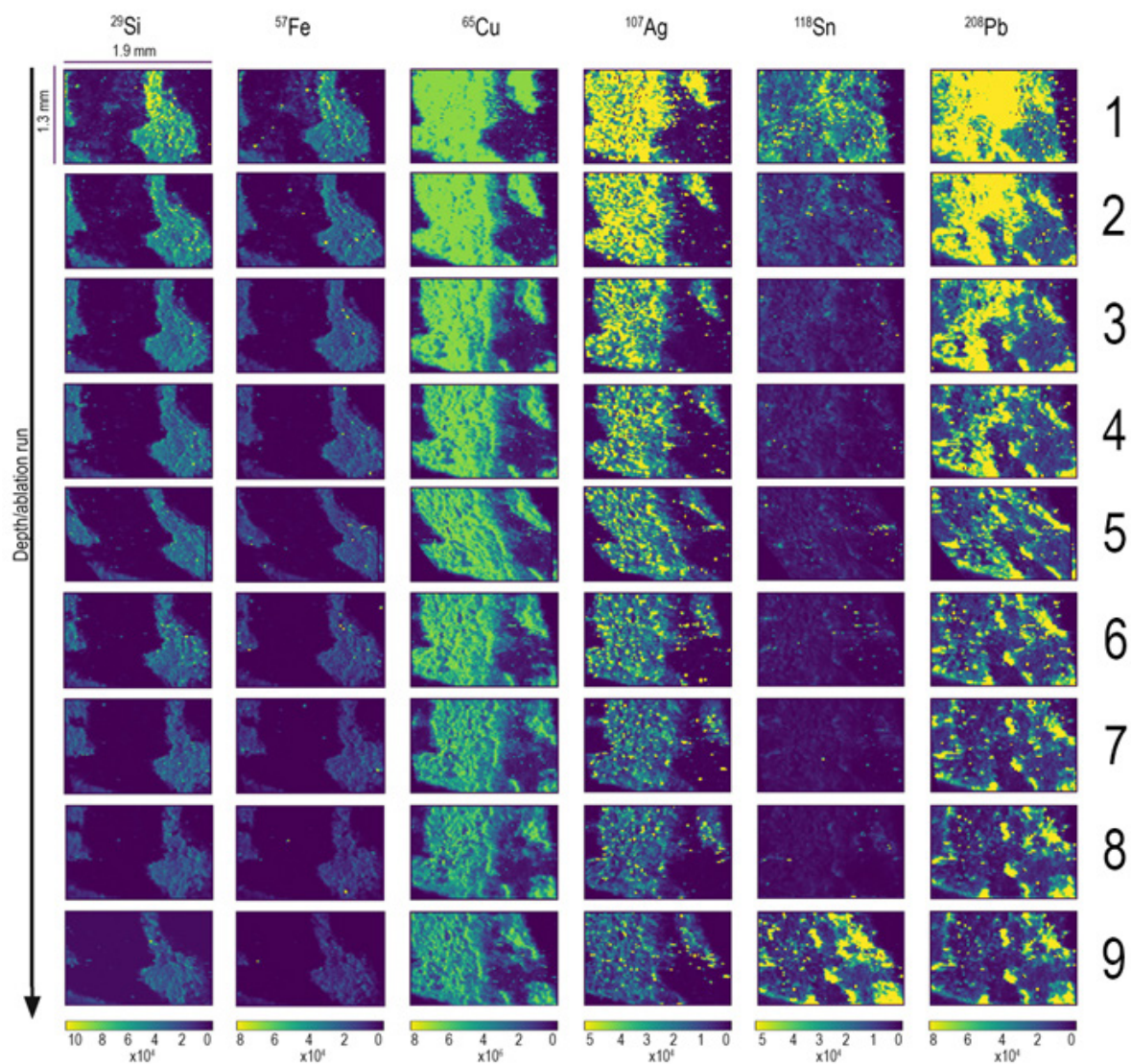


Figure 72 3D LA-ICP-MS datacube, exploded layer by layer. Each row represents one ablated layer. Data are divided per element column-wise.

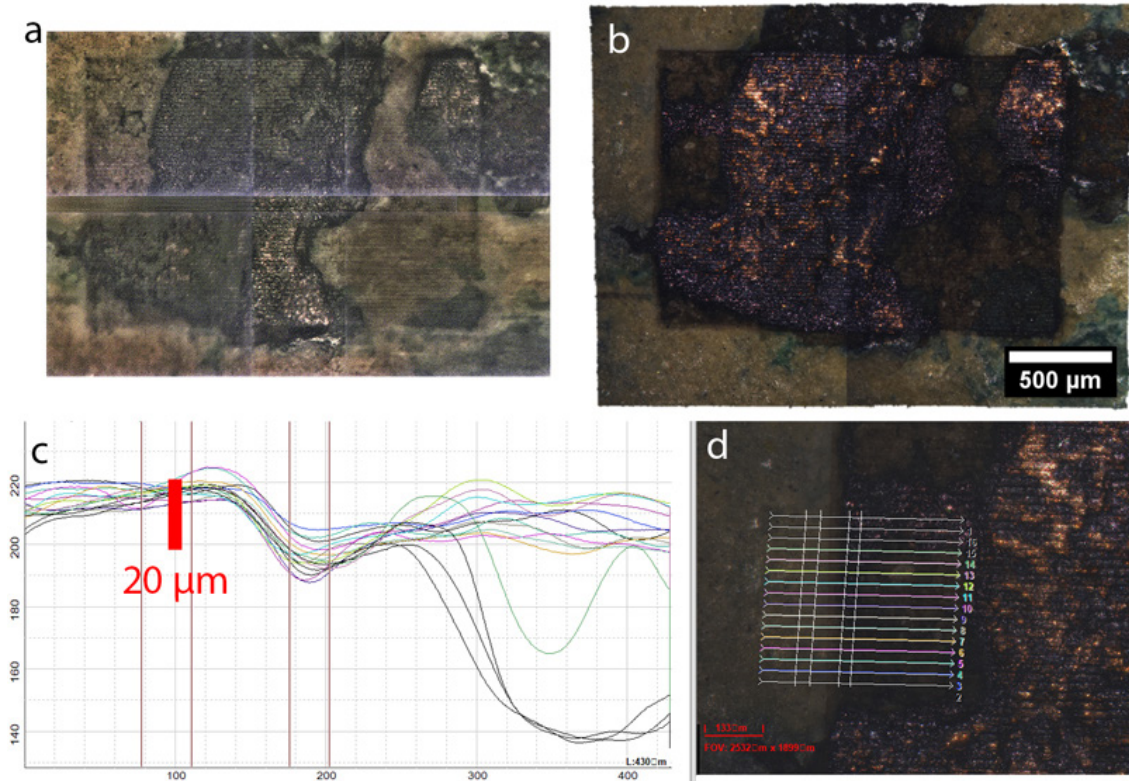


Figure 73 a) Analysed area after the ablation of the first two layers, seen with the internal camera of the LA-ICP-MS instrument. b) The same area at the end of the ablation process, imaged with the optical profilometer. c) Set of 16 profilometric cross-sections along a set of parallel lines (indicated in (d)) across the ablation border. The red bar indicate the depth achieved by the ablation process.

Distortion effects are visible in layers 5 and 9. From the kind of shift, gradually changing pixel by pixel, it can be argued that the origin of such distortions is in a misalignment between the laser ablation and ICP datasets. Ideal samples present an ICP signal as near-perfect square wave and are easy to match with the square-wave of the laser ablation pulse. The archaeological sample investigated here, instead, show a partially irregular ICP signal in respect to standard sample but also other archaeological objects, such as glass [38]. Such ICP signal is complex to align with the LA signal. This inevitably causes some mismatch, which propagates in the dataset finally causing a gradual drift in the maps (Figure 74). The best way to minimise this effect is to rise the time for the ICP to analyse the material coming from the ablation of each laser pulse. This would guarantee a more defined ICP signal, at the cost of an increased time of analysis.

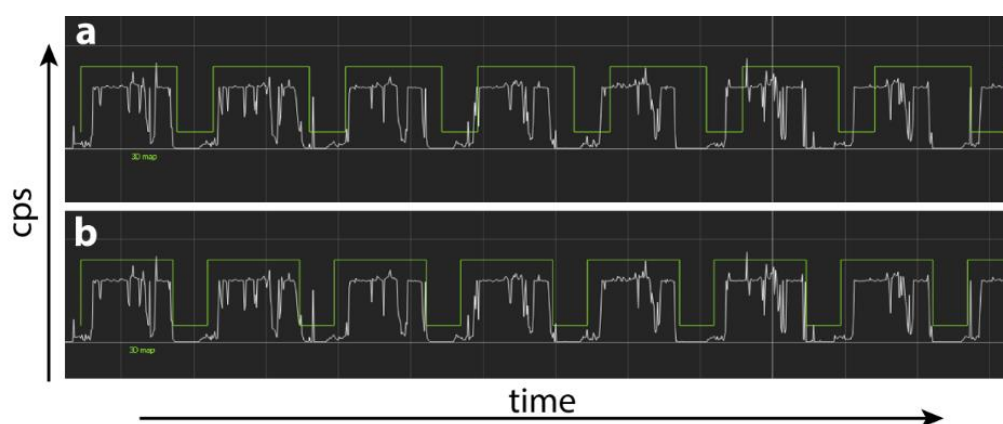


Figure 74 Example of mismatched (a) and aligned (b) ICP and LA signals (white and green, respectively) from the dataset used in this work (screenshot from HDIP software).

III.2.3 Discussion

III.2.3.1 FIB Deep-trenching

The optimised strategy proposed in this chapter allows to produce FIB deep-trenches, with a depth up to 150 μm , on archaeological copper-based samples. The preparation of CSs with an analytical area of 150 x 130 μm^2 represents a huge leap forward in respect to what has been obtained in literature with FIB until today (as evidenced in par. I.3.3). The case study of an ancient Roman coin reported herein demonstrates how this method can be used to achieve depth-resolved information on corrosion and near-bulk feature in a minimally invasive way. The same information cannot be achieved with standard small trenches, given the size and the depth of the features to be observed. This method increases the representativeness of a single CS, without aesthetic impact on the object.

Two major problems have been faced and sorted out during the preparation of deep trenches. The first issue is the large time consumption required for milling large trenches. The milling parameters defined after extensive testing (X-Y aperture parameters 150-200 μm , depth of 150 μm , total time of drilling of about 14-16 h, as reported in par. III.2.1.2) satisfy the criteria of machine time optimisation, requiring for the trench opening just an overnight shift.

Moreover, severe milling effects, consisting of stalagmite-like feature on the surface of the CS, have been observed for deep trenches above tens of μm . This phenomenon is called “curtaining effect” and is a known issue in Ga^+ -FIB technology. In literature, few solutions have been proposed that require the

use of an additional goniometer on the sample holder, or image post-processing [39]. In this work, we adopted a targeted cleaning procedure to curb curtaining effect. Even though a complete removal of these milling effects could not be achieved in the deepest regions of CSs, the impact of residual curtaining effect on the SEM-EDS analysis is minimal when working at 20 kV, only hindering signal from low energy lines at great depths, where curtaining effects are more sever.

The investigation on EDS parameters indicates that 20 kV of accelerating voltage are the optimal conditions for performing the overview analysis of the CS. At this high voltage, the electron beam penetrates deep inside the sample, exciting up to 1 μm of material below the CS surface (Figure 75) [40–42]. This helps in reducing possible negative impact of curtaining effect on SEM and EDS data, because the information is attained from a thickness higher than the characteristic size of such features. When a good level of CS cleaning is achieved, or a specific detail from well-cleaned areas wants to be highlighted, instead, working at 8 kV allows to limit the interaction volume behind the surface of the CS, enhancing lateral resolution and giving to data acquired in this working condition to be limited to sub-surface. This is further accentuated by the fact that, at 8 kV of accelerating voltage, L lines are used for Cu (and Fe and Zn) instead of K lines, because the mean free path inside the analytical volume of lower energy X-rays is lower in respect to higher energy X-rays. For all these reasons, 8 kV of accelerating voltage can be convenient if the analysis has a special focus on the fine distribution of Ag and Sn as alloying elements, or on the presence of soil contaminants.

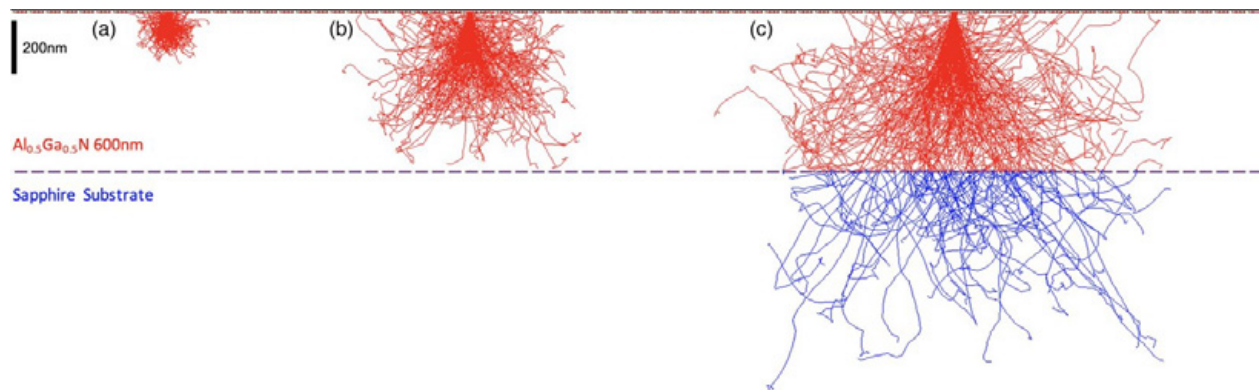


Figure 75 Monte Carlo simulation of electron penetration depths within semiconductor film (AlGaIn over a sapphire substrate) using a beam acceleration voltage of (a) 5 kV, (b) 10 kV, and (c) 15 kV [41]. While absolute values relates to the specific sample, the increase in the penetration depth with the accelerating voltage is a general behaviour.

During EDS analyses on FIB trenches, a slight drifting effect has been noted. The ultra-high vacuum (UHV) conditions and the extreme magnification at which a SEM-EDS operates require the sample to be perfectly still during the acquisition time. Usually, such requirement is met by securing the sample to the stub by means of strong adhesive. Indeed, carbon or copper tapes are able to ensure enough

adhesion, however they are also likely to remove part of the patina once the sample is removed from the stub.

The use of a clip holder avoids issues related to tapes. However, the uneven surface of the sample in contact with the stub may leave to the sample minimal degrees of freedom, depending on the actual sample mounting (i.e. screw fastening, coin positioning, specific coin unevenness). However, it must be underlined that no drifting has been observed during the FIB milling steps of the trenches showed herein, as verified after each milling directly on the instrument. Moreover, the crucial step that determines the final output of the trenching process are the last cleaning phases, which last as little as few minutes. It is thus unlikely that drifting may play a role on the final quality of FIB trenches, while it is more conveniently explained by focus-depth effects and sample heterogeneity [34].

Since EDS detectors are designed only for surface analysis of flat samples, attention must be paid in understanding the exact configuration of the SEM-EDS system in use. FIB trenches have to be designed accordingly in terms of position, orientation and size, otherwise shading effect on the EDS maps of the CS may occur. For instance, this may represent a limit in samples with very high roughness, or with reliefs on the surface, which may obstruct the EDS view of the wall trench. Such factors must be kept into account during the experiment design.

One of the most important concerns regarding the use of FIB cross-sectioning for metal artefacts is the limited representativeness of such a small-spot analysis against high heterogeneous samples. The small size of this (micro-)invasive analysis is however also its major positive point, because it limits the invasiveness to a minimum. Certainly, the possibility to prepare CSs with a wide analysable area like the one illustrated in this work helps balancing these pros and cons towards a more fruitful level, and was the missing point for opening the use of FIB-CS as an alternative to total cross-sections in specific cases, like the one reported in par. III.2.1.4. The use of complementary techniques can further support the representativeness of the analysis, by selecting ROIs in which prepare the FIB CSs based on specific surface features. Here, the potential of μ XRF mapping in localising points of interests has been highlighted, supporting the identification of surface enrichment in Ag or soil encrustation with high precision and ease. The latter are just two examples of how μ XRF mapping can support FIB cross-sectioning. Moreover, the same concept can be easily extended to any other complementary technique with mapping or imaging capabilities.

In particular, the identification of ROIs on the sample surface rich in soil compounds by μ XRF mapping can be exploited in two different ways. On one side, this can prove useful if the aim is to attain a region inside the sample as close as possible to its bulk, by avoiding regions covered by a lot of exogenous materials, which would reduce the depth of the trench analysable.

On the other side, the soil-rich ROI can be selected for FIB cross-sectioning, if information about the burial environment are desired. In this regard, the difficulty to prepare well-defined trenches in soil contaminants-rich ROIs with thick encrustations may be tentatively attributed to two different phenomena. On one side, this could be determined by the different properties between the various materials present in such ROIs. This may induce very irregular milling shapes. On the other side, this may also be linked to charging effects in presence of completely insulating materials, such as aluminosilicates. While very thin (1 μm or less) Si-rich layers have often been observed in most of the CS produced on top of corrosion *patinas* showing only partial charging, fairly thick layers may instead cause massive charging. Such surface charging may cause primary ions deflections and image drifting, generating bad milling shapes. No major solutions can be proposed in the framework of Ga^+ -FIB, apart from repeating multiple times trenching and cleaning phases, ensuring an adequate result but also increasing operation time. Nonetheless, next generation Laser-FIB may represent a huge leap forward on this, thanks to the fact that they make use of an optical beam instead of a particle one [43].

The protocol presented in this work can be applied to all copper-based alloys, and especially highly corroded ones, given that their size allows them to fit in a FIB chamber. Common chambers are able to handle samples up to 150 mm in diameter and 50 mm in thickness. It makes use of EDS as analytical technique, but the FIB-prepared CS can be potentially investigated with many other techniques with micrometric and sub-micrometric resolution capabilities, in particular synchrotron-based ones. In fact, even though not visible by naked eye, the CSs are easy to be found under an optical microscope, provided that the region in which they have been made is known. The method itself still has room for improvement. In particular, the influence of EDS detector position needs to be further investigated, and a more efficient solution for the removal of milling effects removal is advisable. Moreover, its applicability to other corroded substrates, like iron or silver, or even gilded objects, have still to be assessed. These will be the focus of future research.

As additional output, SEM investigations conducted on many archaeological coins revealed the presence of diffused cracks and pores, which develop along both the surface and inward. This is a potential key factor to take into account for the future development of a protective treatment.

III.2.3.2 LA-ICP-MS for metallic heritage study

The drilling test on an archaeological copper-based coin reveals that the ablation process does not follow a linear path across subsequent shots. A linear trend has been observed only over a limited number of shots, and after the ratio between ablation depth and number of shots tends towards a logarithmic

behaviour. However, a strong dispersion of the data makes difficult to extract a real analytical relation between the two parameters. Such dispersion can be attributed to the high heterogeneity that real archaeological *patinas* show, being constituted by materials with very different ablation behaviours and yield, such as soil contaminants, corrosion products and alloying elements. This, along with the variability in the thickness of the various layers of which a *patina* is composed, causes a large variability between the ablation on apparently similar spots. Despite the effect of heterogeneity in the sample, the laser proved to be able to create drilled volumes with a regular shape, a wide and flat bottom side, and growing conical effects only noticeable from ca. 100 μm of ablation depth.

Depth profiling proves to be promising for investigating enrichment, depletion and clustering phenomena along the depth axis, as well as qualitatively investigate the presence of a layered system. However, it presents also various critical points. The most prominent is that, even if it allows to study the composition and thickness of subsequent layers, it does not allow to evaluate the difference between a corroded layer and a bulk metallic layer. This is because sharp changes in elements signals cannot be univocally marked as the interface with the bulk metal, and the system is not able to monitor the anionic part of corrosion compounds. This hinders at the moment possibility to use LA-ICP-MS for bulk analysis without a complementary technique.

The choice for a 110 μm laser spot as optimal working condition in this case is linked to the representativeness of the analysis. As evidenced also for FIB-SEM, alloy features commonly have characteristics size in the order of tens of μm . Going below 100 μm of spot size can be thus detrimental, while a 100 μm spot is still not visible by naked eye. The comparison between two runs at different fluence evidences a reproducible and scalable behaviour of the ablation process. Reducing the working fluence can be interesting in order to rise the depth resolution of the analysis and better resolve phase transitions. Moreover, the use of a lower fluence proved to reduce the formation of redeposited material around the laser spot. Further study on the influence of laser power and shot frequency are advisable.

Other than for corrosion studies, depth profiling proves to be promising also for micro-invasive authentication procedures, thanks to its capability to investigate even very thin layers. Possibly, also ICP-MS capabilities for the monitoring of trace elements can be exploited for authentication purposes, coupled with the micro-invasivity of the laser ablation.

The 3D mapping obtained in this work is the first reported in literature of an archaeological metallic *patina*. This proves that such result is feasible, allowing for the 2D localisation of elements on wide areas, coupled with the depth profiling capabilities discussed above.

The duration of the acquisition process is a critical parameter. This experiment was designed as a proof of concept for the 3D reconstruction of the corrosion patina from an archaeological copper-based object. In the working conditions adopted (dosage 7, 6 J/cm² of fluence 6, 1.9x1.3 mm² of analysed area) an ablation yield of 1.5-3 µm per layer has been achieved (for a total of ca. 20 µm). Considering that the ablation (and ICP acquisition) of one layer took around 4 minutes in our working conditions, it is reasonable to propose LA-ICP-MS for 3D analysis of corrosion patinas of 100 µm or above. Next experiments will point towards this achievement. Clearly, areas as big as the one investigated in the present case are visible by naked eye. A next challenge will be to test the ablation on smaller areas, at cost of some representativeness of the analysis.

This work also highlights a high complementarity with optical profilometer. The latter represents a simple way for bridging some of the gaps of LA-ICP-MS, in particular giving a detailed visual information and quantitative data on ablation depth and ablation shape.

Overall, the proposed case studies on LA-ICP-MS well point out its strong potential for corrosion studies, but also reveal some critical aspects that have to be addressed before considering this technique as a possible new standard in the field of diagnostics and archaeometry. By doing so, this work opens many interesting paths for future research on this topic.

III.3 SPEM for ancient metals: identification of a new form of corrosion and exploration of new methodological synergies

SPEM investigations were conducted on two ancient Roman coins, with the aim of assessing the capabilities of SPEM on the analysis of the small-scale heterogeneities of archaeological *patinas*.

A new form of corrosion for Cultural Heritage objects (i.e. metallic whiskering) was revealed on one coin using SPEM. This was made possible by the SPEM capability to image the differential charging over the sample surface, generated by *patina* heterogeneity. Whiskering was further investigated by SEM-EDS, FIB-SEM, lab-based XPS and μ XRF mapping, to understand its chemical origin and evaluate potential diagnostic features for its detection.

On the second coin, two micro-digs were prepared by laser-ablation and analysed with SPEM in order to verify whether the ablation process had allowed to expose the metallic bulk of the sample. Lab-based XPS analyses on pellets of reference materials were also performed prior and after ablation with laser, in order to check the possible impact of the laser preparation step on the sample.

III.3.1 First observation of metallic silver whiskers as corrosion product

III.3.1.1 SPEM observation of whiskers

Silver whiskers have been found on a region on coin 582405 while imaging large areas of the sample using SPEM. As visible in Figure 76 a, the low border of the coin showed a much higher signal output, due to a reduced charging effect. When investigating closer this ROI, small Ag-rich features of typical diameter below 10 μ m have been detected (Figure 76 e).

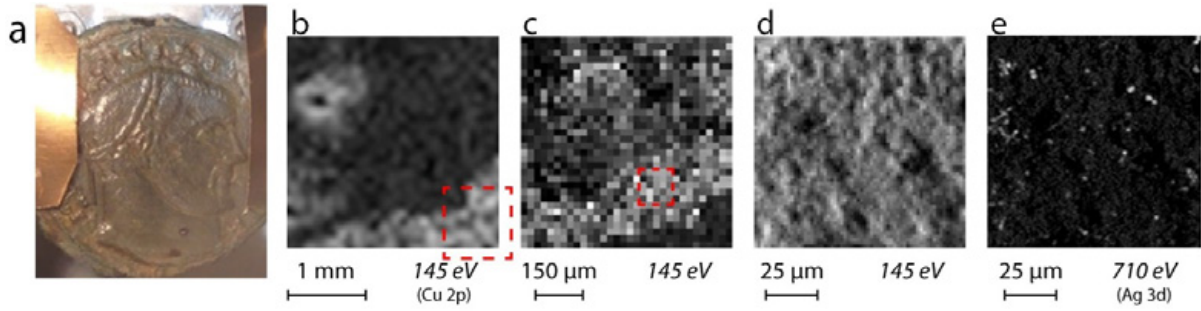


Figure 76 Observation of whiskers presence on the surface of coin 582405. a) Coin 582405, as mounted on the SPEM sample holder. b) SPEM map at 145 eV (Cu 2p), $3200 \times 3200 \mu\text{m}^2$, of the bottom region of the coin face. c) SPEM map at 145 eV (Cu 2p), $640 \times 640 \mu\text{m}^2$, of the region marked in red in b). d) SPEM map at 145 eV (Cu 2p), $96 \times 96 \mu\text{m}^2$, of the region marked in red in c). e) SPEM map at 710 eV (Ag 3d), $99.8 \times 99.8 \mu\text{m}^2$, in the same region as d).

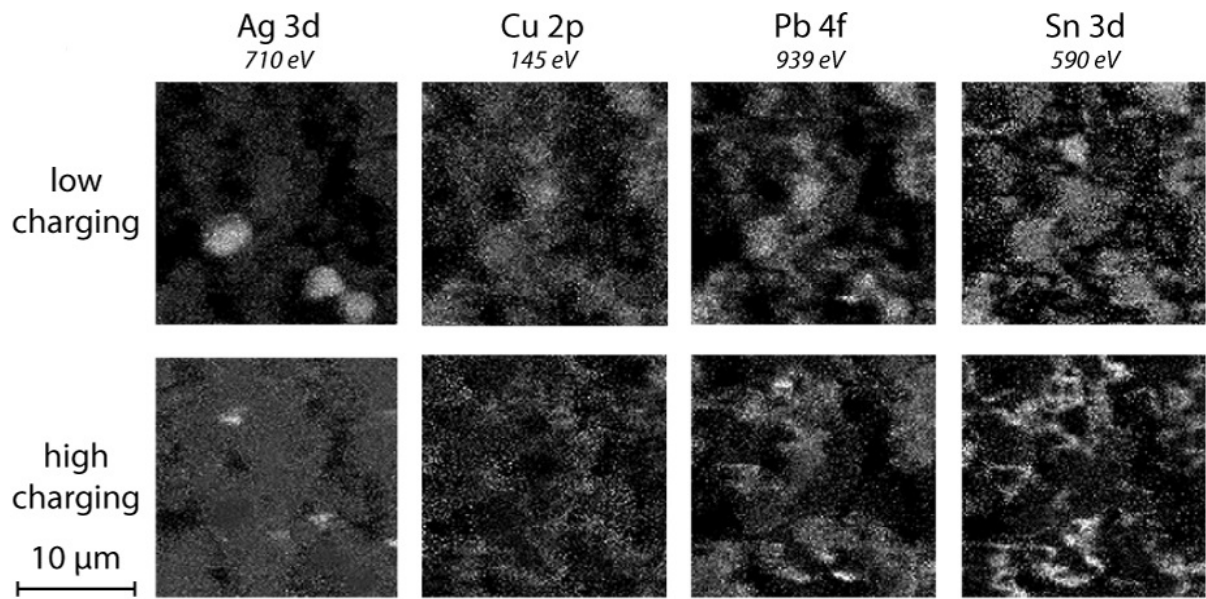


Figure 77 SPEM high-magnification maps collected in a sub-region of Fig. 37e. Each map is $20.5 \times 20.5 \mu\text{m}^2$. Top row) Areas with lower charging effects (the peak considered for normalisation is in the upper part of the energy window of the map) and bottom row) areas with higher charging effects (conversely).

High magnification maps better highlight the micrometric size of Ag-rich features, and further reveal a highly different charging behaviour of the surface nearby (Figure 77). The presence of two differently charging domains appears plausible to explain this feature, separated one from the other by ca. 5-6 eV due to charging shift, with the one at higher energy (lower charging effects) presenting also more intense signal. Even though the spectra extracted from SPEM maps (not shown here) have too low resolution to allow for further conclusions, this difference in energy underlines the need of further investigations with complementary techniques to explore the phenomenon. Ag-rich larger feature show up in the domains with low charging effects, while there are also small Ag-rich features in domains with high charging effects.

III.3.1.2 Investigation by SEM-EDS and FIB cross-sections

The ROI highlighted by SPEM has been further investigated by SEM-EDS in order to understand the nature of the Ag-rich features.

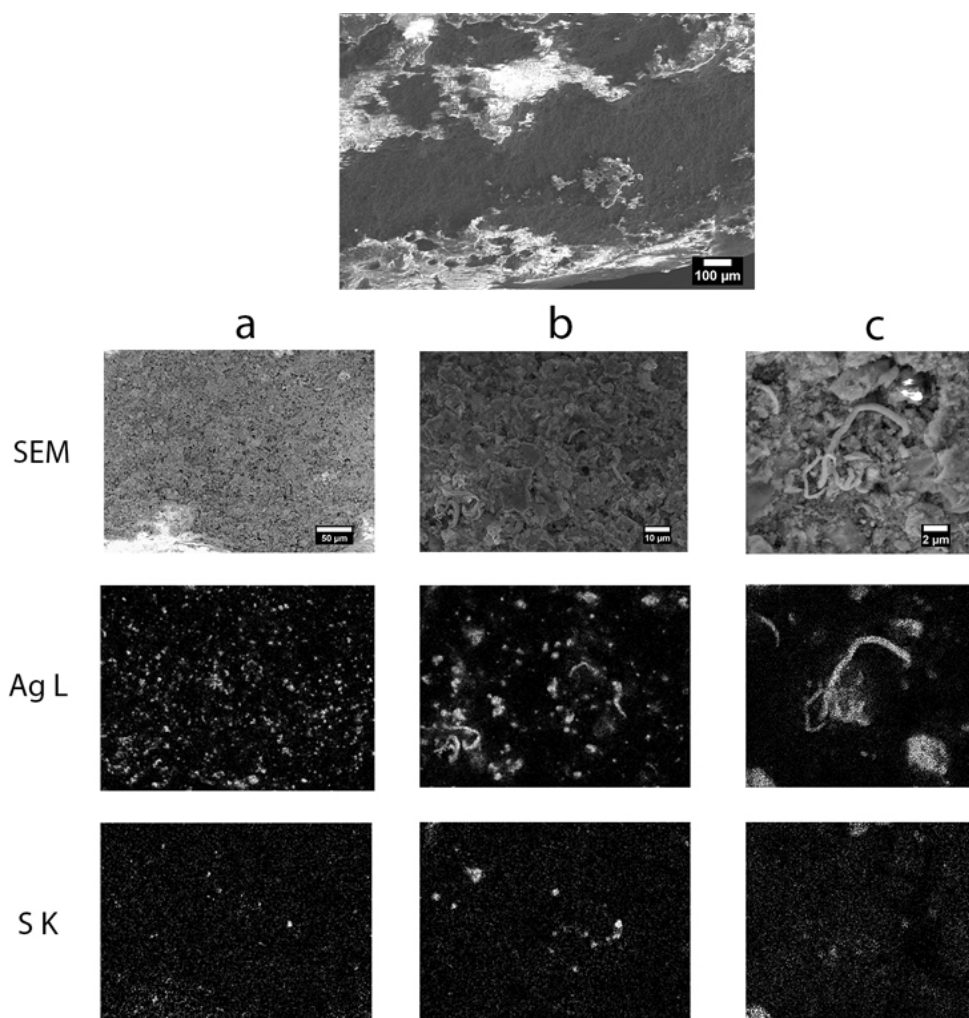


Figure 78 SEM-EDS investigation of the ROI with Ag-rich feature identified with SPEM. (Top image, first line) a SEM-SE image of the ROI at low magnification. In the three rows below, (second line) SEM-SE images at increased magnification, along the respective Ag L (third line) and S K (fourth line) elemental maps. Data on columns a and b were acquired with the ZEISS system, 20 kV. Data on column c were acquired with the FEI system, 18 kV.

This specific region of the coin appears particularly porous and covered by powdery deposits (Figure 78). On it, tiny filaments (thereby “whiskers”) on the micron-size, clearly made by Ag, are easily visible both at medium magnification, and further confirmed with the support of EDS maps.

Such Ag-whiskers present an elongated form, decreasing in diameter until an eventually visible tip. They also show a striated morphology, similar to objects extruded through a mould (Figure 79). In some cases, they have been found in correspondence with localised high amount of S.

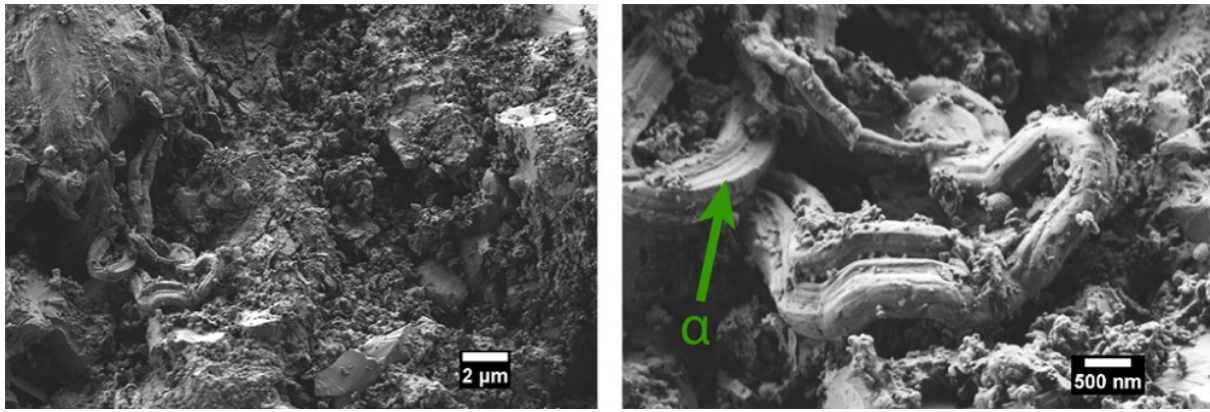


Figure 79 High-magnification SEM-SE images of a whisker (ZEISS system, 1 kV). The green arrow identifies where point α in Table 13 has been taken.

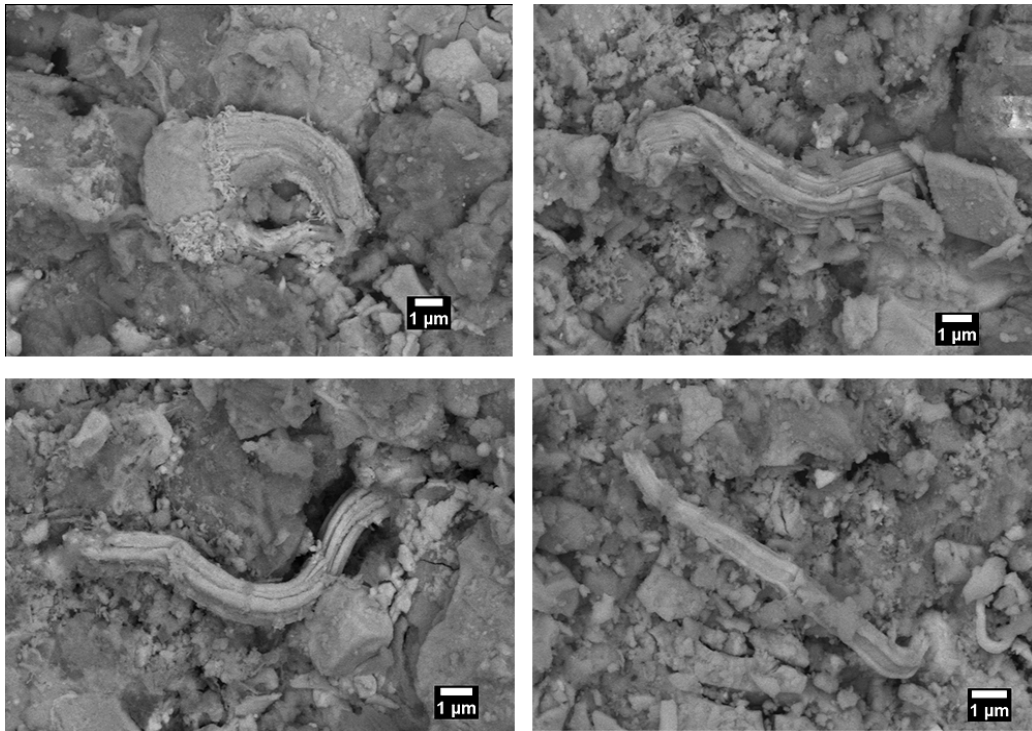


Figure 80 SEM-SE of some other whiskers found in the same ROI (ZEISS system, 10 kV).

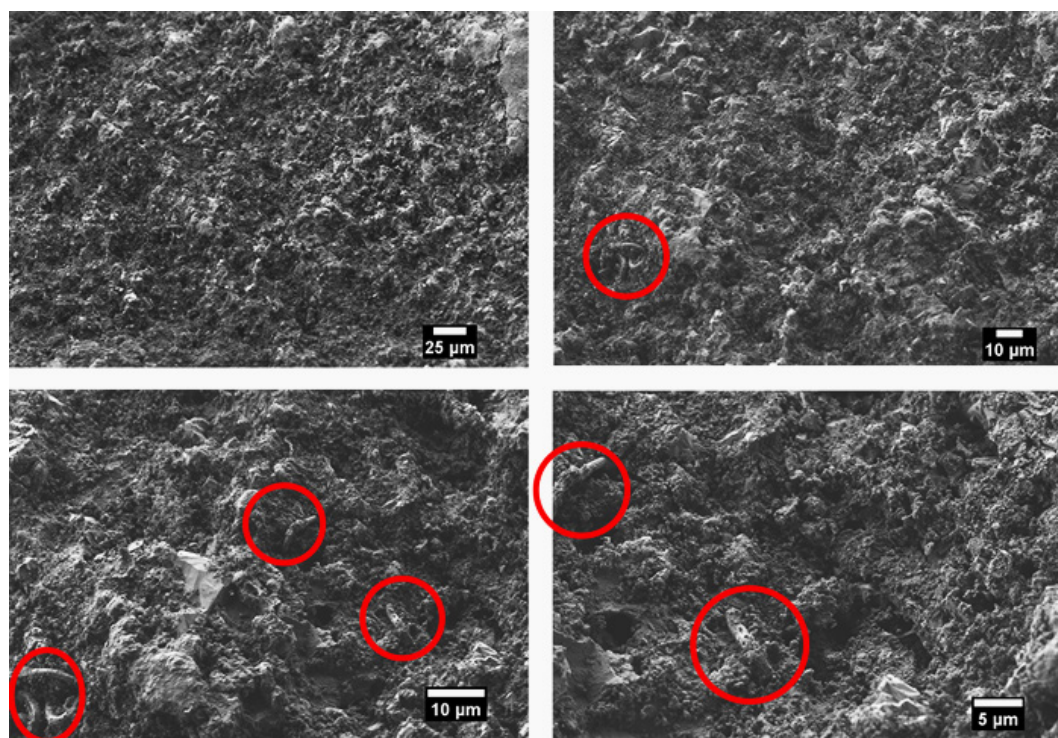


Figure 81 SEM-SE images of whiskers and their context (ZEISS system, 1 kV). Some of the whiskers spotted are marked by red circles.

In particular, the observation of Figure 80 and Figure 81 clearly shows that whiskers have grown from the sub-surface region in outward direction, closely intertwining with other corrosion aggregates, to finally lay on the top of the external surface. They are also covered by fine corrosion and soil residues particles. This suggests that whiskers formation has happened simultaneously with the growth of the outer corrosion layer or right after its stabilisation, but, in any case, prior to the excavation of the artifact and its cleaning. Moreover, whiskers have been observed on coin surface also outside the specific ROI investigated, even if with far lower frequency (Figure 82).

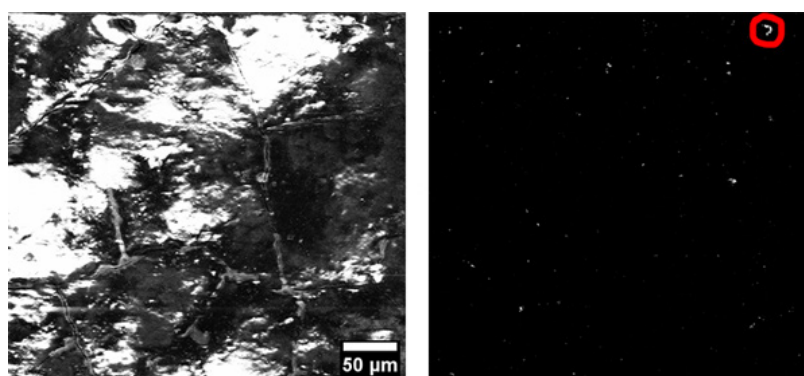


Figure 82 Example of whisker found in another region of the coin surface. The strong charging effects are due to the isolating nature of the thick patina (FEI system, 20 kV). (left) SEM-SE image and (right) corresponding Ag L line map.

EDS semi-quantitative data from the whisker in Figure 79 reveals a composition mostly made of Ag (ca 72 wt%), with a limited amount of O and Cu (point α in Table 13). However, EDS have a depth of analysis that is comparable in size with the diameter of the whiskers ($\sim \mu\text{m}$), and this requires the use of different approaches to investigate the phenomenon more in detail. To address this, FIB cross-sectioning has been performed on a whisker and on a larger surface (exploiting the deep-trenching procedure previously developed and presented in par. III.2.1).

	C	O	S	Fe	Cu	As	Ag	Sn	Pb	Total
α	3.8	10.4			8.3		71.9	2.0	3.7	100
β	1.7	1.4			2.6		94.3			100
γ	0.9	5.4			23.4		70.3			100
δ	3.2	3.8	10.0		44.2		38.8			100
ϵ	3.6	14.7		4.8	39.6	1.6	5.2	22.8	7.6	100

Table 13 Semi-quantitative EDS data from the respective points indicated by a Greek letter in various figures. All data are expressed in wt%.

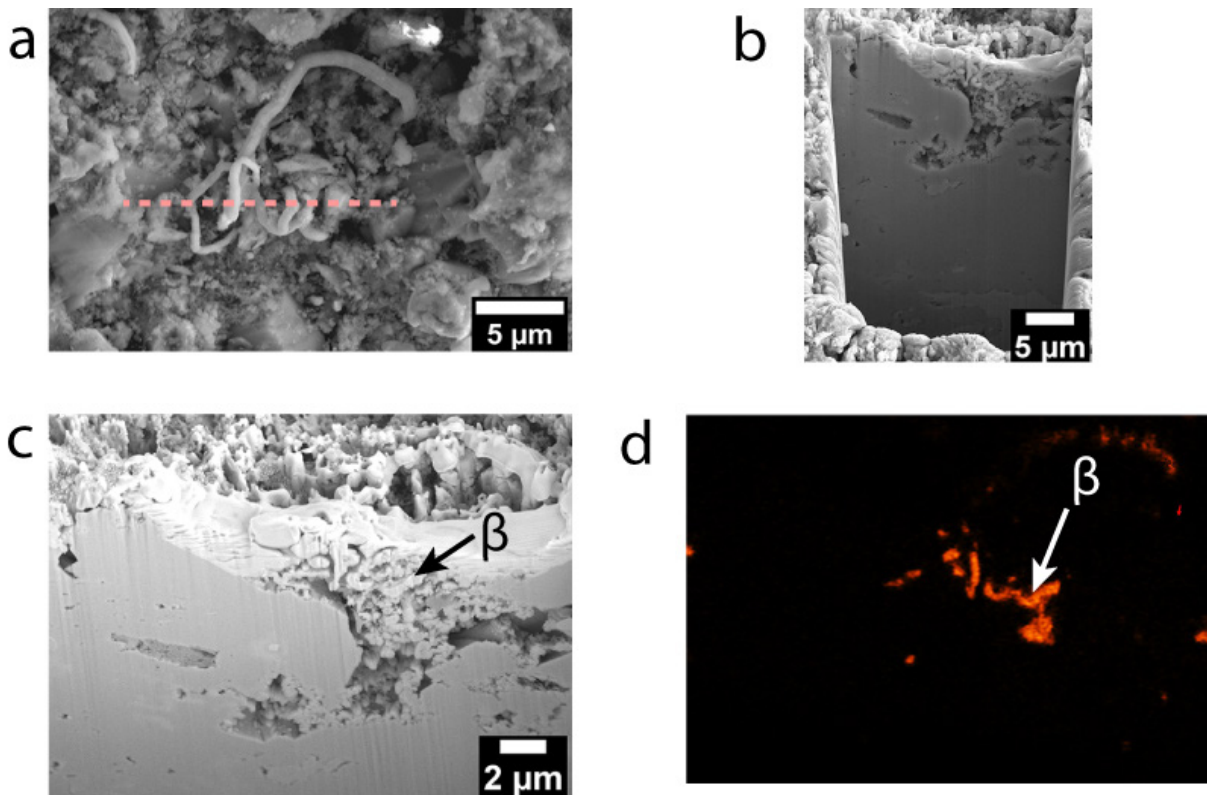


Figure 83 FIB cross-section of a whisker. a) SEM-SE of the trenching location (red dashed line). b) SEM-SE full cross-section view. c,d) SEM-SE and Ag L line EDS map of the cross-sectioned whisker. (a,b) images are taken using the FEI system at 18 kV. (c,d) images are taken using the ZEISS system at 8 kV. The arrows identifies where point β in Table 13 has been taken.

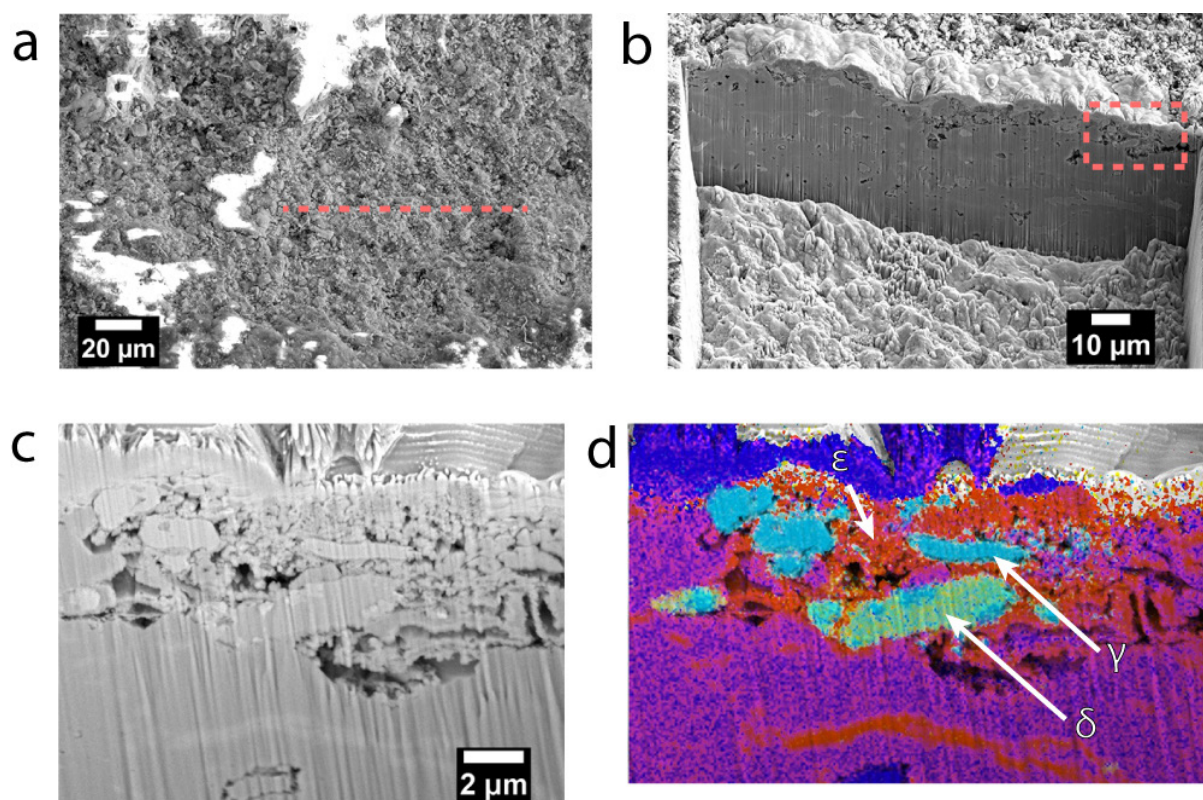


Figure 84 Larger FIB cross-section. a) SEM-SE on the trenching location (red dashed line). B) SEM-SE of the cross-section. c,d) SEM-SE image and EDS map of the area marked by the red rectangle in (b). EDS colour references: Ag L (light blue), Cu K (blue), O K (orange) and S K (yellow) lines. (a,b) images are taken with the FEI system at 18 kV. (c,d) images are taken with the ZEISS system at 8 kV. The arrows identify where points for quantitative results in Table 13 have been taken.

From the cross-section made in correspondence of a selected whisker (Figure 83), the intertwining between the whisker and the corroded area is even more intimate than expected. The whisker does not penetrate more than 5 μm in depth. In cross-section, the whiskers appear to be made exclusively of Ag (> 94 wt%, point β), suggesting a metallic nature of the object (i.e., Ag^0).

In a larger cross-section (Figure 84), one whisker has been cut on the right side (point γ). The study of its elemental surrounding interestingly reveals the presence of a grain made of Ag, S and Cu, most likely Ag_2S or mixed Ag-Cu-S compounds (point δ). Ag-rich non-oxidised phases with similar features seem located only at the surface, as they have not been found in deeper regions of the cross-section.

III.3.1.3 Lab-based XPS and μXRF mapping

The lab-based XPS investigation of the ROI characterised by the presence of high number of whiskers revealed an unexpected behaviour. As visible in the XPS spectra in Figure 85, all the metallic elements

found on the sample (Ag, Cu, Sn, Pb) present a splitting of their XPS lines in two. Consequently, Cu 2p doublet appear as a two distinct doublets, and similarly for Sn 3d and Pb 4f. Ag 3d doublet is further split into three doublets. The conjugated nature of the additional peaks into doublets is confirmed by the preservation of the spin-orbit splitting value among each doublet. The energy separation between main and “split peaks” is variable among different elements: 2.2 eV for Cu 2p, 1.9 eV for Sn 3d, 2.0 for Pb 4f and 2.5/0.9 eV for the two split doublets of Ag 3d. In addition, the difference in the integrated areas below the peaks is not consistent among different elements: Cu presents a more balanced situation with a surplus of the lower binding energy doublet, whilst Ag has a slightly more marked presence of the latter, and Sn and Pb show a 1:10 ratio between the two doublets. It must be noted that, in lab-based XPS experiments, energy is commonly expressed as binding energy, while in SR-XPS experiment the kinetic energy is used. Such two scales have an opposite behaviour, thus lower binding energy means higher kinetic energy. This must be kept in mind when comparing SR and lab-based data. The insurgence of peaks splitting seems highly reproducible, as it has been observed multiple times in various conditions. Results have always been consistent to what showed in Figure 85.

By varying the charge balance voltage of the neutralizer from the optimum value (3.5 V, determined according to the procedure described in par. II.4.5), towards higher values, the main doublet of Ag 3d gradually shifts towards lower binding energy, while the second main doublet remains in the same position (Figure 86). The same shift occurs to the main peak of C 1s, related to amorphous carbon present on the patina. When lowering the charge balance voltage below the optimum value, instead, the intensity of the main doublets of Ag 3d plummets and a new doublet appears at higher binding energy (Figure 87). At the same time, the second main doublet remains at the same energy position. It must be noted that, in the sub-compensated conditions, the sum of the areas of the new doublet and of the one still present in the position of the original main doublet (i.e. the blue and red lines in Figure 87, respectively) equals to the original area of the main doublet in optimum compensated conditions (green line). Meanwhile, the relative area of the second main doublet remains constant (**Table 14**).

One possible explanation for this behaviour is the different conditions in which Ag atoms are present: a region that suffers from surface charging, and is thus influenced by the level of charge compensation, and another region that does not suffer from surface charging. In addition to this, experiments conducted by varying the spot size of the primary beam (Figure 88) suggest that this different localisation of Ag in two regions remains also on a small scale, at least lower than 50 μm i.e.: the smallest size of the beam spot used.

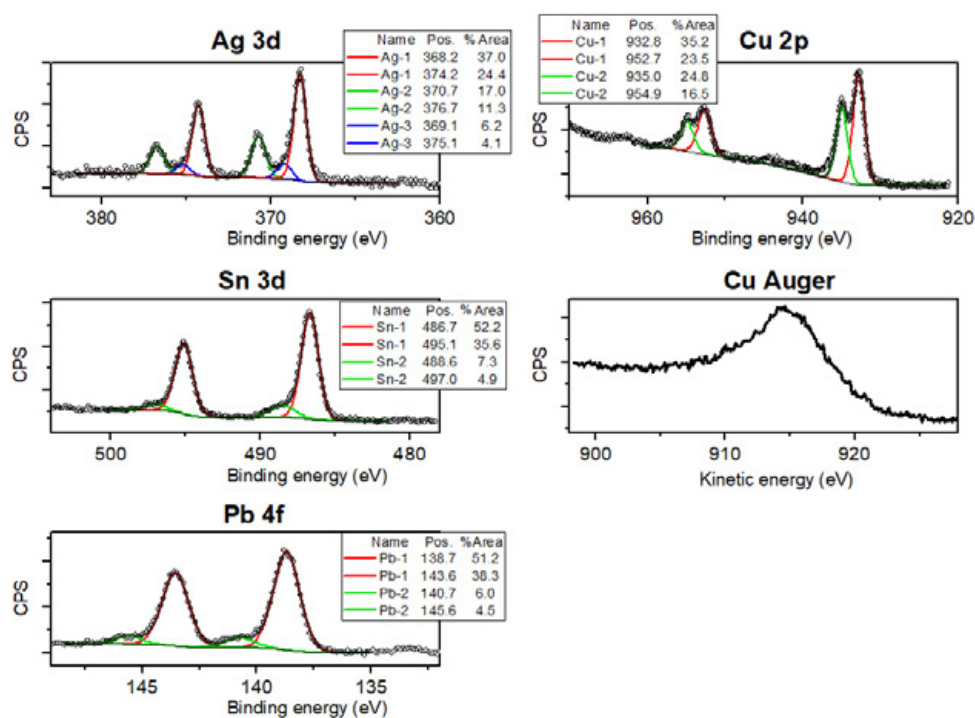


Figure 85 XPS spectra of metallic elements in the whisker's ROI. The respective XPS lines are indicated in each spectrum title. For Cu, also the Auger spectrum is reported. The binding energy position in eV and the relative percentage area is reported for all peaks of every spectrum.

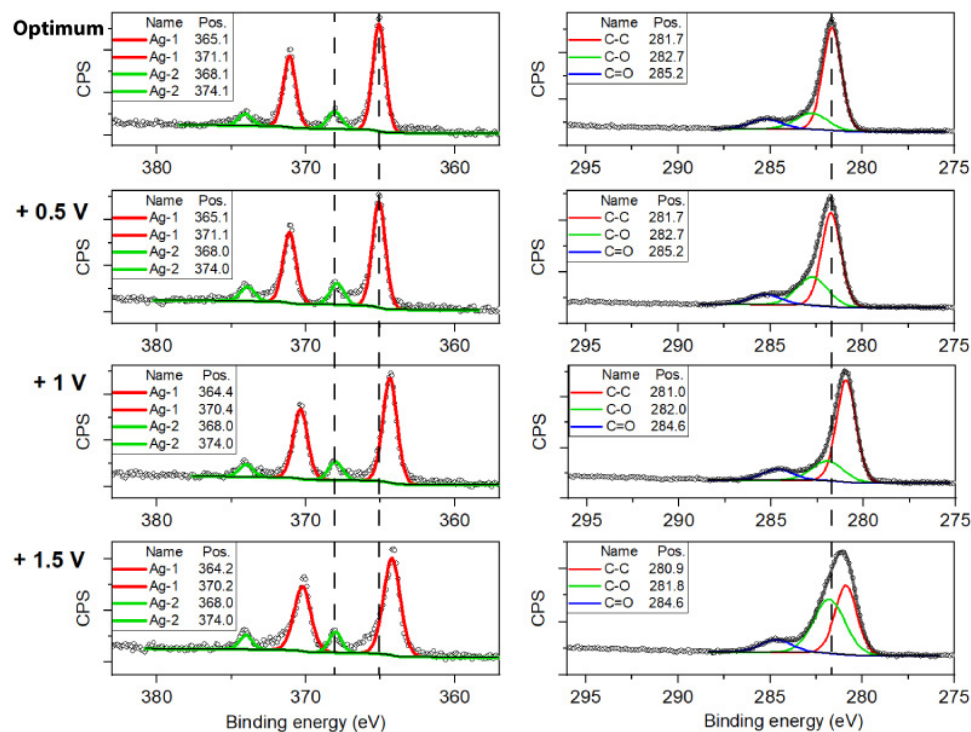


Figure 86 XPS spectra of Ag 3d and C 1s, by varying the charge balance voltage of the neutralizer from the optimum value towards higher values. The optimum value (3.5 V) was determined according to the procedure described in the Experimental chapter. The binding energy scale is not calibrated. The binding energy position in eV is reported for all peaks of every spectrum.

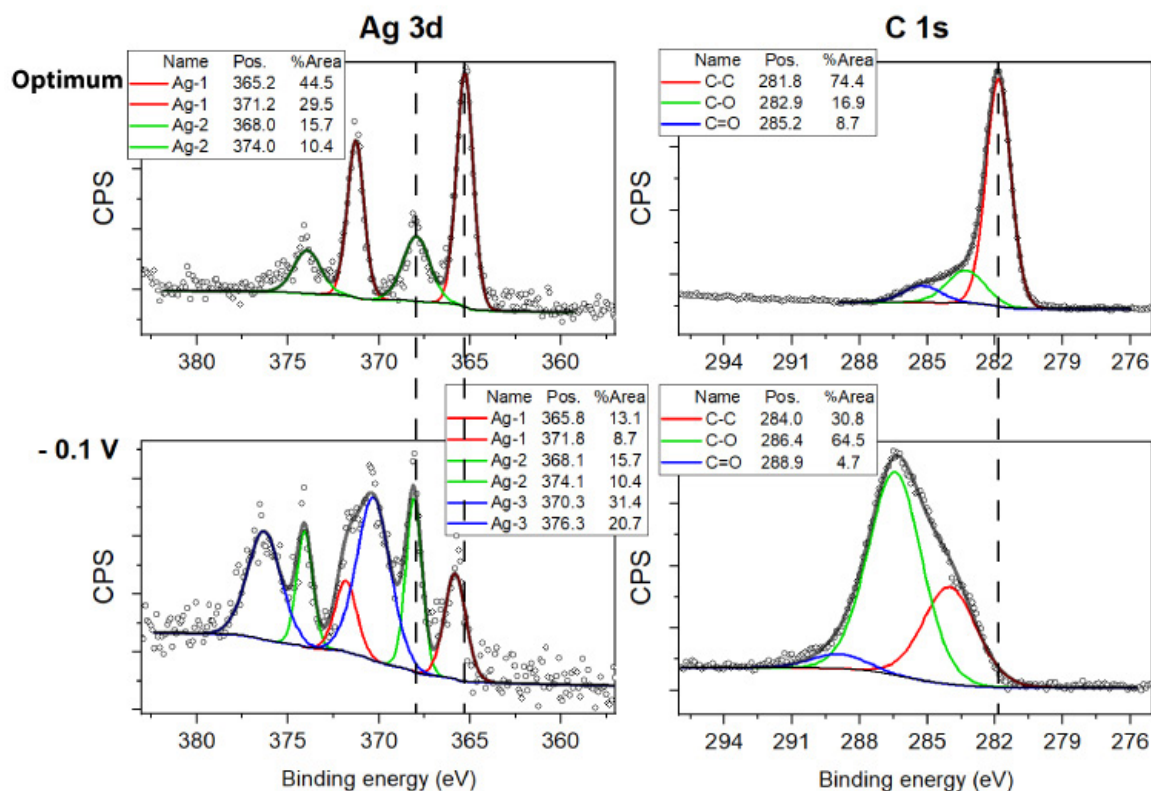


Figure 87 XPS spectra of Ag 3d and C 1s, by varying the voltage applied to the charge neutraliser. The optimum value (3.5 V) was determined according to the procedure described in the Experimental Section. The binding energy scale is not calibrated. The binding energy position in eV and the relative percentage area is reported for all peaks of every spectrum.

Charge balance	Doublet label	Ag 3d _{5/2}	Ag 3d _{3/2}	TOT
		%	%	%
+ 0 V	Ag-1	44.5	29.4	73.9
	Ag-2	15.7	10.4	26.1
- 0.1 V	Ag-1	13.1	8.7	21.8
	Ag-2	15.7	10.4	26.1
	Ag-3	31.4	20.7	52.1
	Ag-1 + Ag-3	44.5	29.4	73.9

Table 14 Quantitative values for Ag 3d spectra in Figure 87.

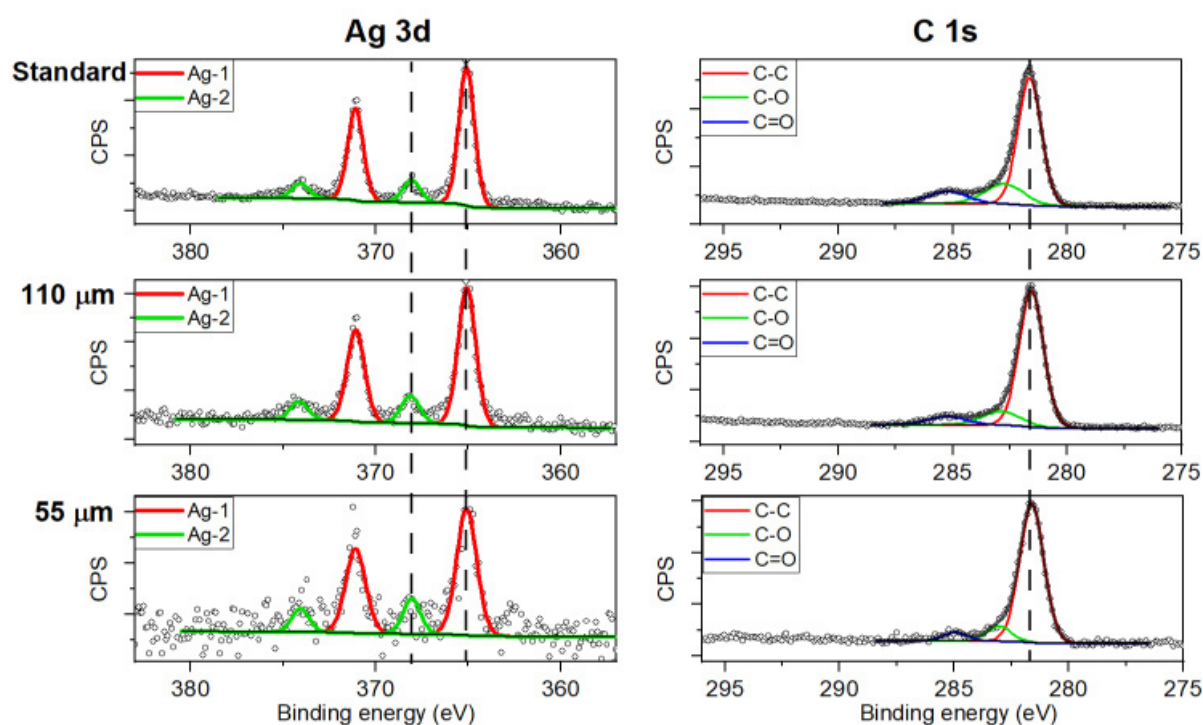


Figure 88 XPS spectra of Ag 3d and C 1s by varying the spot size. The binding energy scale is not calibrated.

μ XRF maps further proved that there are other areas enriched in metallic silver whiskers, on coin 582405. Indeed, a second region with a totally similar behaviour, clearly marked by its high $^{Ag}L/_{Ag}K$ ratio (Figure 89) has been identified.

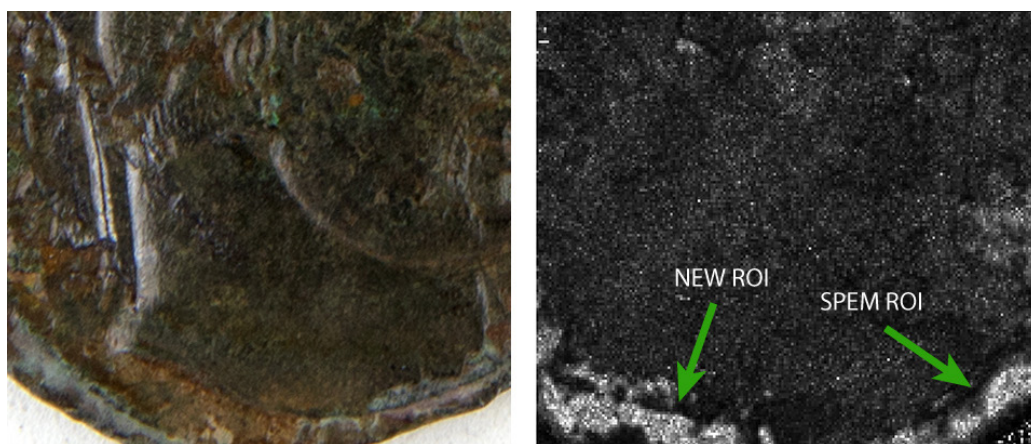


Figure 89 (left) Optical image and (right) $^{Ag}L/_{Ag}K$ ratio from μ XRF mapping data. SPEM ROI is the area that was previously identified by SPEM and investigated throughout this paragraph. NEW ROI is the new area with whiskers identified by XRF.

III.3.2 Validation of laser-ablated micro-digs for electrochemical applications

III.3.2.1 Profilometric characterisation of LA-microdigs

Laser ablated micro-digs observed under an optical profilometer reveal a well-defined rectangular dig, with a hilly bottom created by the overlapping of not-perfectly collimated laser spots (Figure 90). The maximum depth achieved is slightly below 100 μm . It must be underlined that the 375 μm -wide dig was necessary for the scope of achieving the present SPEM data, due to the geometry of the experimental setup.. Digs can be easily tuned depending on the applications. For EIS techniques (the primary scope for the present digs) dig size can be made far smaller, highly reducing the overall aesthetic impact.

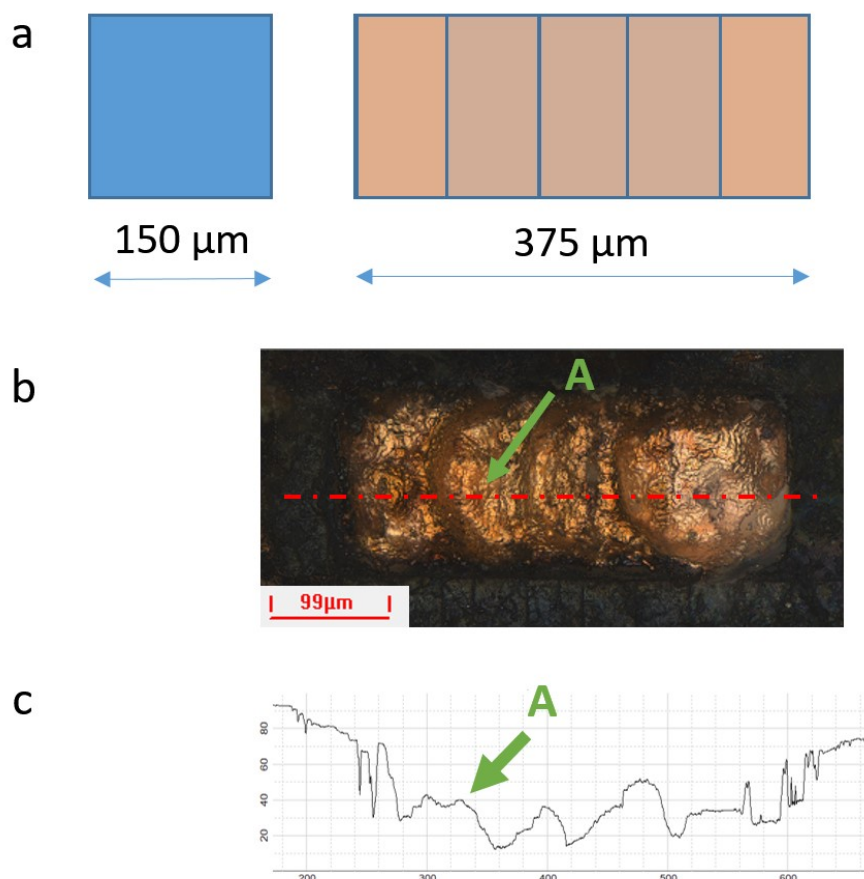


Figure 90 a) Scheme of the dig (top view) b) All-in-focus microscopic image of dig X. (c) Profilometric cross-section of dig X along the red line in b). The point marked with 'A' refers to the same point A in Figure 92.

III.3.2.2 SPEM investigation of LA-microdigs

Figure 91 reports an example of XPS spectra taken directly on the outer surface of coin 587202 using SPEM. As clearly shown, the XPS spectra is shifted of ca. 700 eV, indicating a severe surface charging phenomenon. Synchrotron-based SPEM setup does not allow for the use of a charge neutraliser, as in lab-based XPS. The reason lies on the technical difficulties to obtain a neutralisation beam perfectly collimated as the main X-ray beam, able to hit exactly the same point on the sample. This represents a major challenge in terms of engineering implementation. Therefore, SPEM instruments are not equipped with charge compensation systems.

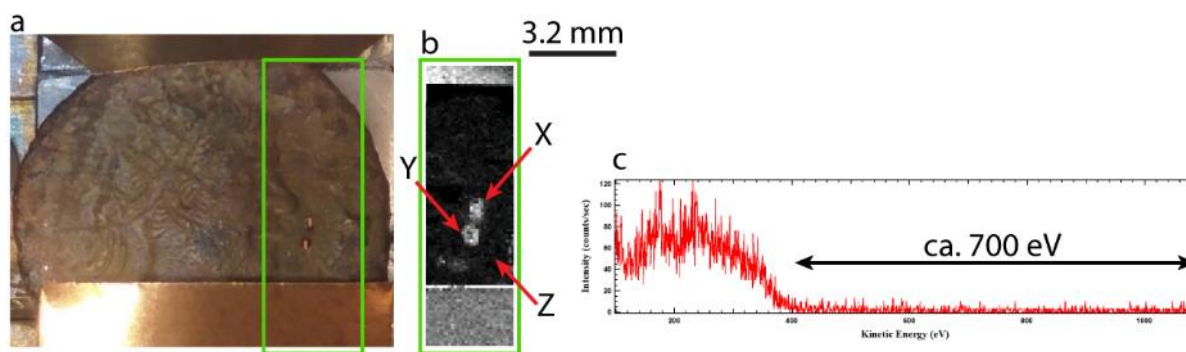


Figure 91 a) Coin 587202, as mounted in the SPEM chamber. b) SPEM maps (793 eV) at low magnification of the LA-digs region (green rectangle marks the corresponding area on a). c) XPS survey spectrum taken at point Z (as marked in b), showing a charging effect equal to approx. 700 eV. X and Y points mark the position of the two digs investigated.

Nonetheless, SPEM was fully able to locate, image, and analyse LA micro-digs. In particular, Cu^0 was easily identified at the bottom of the microdigs, as is particularly evident in the point A (Figure 92 a) inside dig X (Figure 90) by comparison with reference spectra taken in the same experimental conditions. In detail, from Cu 2p 3/2 region, the absence of Cu^{2+} component has been observed, given the absence of shake-up satellite peaks ca. 7 eV higher in binding energy with respect to the main peak (Figure 92 c). Moreover, the position of the main peak (932.5 eV), and its FWHM are very similar to the ones of Cu^0 and Cu^+ reference spectra. From the Auger line, the presence of Cu^0 , together with Cu^+ species has been unequivocally confirmed (Figure 92 b). In fact, from a comparison with Cu^0 and Cu^+ Auger reference spectra, the peak at 917.8 eV, together with the small shoulders at 913.2 eV and 920.4 eV, can be attributed to Cu^0 , while the feature at 915.9 eV is due Cu^+ species.

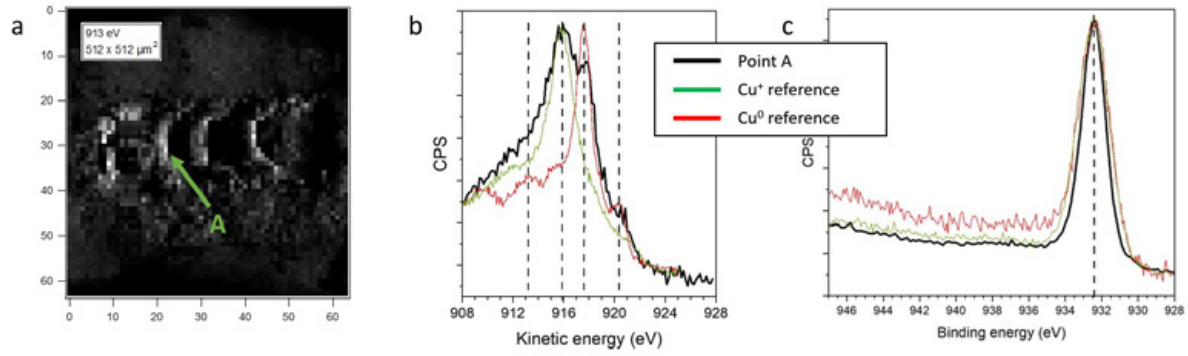


Figure 92 Cu⁰ observation at point A, dig X. a) SPEM map at Cu LMM (Auger) energy. b) Cu LMM high-resolution spectra taken in point A (black), overlapped with reference spectra for Cu⁺ (green) and Cu⁰ (red) taken at the same beamline in equivalent working conditions. c) Cu 2p 3/2 region high-resolution spectra (same legend as for b)).

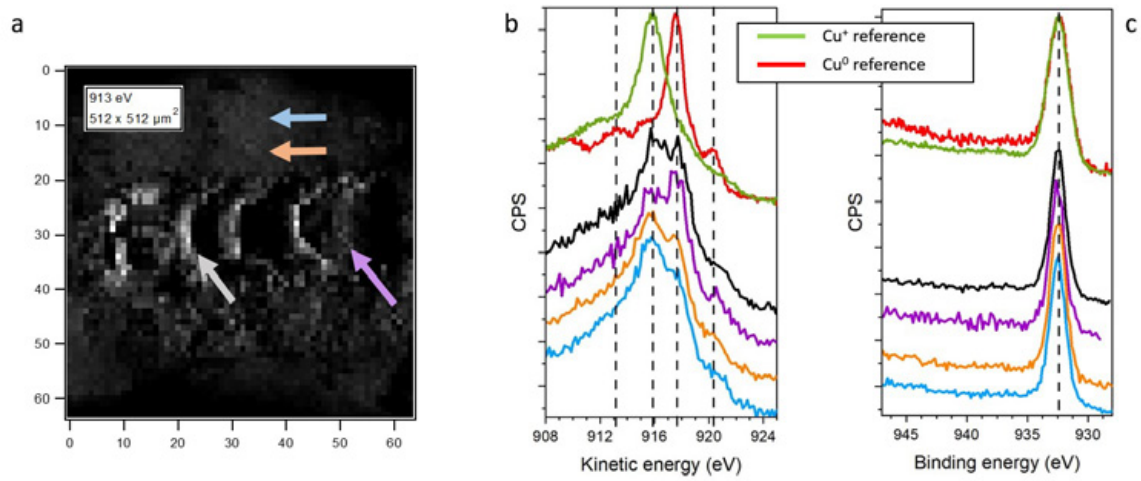


Figure 93 Further Cu⁰ observations inside and around dig X. a) SPEM map at Cu LMM (Auger) energy. b) Cu LMM high-resolution spectra taken in the points indicated by arrows of same colour in a) (black line correspond to grey arrow), overlapped with reference spectra for Cu⁺ (green) and Cu⁰ (red) taken at the same beamline in equivalent working conditions. c) Cu 2p 3/2 region high-resolution spectra (same legend as for b)).

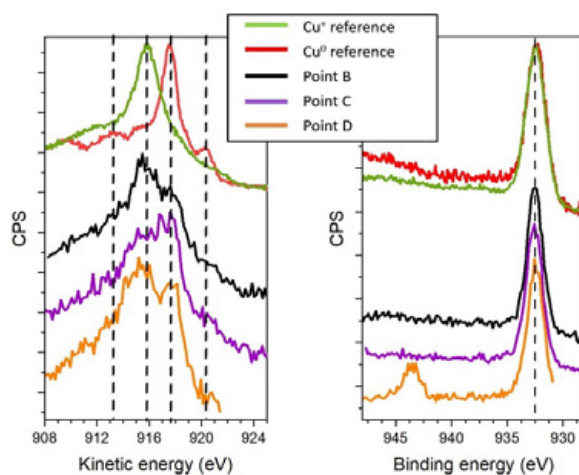


Figure 94 Cu⁰ observations inside dig Y. a) SPEM map at Cu LMM (Auger) energy. b) Cu LMM high-resolution spectra. c) Cu 2p high-resolution spectra.

Figure 93 and Figure 94 report additional observations for metallic Cu inside both LA-microdigs. Interestingly, in Figure 93 it is possible to note that Cu⁰ is present also at the border of dig X, creating a halo effect in its surroundings. Still, no signal from Cu²⁺ was detected.

III.3.2.3 Effect of the laser ablation process on the oxidation of Cu compounds

In order to exclude any influence on the presence of Cu⁰ due to the sample preparation via laser ablation, a set of pellets made of pure chemicals representing the common (and expectable, in the case of the coin) Cu corrosion products have been analysed using lab-based XPS as pristine, and after a raster-scan ablation over the pellets surface (Figure 95).

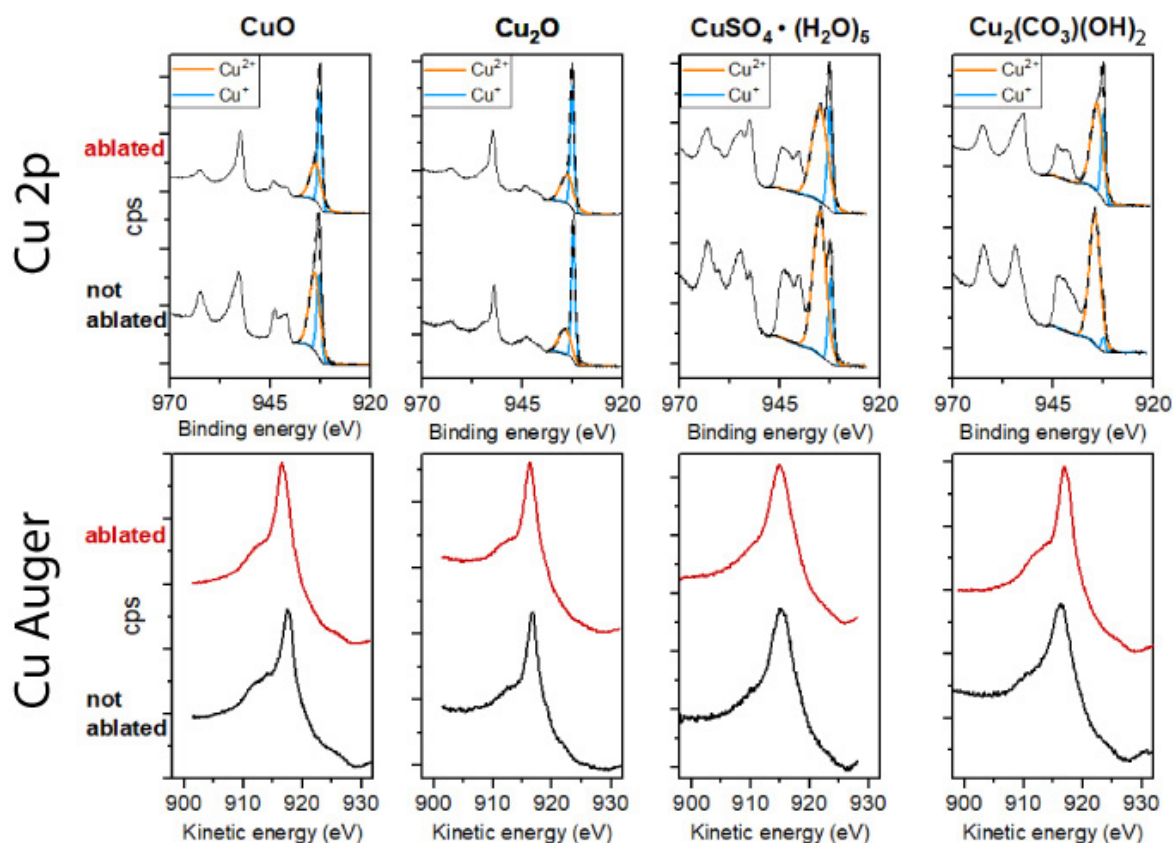


Figure 95 Verification of laser ablation effects on the stability of pure Cu compounds by lab-XPS. Cu 2p (top row) and Cu LMM (bottom row) for (from left to right): CuO, Cu₂O, CuSO₄·(H₂O)₅, Cu₂(CO₃)(OH)₂. Inside each plot, the spectrum of the pristine material is shown at the bottom, while the one of the ablated material is shown at the top. In Cu 2p plots, blue and orange lines represent the fitting profiles of Cu⁺ and Cu²⁺ components. For simplicity, only the 2p 3/2 sub-region of the Cu 2p spectrum without shake-up satellites was fitted for all spectra collected.

The analysis demonstrate that the laser ablation process only provokes reduction of Cu²⁺ to Cu⁺, as can be seen from Cu 2p spectra. Considering only the 2p 3/2 sub-region for the sake of simplicity, the Cu²⁺ component (in orange) decreases, together with shake-up satellites, in favour of the Cu⁺ component (in blue). This is evident in the case of CuO, but it is partially visible also for CuSO₄·(H₂O)₅ and Cu₂(CO₃)(OH)₂. In the case of CuO, the Cu²⁺ component, found at 933.5 eV, decreases of about 35% in favour of the Cu⁺ one, found at 932.5 eV [44]. Moreover, the Auger peak moves about 1 eV towards lower kinetic energy, but its shape does not change. This result is consistent with the presence of a higher amount of Cu⁺ at the expense of Cu²⁺, whilst it excludes the formation of metallic Cu, that would cause the Auger peak shift towards higher kinetic energy and the appearance of two new features on the sides of the main peak [44]. For CuSO₄·(H₂O)₅ and Cu₂(CO₃)(OH)₂, the decrease of the Cu²⁺ component is lower, around 10 % and 15 %, respectively. In the CuSO₄·(H₂O)₅ sample, the Cu²⁺ component is found at 935.1 eV, while the Cu⁺ is at 932.5 eV, according to the data reported in the literature [44]. Instead, for Cu₂(CO₃)(OH)₂, the Cu²⁺ peak moves from 934.7 eV (pristine sample) to 933.8 eV (after ablation), while the Cu⁺ peak stays at 932.5 eV as the other samples. Considering the

Cu^{2+} component, the first value (934.7 eV) agrees quite well with the data reported for CuCO_3 species, while the second one (933.8 eV) is nearer to the position reported for CuO , as discussed above. The degradation of $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ into CuO is confirmed also by the change of the Cu Auger peak shape: it matches the one of CuCO_3 species for pristine sample, but it becomes compatible to the one of pristine CuO after ablation.

Finally, in the case of Cu_2O , the Cu 2p and Cu Auger spectra remain almost unaltered, except for the degradation of the small peak at 933.6 eV and its satellite due to impurities of Cu^{2+} specie in the pristine sample. Therefore, the reduction of Cu^+ to Cu^0 can be excluded for Cu_2O .

III.3.3 Discussion

III.3.3.1 Silver whiskers

SPEM is a powerful technique that has been scarcely applied to Cultural Heritage object, but that can be key in studying heterogeneity on archaeological samples. Indeed, we have proven that SPEM can be determinant in first locate peculiar surface structures such as metallic silver whiskers on the surface of coin 582405, otherwise difficult with other techniques. On the other hand, SPEM has proven not ideal to directly investigate the outermost layers of the patina of an archaeological copper-based item, due to the impossibility to couple it with a neutraliser, and the consequent excess in surface charging generated by the thick and insulating patina (Figure 91).

Thanks to the synergy with XPS and SEM-EDS (both on the surface and on FIB cross-sections), it was possible to confirm the presence of silver whiskers in metallic state on the surface of the Licinius' *folles* (coin 582405). In particular, SEM-EDS on the surface confirms their morphology as striated protrusions of about 10-20 μm in length and 1-2 μm in diameter, growing in irregular directions in their characteristic “whisker-like” form. Finally, EDS on small and deep FIB cross-sections confirms the absence of oxygen, sulphur and other elements, pointing towards a metallic state of the whiskers. From EDS data both from the surface and from FIB cross-section, it appears evident that whiskers are often found in the same area with Ag_2S .

Whiskers of silver and other metals (Sn, Pb, Cd to cite some) were first observed in 1951 [45], representing a prominent issue in the electronic industry for decades. The thermodynamics behind metallic whiskering is still unclear, as it is listed as one of the open problems in condensed matter

physics [46–48]. This phenomenon is new for the field of Cultural Heritage, as it has never been observed before as corrosion product on heritage objects in its metallic form. Instead, only the growth of macroscopic silver sulphide been reported in the past, even though with very different morphology (Figure 96) [49–51]. We should also stress that it is never been observed before also on samples buried in soil.

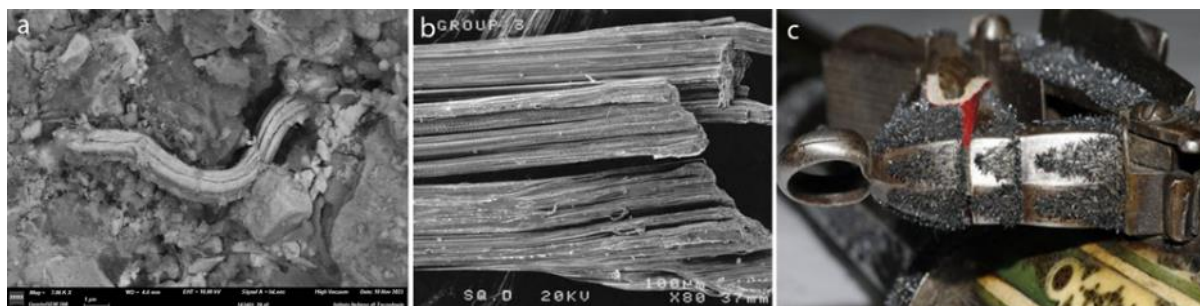


Figure 96 a) SEM (SE) of a whisker on coin 582405. b) Example of metallic silver whiskering from literature [52]. ©2002 IEEE. c) Example of silver sulphide whiskering on heritage object (reproduction from the original version available at [51]).

The presence of metallic silver whiskers has been observed only in two specific contexts: in high sulphide environment [52–54], or in vacuum under e-beam irradiation [55–59]. However, the latter option can be easily excluded as extensive SEM analyses performed on the object did not cause dynamic growth or modification of whiskers, contrary to the cases reported in literature for Ag-nanowires on a support of TiO₂ [59].

Most likely, here the whisker phenomenon is linked to an environment rich in sulphur, given the presence of Ag₂S grains in the areas nearby (Figure 84 d). The role of the handling and storing after excavation can be excluded. The coin has been excavated in 2012 and, since then, it has been stored together with other coins in their same conditions. The present investigation has been made across the 2023. We did not observe whiskering on similar kind of coins, found and stored in a similar way, so far.

The insurgence of whisker has thus to be traced back to the original burial context of the artifact. Even though other coins were found during the same archaeological survey and further stored together, they were retrieved from field even kilometres away one from the other. Chemical variations in the burial context are common even for close locations [60]. Consistent variability has been observed in the same Aquileia surroundings where the artifact was found [61]. The specific finding location is an agricultural field. The use of sulphates as fertilisers is largely attested in agriculture [62]. Locally Sulphide-rich environments can also form in presence of microorganism, such as sulphate-reducing bacteria [63].

These bacteria are capable, in anoxic sulphate-rich environments such as the deep layers of agricultural fields, to produce significant amounts of H_2S , as happens for microbially induced corrosion (MIC) [64].

Consequently, the most reasonable explanation for the insurgence of silver whiskering as corrosion product on the surface of the coin investigated is the presence of high levels of sulphides in the burial context of origin. From this point of view, whiskering can be linked to the original burial environment of the artifact. Despite the fact that silver whiskering has never been associated with a microbiological action, this eventuality cannot be excluded, also because whiskering was never observed in burial context before.

The doubling of XPS peaks of metal elements observed in surface regions with dense silver whiskering is rather unusual. There are many instrumental-related and sample-related factors that can cause shift and shape distortion of XPS peaks in heterogeneous insulating materials. Among the first ones, there are effects associated with the XPS measurement, including interactions with X-rays, secondary electrons, or interactions between neutralization electrons and sample constituents. Between the sample-related causes, instead, there are differences in chemical composition and/or degree of conductivity across the surface, charge localization, sample thickness variations, and charge trapping at interfaces [65]. The main consequence of these factors is a non-uniform (also named differential) surface charging, i.e. the coexistence of surface moieties with different degree of insulation across the area analysed by the XPS beam. In the case of differential charging, photoelectrons coming out from the surface are slowed down each of a slightly different amount, resulting in an XPS peak that is broadened across a large range of energy. However, this is not what happens in the case of whiskers-rich areas. There, the Ag 3d doublet, as well as Cu 2p, Sn 3d and Pb 4f, are all further split in two sharp doublets, both doublets showing with the same spin-orbit splitting values, as well as the similar peak area ratio, and similar peaks FWHM (Figure 85). A fairly similar case has been reported for impurities on pyrolytic graphite, however the phenomenon has not been properly explained [66].

What the data could be suggesting here is that, inside the surface area analysed by the XPS, there are two different regions each with a well-defined charging behaviour. Test done by varying the XPS spot size (Figure 88) tells that the clustering of these two regions cannot be on a macroscopic scale (i.e.: the analytical spot is across the border between two macro-regions), but on a microscopic one (i.e.: there are clusters of one region uniformly dispersed into the other, or there are small domains of both regions mixed at a small scale). Furthermore, the acquisition made at different charge compensation levels (Figure 86 and Figure 87) clearly point out the fact that only one of such regions is being affected by compensation. This indicates that one part of the signal (i.e. one of the doublets), the one compensation-dependent, stands on a charging region, while the other part (i.e. the other doublet), stands on a non-charging region. The last observation that can be made is that the ratio between non-charging vs

charging doublets is far higher for Ag than for other secondary alloying elements (Pb, Sn), suggesting a primary role of Ag in the non-charging domains.

Overall, what could be hypothesized is that metallic silver whiskers determine locally non-charging domains, while the rest of the surface shows normal charging effects due to presence of a thick *patina* beneath. SPEM high-resolution maps in whiskers region partially support this interpretation, by highlighting regions with different surface charging effect clustered below the microscale and in proximity of silver clusters (Figure 77). There, large Ag-rich features may represent silver whiskers, belonging to less-charging surface domains, while small Ag-rich features may represent Ag oxidised phases, such as Ag₂S. If the link between whiskers and XPS-peak doubling stands true, then the latter phenomenon can potentially be used as a diagnostic indicator for their presence. However, further experiments are needed to definitely confirm such hypothesis, which remains for now tentative.

Apart from XPS, also μ XRF mapping proved interesting potential as diagnostic tool for the presence of whiskering. In fact, areas with dense whiskering clearly emerge when the ratio between Ag L and Ag K lines is plotted. A high $^{Ag L}/_{Ag K}$ ratio is a general indication of an enrichment in silver from the bulk towards the surface of the sample, so it cannot be univocally linked to whiskering. However, starting from a relatively fast XRF map to localise ROIs, then followed by a targeted SEM analysis, could be a smart strategy for fast screening whisker presence on ancient objects.

III.3.3.2 Synergistic use of SPEM and Laser ablation

SPEM univocally identifies the presence of metallic copper inside the laser-ablated micro-digs. Indeed, Cu⁰ component is clearly visible in both the digs in coin 587202 (Figure 92, Figure 93 and Figure 94). Since Cu²⁺ is well-known to be susceptible of photo-reduction [67–73], ablation tests on reference materials similar to the one present in the analyses patina have been performed (Figure 95). The results prove that, even if a reduction of Cu²⁺ to Cu⁺ can occur, no formation of Cu⁰ is observed and thus, the formation of Cu⁰ revealed by SPEM cannot be re-conducted to sample preparation procedure. The laser-induced reduction could explain the absence of any Cu²⁺ signal in SPEM spectra, together with Cu²⁺ photoreduction induced by X-rays. The presence of Cu⁰ represents the principal achievement expected by the experiment, i.e. demonstrating how the laser ablation procedure is viable for the micro-invasive preparation of samples to be analysed with the carbon-brush EIS setup (see section III.4 for further details on its application).

Nonetheless, the successful design of the digs to achieve SPEM analysis from a depth of almost 100 μm can have implications that extends far beyond the Heritage Science field. Until now, the synergy between SPEM and LA was tested before only to study alterations suffered by a surface due to laser irradiation [74–77]. This is the first time that SPEM and LA are used to micro-invasively investigate features that are at almost 100 μm depth. Thereby, the results achieved here open the way to a new experiment design strategy, which couples SPEM with a micro-invasive preparation technique (LA, FIB, etc.) in order to make SPEM not only a surface technique, but also capable for investigation of subsurface and of deep features inside materials. Of course, attention must be paid to possible alteration suffered by the sample due to the preparation step, as it has been done in the present case.

As last note, SPEM imaging also confirms that the halo around laser-ablated digs, already observed in the previous experiments with LAICPMS, is actually made by re-deposited material from the ablation process. In fact, there is Cu^0 all over this surface region, gradually reducing moving away from the dig. The gradient in Cu^0 is further accompanied by an inverse gradient of surface charging, which is clearly influenced by the presence of metallic powders.

III.4 New EIS Setups tailored for heavily corroded metals

Two new setups for the execution of Electrochemical Impedance Spectroscopy (EIS) were designed, developed and validated. The goal of this work was to achieve reproducible and reliable EIS measurements on samples that are completely covered by a thick insulating layer, for which the electrical contact with their metallic bulk cannot be achieved without invasive removal of this layer, as in the case of archaeological copper-based artifacts. The two setups proposed exploited distinct designs: one utilised a micro-invasive preparation step (validated in the previous par. III.3) and a brush-like electrode made by carbon fibres (CB), in a three-electrode configuration; the other, instead, exploited a four-electrode configuration (4E), mimicking the approach used for membranes studies. To achieve the intended goal, the setups were first tested on an archaeological item and compared against a standard setup. The more promising of the two (i.e. the 4E setup) was further applied to a set of archaeological samples, and its performance were evaluated in detail.

III.4.1 Validation and comparison of the CB and 4E setups

The CB and 4E setups were validated on coin 587202 and the results were compared with those recorded with the standard approach. Figure 97 a shows the Nyquist plots acquired with the different configurations. The spectra obtained with both CB and 4E setups are highly similar, and present a strong depressed capacitance semicircle at high frequency, likely followed by a much smaller second one, even more depressed, at low frequency. The first semicircle can be conceivably assigned to the insulating patina layer. The Bode plots shown in Figure 97 c,d are also congruent with the above observation. These spectra show features similar to those reported in the literature using the classical direct clamping approach [78].

The linearity, stability and causality of the responses were assessed by the Kramers-Kronig fitting method [79]. The fitted spectra are include in Figure 97 and the residuals are shown in Table 15. The good graphical fit, together with the low χ^2 obtained between experimental and theoretical data ensured that the new configurations adopted did not introduce any fictitious response.

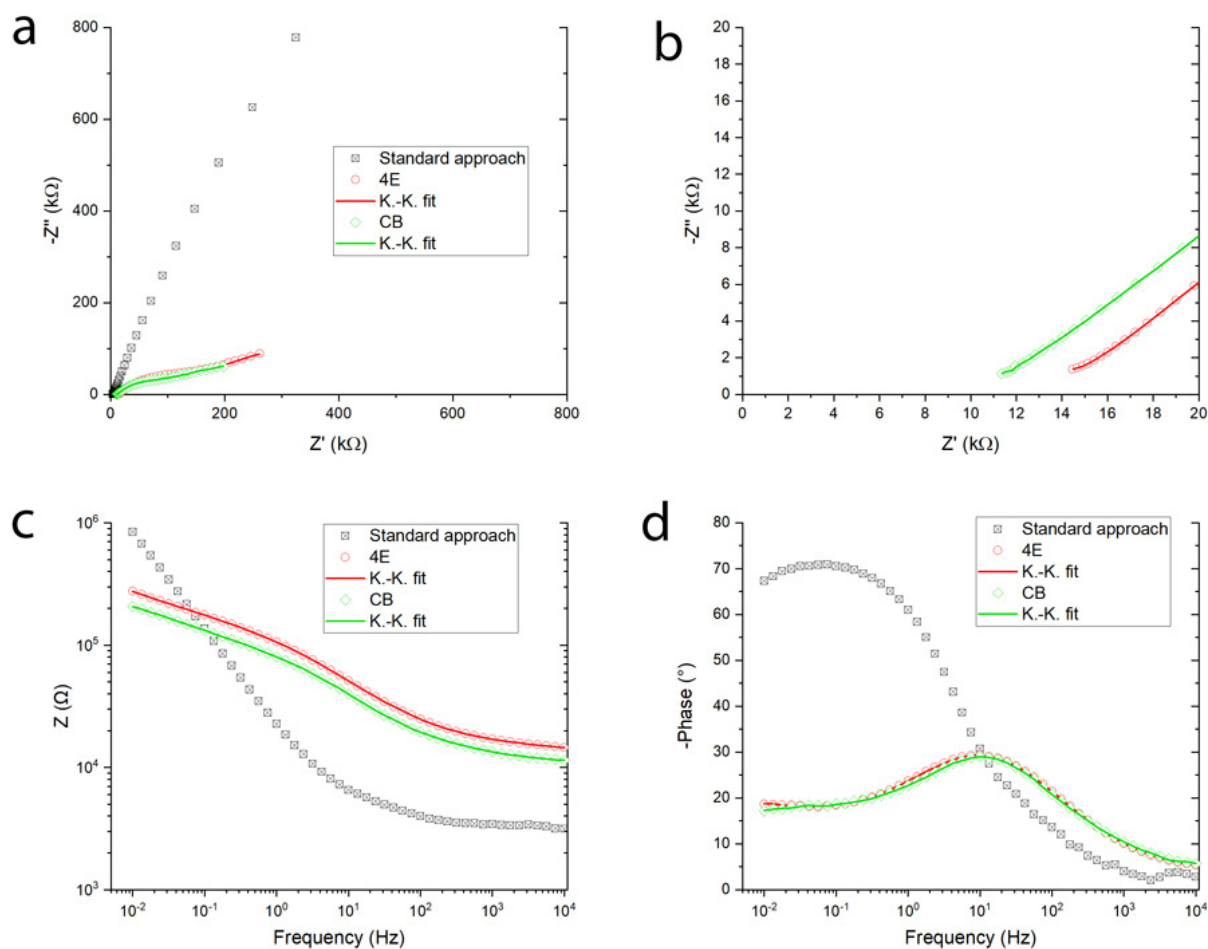


Figure 97 EIS measurements on coin 587202 using three different setups. a) Nyquist plot (0-800 kΩ), b) Nyquist onset (0-20 kΩ), c,d) Bode plots. Black crossed squares: Standard approach. Red circles: 4E. Green rhombus: CB. Continuous lines: Kramers-Kronig fit.

	$\chi^2 (Z')$	$\chi^2 (-Z'')$
4E	$3.3 * 10^{-6}$	$2.8 * 10^{-6}$
CB	$3.3 * 10^{-6}$	$2.8 * 10^{-6}$

Table 15 Residuals of the Kramers-Kronig fit on the real and imaginary part of impedance signals recorded using the 4E and the CB setup on coin 587202.

The same sample was examined using the standard setup and relevant spectra are included in Figure 97. As is evident, the results obtained with the standard setup are different from those obtained with the CB and 4E setups. The Nyquist and Bode plots show only a high capacitance that starts developing from mid frequency, probably linked to the charging of the insulating *patina* and indicating that the pressed Cu-sheet method is insufficient to grant a good electrical contact with the metallic bulk of the sample. On the Nyquist plot, it can be noticed that, at high frequency, the signal is able to pass through

the patina. However, from mid to low frequency the impedance generating from the bad electrical contact is order of magnitude higher than the one arising from internal processes within the sample, hiding the crucial information on charge transfer and thus latent corrosion at low frequency.

An interesting note can be made on the onset of Nyquist plots (Figure 97 b), as well as on the corresponding high-frequency region of the Bode modulus plot. This region is dominated by the resistance in the conductive part of the system, i.e. the reference electrodes, the jellified electrolyte, the clamps and their interfaces. It can be hypothesized that this resistance is principally due to the gel electrolyte resistance, since the resistance of the metallic bulk of the sample is negligible, compared to that. The high-frequency resistance is characterised by a linear segment in the Nyquist, whose extrapolation on the x-axis give an approximate evaluation of its value. As can be seen, the extrapolated value for the CB is lower than the one for the 4E. It is explained by the fact that the 4E setup features two gel semi-cells, so that the electrical signal travels two time across the same of gel in respect to the standard setup, which features only one gel semi-cell. This determines a 2x scale factor for the total electrolyte resistance between the CB and the 4E. Deviations from a 1:2 ratio are explained by an additional resistance given by the carbon-brush, and by the contact resistance between the brush and the sample inside the micro-dig. For instance, the resistance measured at both ends of a carbon brush is ca. 1 k Ω .

The low-frequency region in the Bode modulus plot (Figure 97 c), instead, is generally assumed to be dominated by charge transfer resistance (R_{CT}), which is directly correlated to corrosion in the sample. The value of Z modulus at low frequency recorded for CB is half of that of the 4E. This is congruent to the fact that the current signal, in the 4E setup, crosses twice the interface between the bulk metal and the corrosion layers, where corrosion phenomena take place. This and the previous predictable features are a good indication of the well behaving of the CB and 4E setups.

The overlap of the Bode phase plots (Figure 97 d) of the CB and the 4E suggests that both faces of the coin show similar EIS responses. This is because both faces in the 4E configuration contribute to the signal, while only one face contributes to the signal recorded with the CB.

The good performance of both CB and 4E configurations is provided the by the stability of the E_{OCP} evolution with time, as is shown from data reported in Table 16. The overall stability of the systems has been confirmed by the agreement of replicate measurements performed over time (Figure 98). Furthermore, E_{OCP} measured for the 4E is about 0 V (see par. I.4.2.2.1). This is an expected feature of the four-electrode symmetric configuration, once again highlighting that the system is properly working.

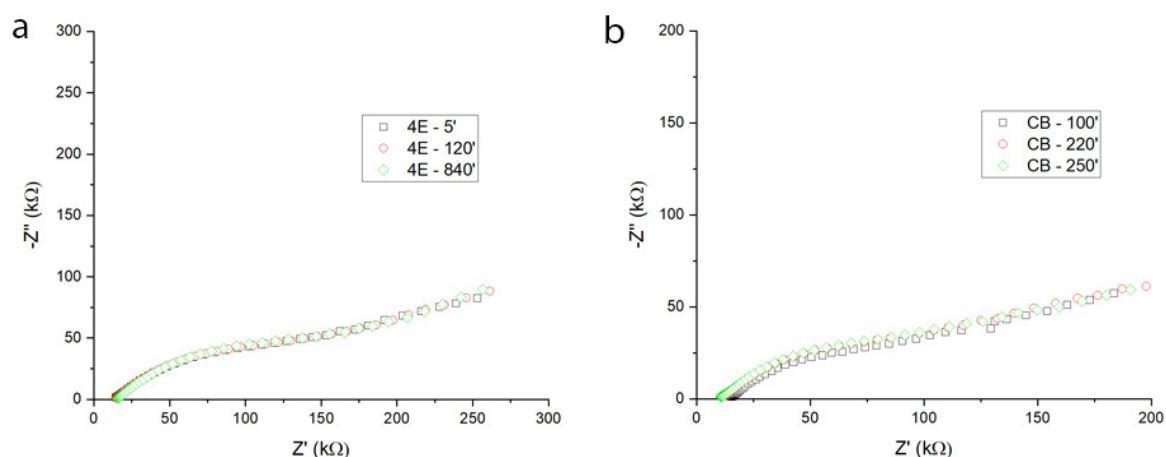


Figure 98 Repeated EIS measures over time on coin 587202 with a) the 4E setup and b) the CB setup. Subsequent measures are taken by keeping the setup mounted, with the coin in contact with the gel.

4E		CB	
Time (min)	E_{OCP} (V)	Time (min)	E_{OCP} (V)
5	0.011	0	-0.190
120	0.014	120	-0.193
840	0.020	240	-0.197

Table 16 E_{OCP} evolution over time during the measurements conducted on coin 587202 with the 4E and CB setups. The time is expressed in reference to the moment in which the sample has been mounted in the cell.

The aesthetic alterations due to sample exposure to gel, as well as to the EIS measurements have been visually evaluated. In any case, no visible alterations at the end of the measurements has been observed compared to the original sample conditions (Figure 99).



Figure 99 Visual evaluation of the invasivity of the EIS measurements conducted on coin 587202. For reference, the max diameter of the coin is 16 mm. Reproduced upon permission of the Ministry of Culture, Regional Directorate of Museums of

Friuli Venezia Giulia. Any further reproduction of such images, duplication by any means, as well as downloading and subsequent manipulation, is strictly prohibited.

III.4.2 4E setup: reproducibility, invasiveness and gel properties

The 4E setup has been selected for further measurements on a set of three archaeological coins (coins 579666, 579679 and A3).

EIS measurements with the 4E setup have been repeated on approximately the same spots on two different coins in different days, and after approximately the same time from sample mounting (Figure 100). The electrolyte and gel were freshly prepared before each series of measurements. The results obtained have shown a good overlapping between measurements performed under the same experimental conditions, indicating a good reproducibility and that their execution has not modified the sample on the long term.

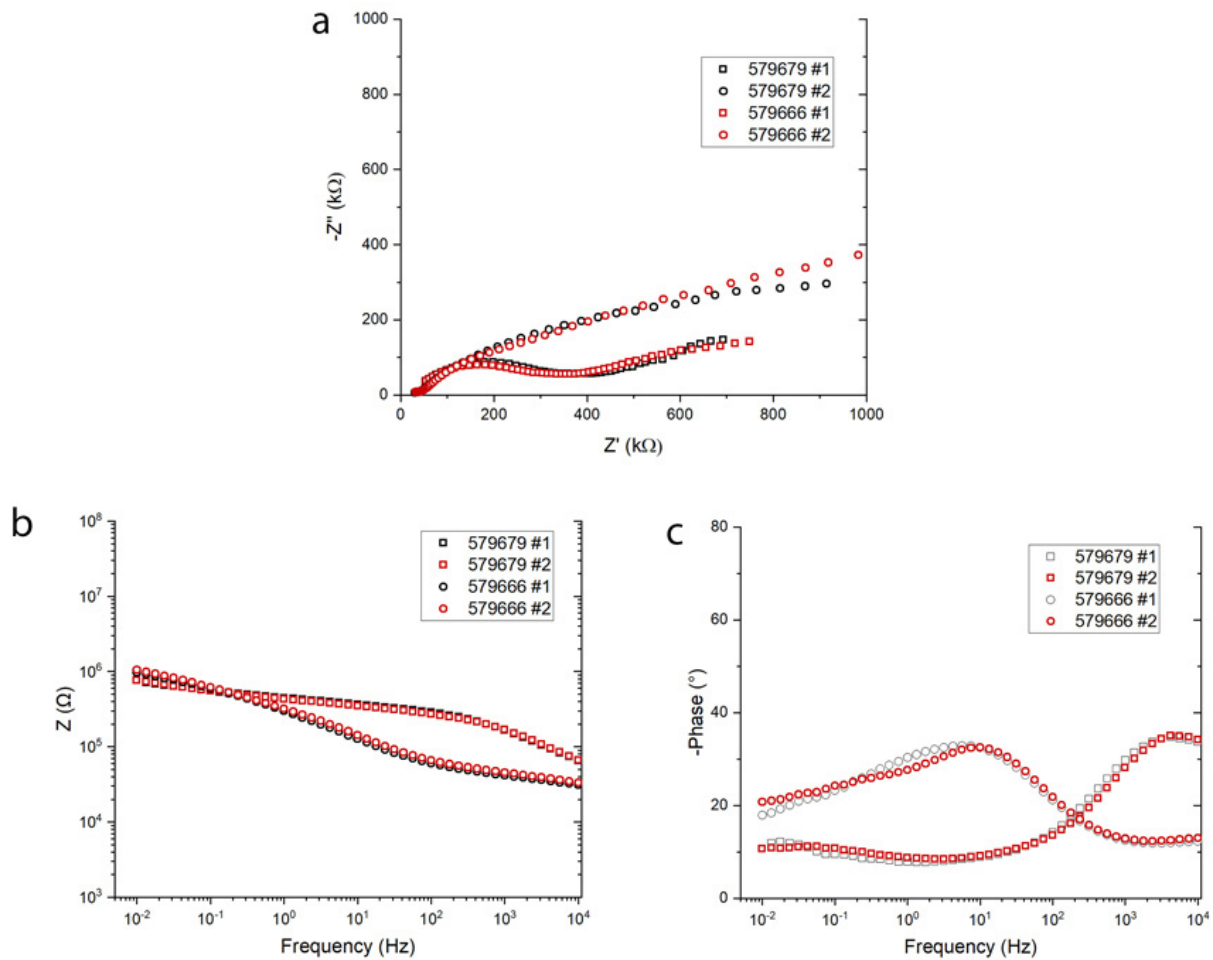


Figure 100 Repeated measurements across different days on the same sample (579666 and 579679). a) Nyquist, b,c) Bode modulus and phase plots.

Another indication for the non-invasivity of the measurements with this setup is shown in Figure 101, where the EIS responses of the sample (coin 579666) evolved over time. In particular, a flattening of the yet depressed main capacitance semicircle and a reduction of the Z modulus at high frequency are observed during time. A possible explanation for this is the wetting of patina due to contact with the small amount of liquid electrolyte released by the gel, or to its penetration inside open porosity. However, this evolution is totally reverted after some time, as has been verified by a second run of measurements taken on the same spot two weeks after the first one. Data of the second run of measurements (Run 2) have been acquired in a range of time (ca. 45 minutes) from the assembling of the setup, while the first measurement of the first run (Run 1) was taken after 45 minutes from the assembling. This explains why impedance values are generally higher than run 1 while showing exactly the same trend, if the latter is due to a reversible interaction between the sample and the gel or the electrolyte. The typical trend of coin 579666 data is further underlined by a third series of measurements, taken on a different spot on the surface of the sample (Point 2, Figure 102).

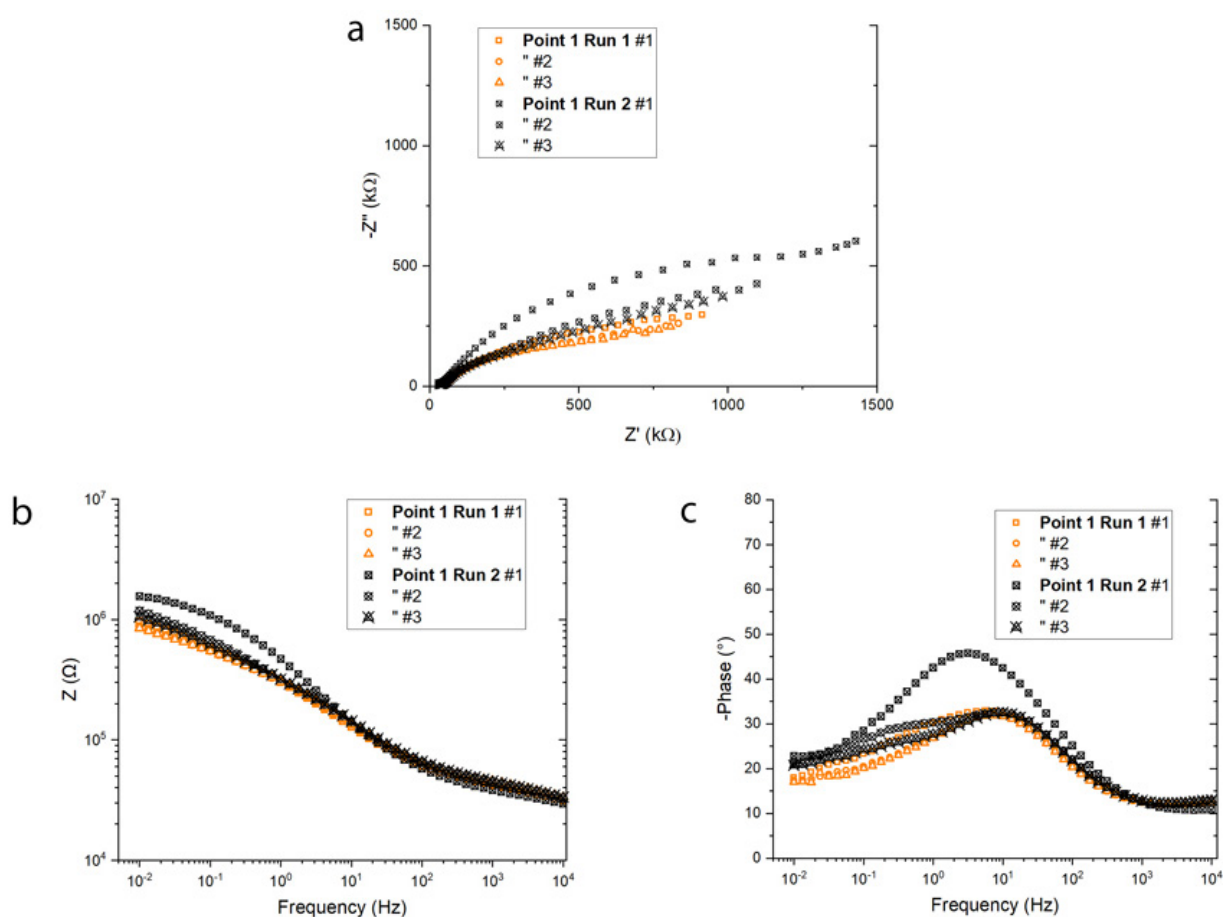


Figure 101 EIS spectra from two runs (orange: run 1, black: run 2) of three subsequent measurements on the same point of coin 579666 repeated 14 days apart with fresh electrolyte and gel. a) Nyquist plot (high frequency region is highlighted in the onset), b,c) Bode plots.

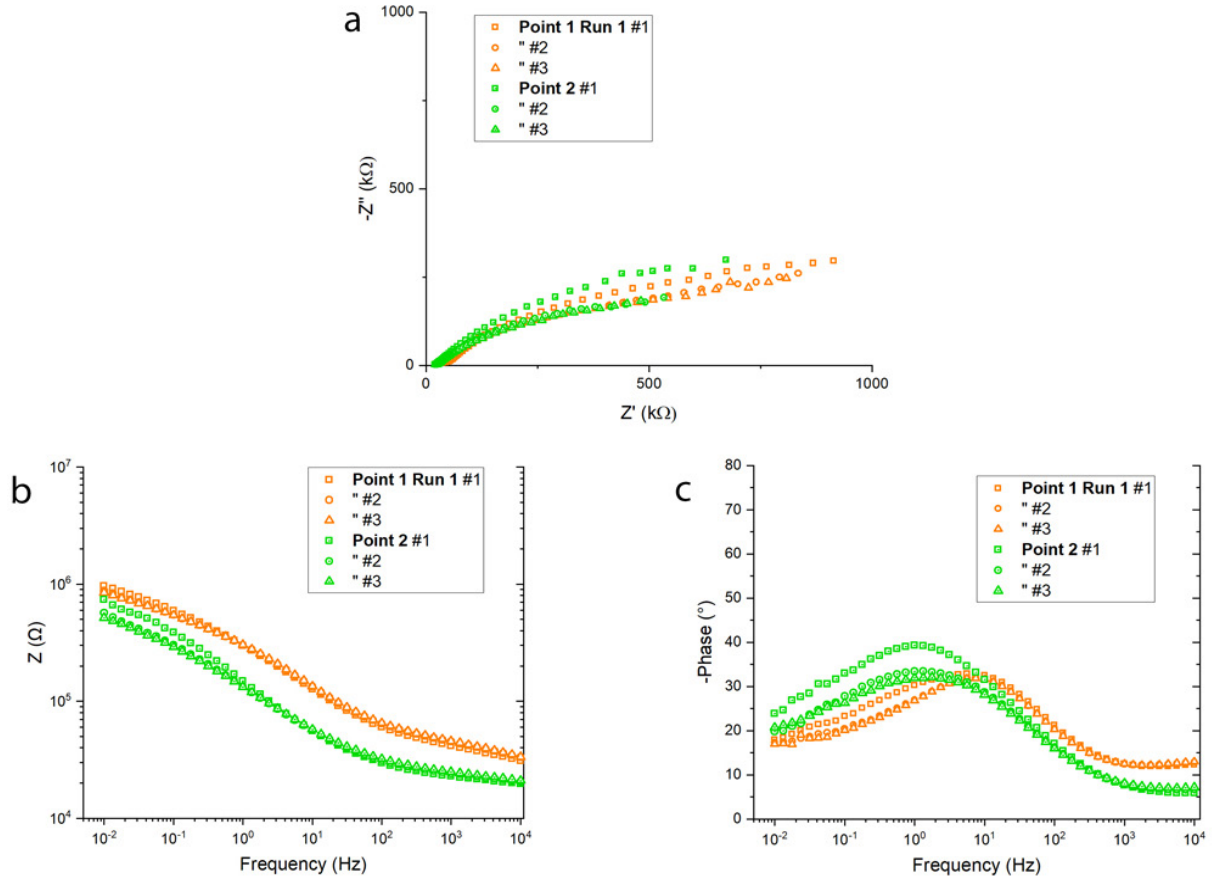


Figure 102 EIS spectra from different points of coin 579666. a) Nyquist plot, b,c) Bode plots. One run of three subsequent measurement for each point.

An irreversible evolution has been observed only in presence of active corrosion on the sample. This is the case of coin A3, which is affected by bronze disease (see coin A3 in section III.1 for reference). From Figure 103, it is evident how the system is evolving over time in the sense of a gradual but continuous reduction of R_{CT} .

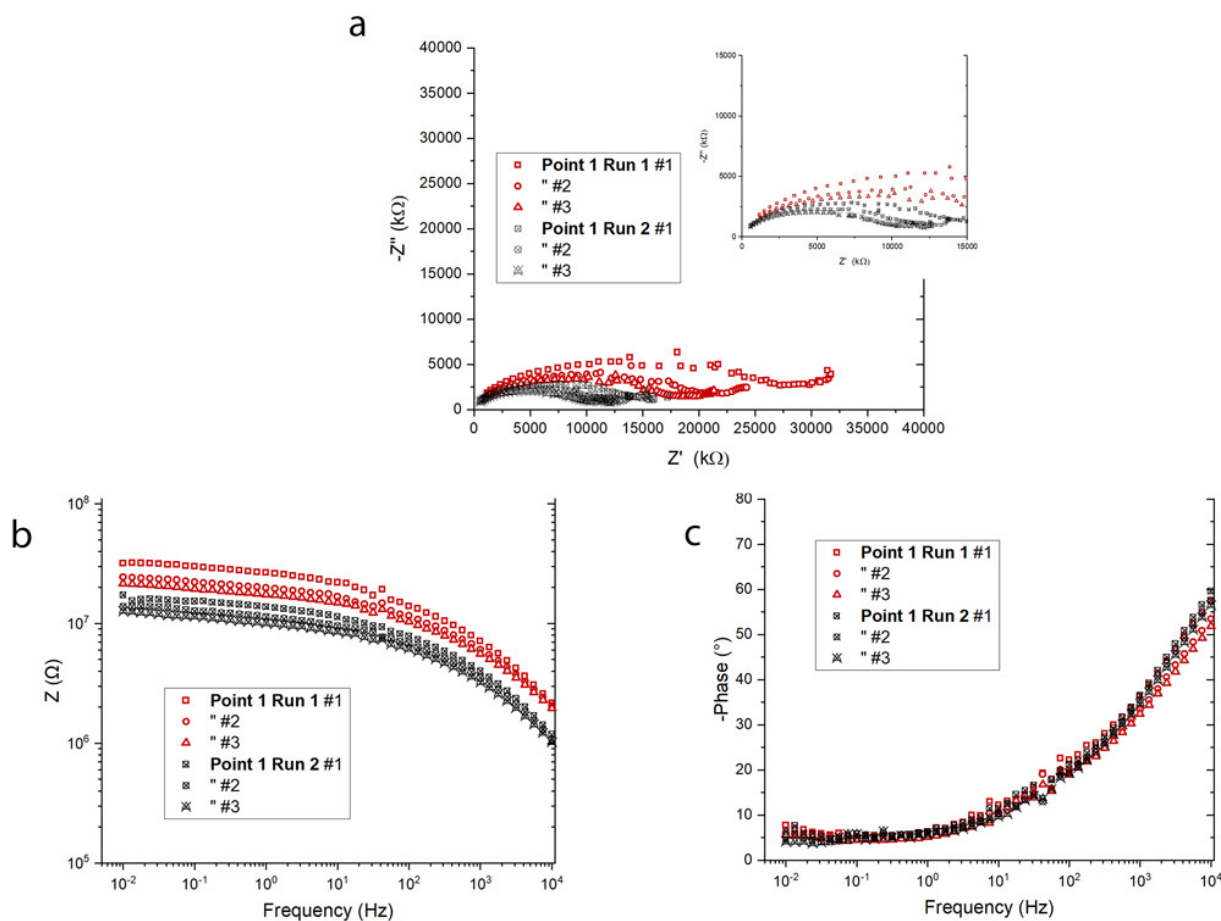


Figure 103 EIS spectra from two runs (orange: run 1, black: run 2) of measurements on the same point of coin A3 repeated three days apart with fresh electrolyte and gel. a) Nyquist plot (high frequency region is highlighted in the onset), b,c) Bode plots.

Replicating the same series of experiments on approximately the same spot, the R_{CT} continue to decrease. Other points on the same sample shown the same evolutionary trend (Figure 104). The evolution of the system was not detectable by naked eye (Figure 105).

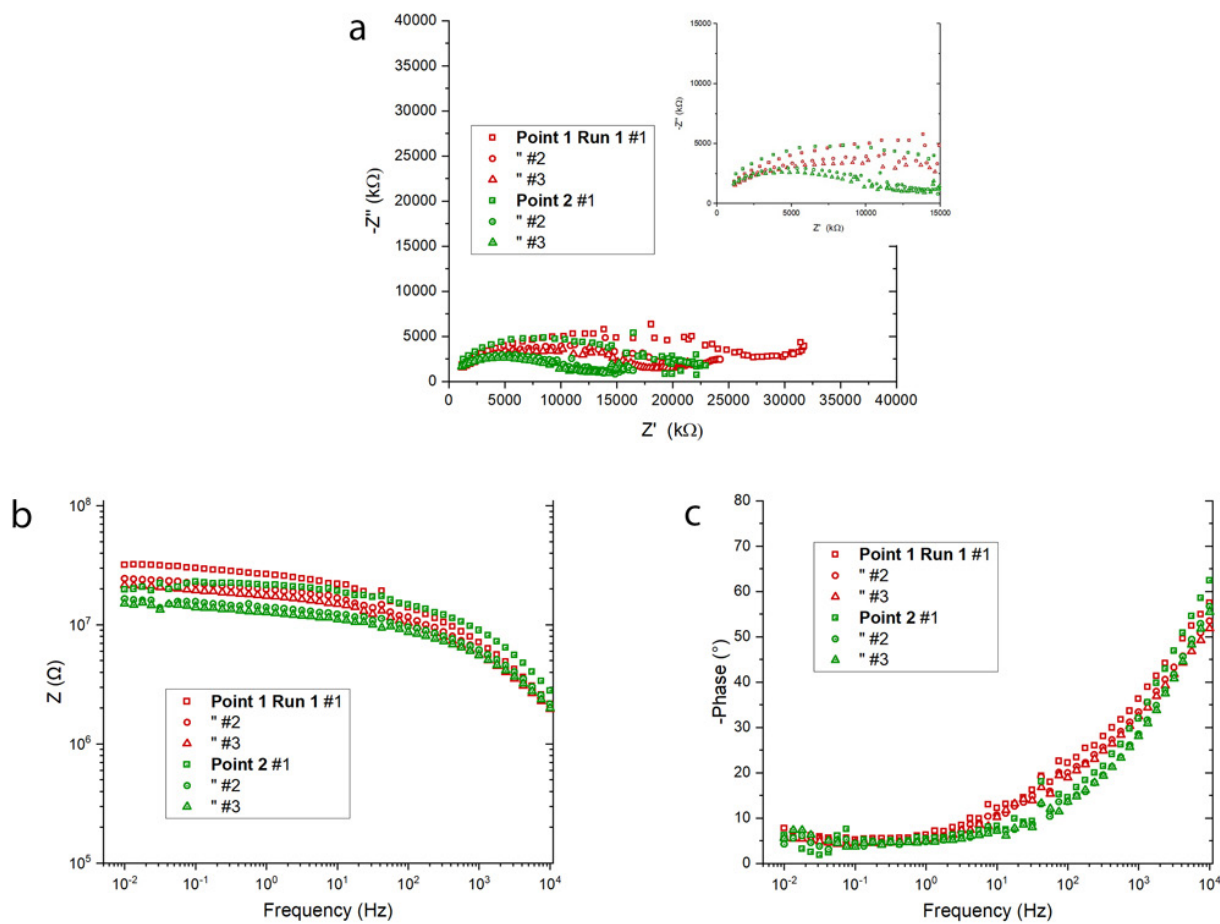


Figure 104 EIS spectra from different points of coin A3. a) Nyquist plot, b,c) Bode plots. One run of three subsequent measurement for each point.

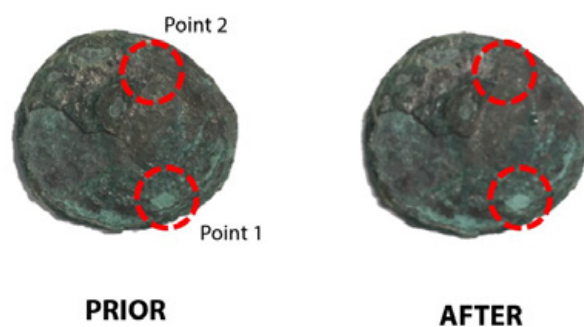


Figure 105 Coin A3 prior (left) and after (right) EIS measurements.

As mentioned in the previous paragraph, the 4E setup should register a 0 V E_{OCP} in ideal conditions. Figure 106 a shows that the E_{OCP} registered on different spots on coin 579679 across multiple days, with the gel renewed each day, is consistently limited around 0 V (0.01 ± 0.02 V). Small deviations from ideality can be attributed to different conditions (species adsorbed, oxidation, etc.) between RE and WS surfaces, and to small variation in gel conditions between the two half-cells, such as pH decrease due

to CO₂ dissolution during gel preparation. For instance, for coin A3, which is affected by bronze disease, the E_{OCP} have reached values over 120 mV, possibly meaning that one of the coin surfaces is significantly different from the other, releasing ionic species in the electrolyte that diffuse through the gel and adsorb on the RE.

The extrapolation to $X = 0$ of the linear starting branch of the Nyquist plots is a good estimate for the resistance of the jellified electrolyte. As can be seen from Figure 106 b, this value is consistently around 10 k Ω across multiple measurements made with the same gel, as well as on different days with renewed gel. In accordance to this, a value of 11 k Ω has been recorded by putting in direct contact the two gel semi-cells. Both the last observations indicate that the working conditions with the 4E setup are reproducible and stable across repeated measurements in the same run.

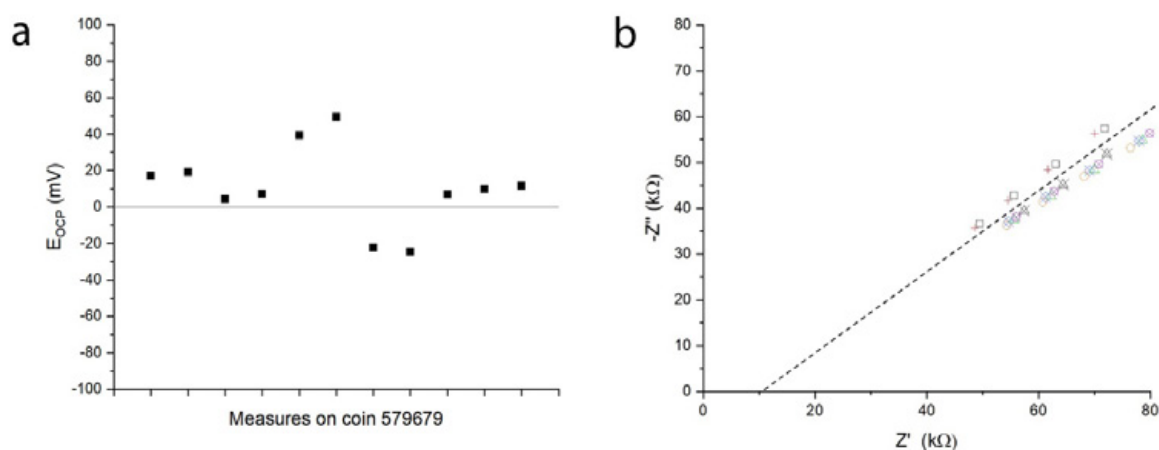


Figure 106 a) E_{OCP} registered during multiple acquisitions on different areas of coin 579679, made across different days with renewed gel. b) High frequency region of the Nyquist plot of multiple runs on the same spot on coin 579679, made across different days with renewed gel. A dashed line is added as visual reference.

III.4.3 Preliminary data fitting

Preliminary fitting of EIS spectra by means of an equivalent circuit (EC) have been performed on coin 579679, as confirmation of absence of artifacts coming from the setup used. In Figure 107, two spectra taken at two different spots on coin 579679 are reported. Spectra have a similar shape but are overall different, indicating that the same processes are occurring in both spots, but with different intensity. Both spectra can be fitted with the same EC in Figure 107 b, constituted by the resistance of the electrolyte (R_{el}) in series with two nested resistance/constant phase elements (R/CPEs). As has been proposed in literature [80], the external R/CPE describes the *patina* capacity (CPE_{pat}) and resistance (R_{pat}), while the internal R/CPE represents the charge transfer resistance (R_{CT}) and the capacity of the double layer at the metal/*patina* interface (CPE_{dl}). The values of fitted parameters are reported in Table

17. In point 1, the CPE_{pat} is much higher than point 2. At the same time, CPE_{dl} and R_{ct} are lower, meaning that point 1 is more active towards corrosion. Although the fittings are preliminary and therefore quantitative values should be treated as such, they help highlighting the similarity and difference between the two spots.

CPE is a generalisation for non-ideally behaving capacitors. They are bi-parametric elements whose impedance is defined as:

$$Z_{CPE} = \frac{1}{Y^0 \omega^N} e^{-\frac{\pi N i}{2}}$$

where N is the parameter governing the degree of deviation from the behaviour of an ideal capacitor. The case $N = 1$ describes an ideal capacitor while the case $N = 0$ describes a pure resistor.

The model used in this fitting is the analogous of the EC commonly used for coated metals [81,82]. CPEs with comparable N values, in the same or similar ECs, have been widely used in the Heritage Science literature [80,83–85]. While the use of CPEs with low N values helps in accounting for sample complexity for fitting purposes, CPEs with such low N coefficient are difficult to justify in terms of real physical mechanisms. Most likely, they hinder the need for much more complex ECs, to fully unveil what happens inside the sample. Nonetheless, the possibility to fit our data with an EC commonly adopted in literature for similar sample underlines the absence of fictitious signals coming from setup components.

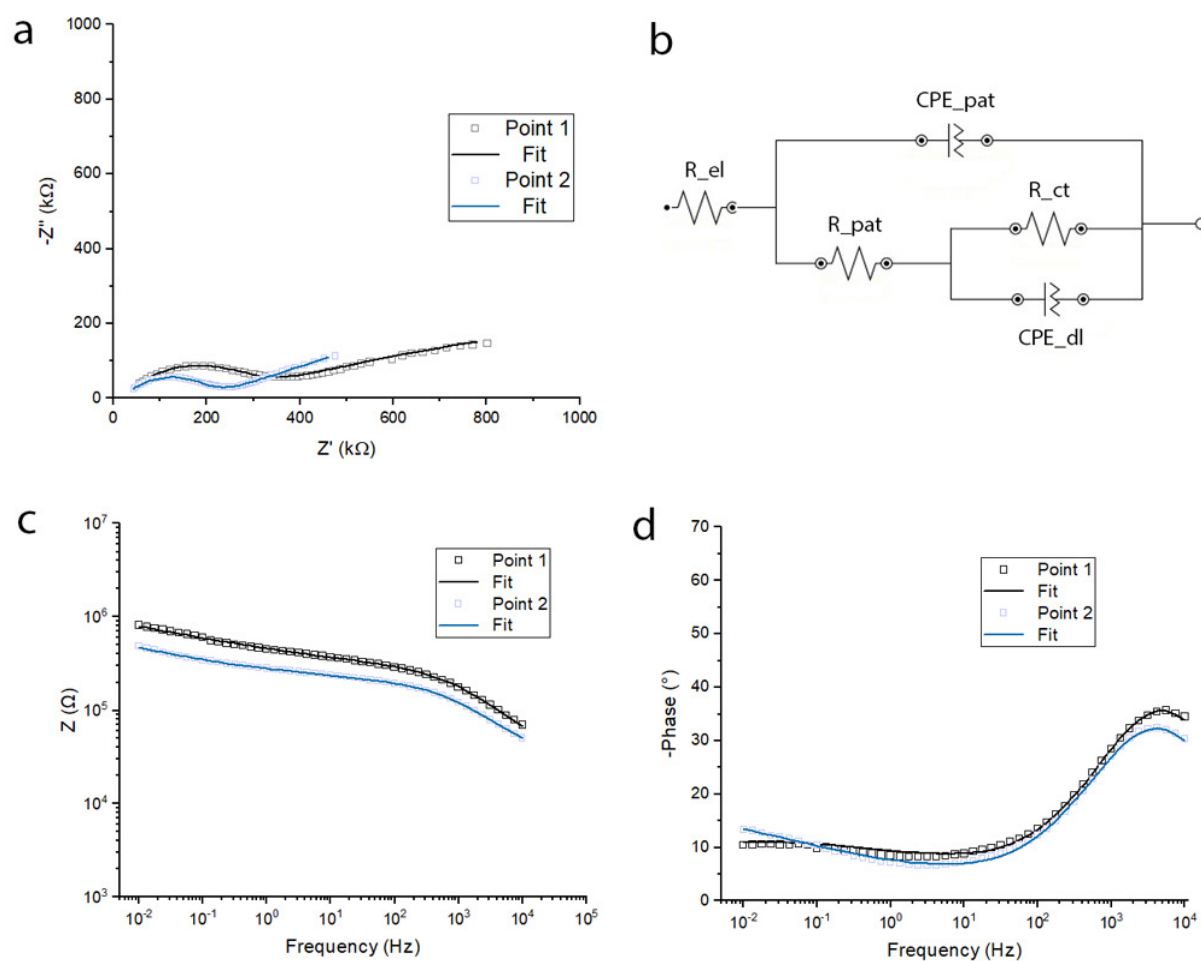


Figure 107 Preliminary data fitting on spectra taken on two different points of coin 579679. a) Nyquist plots. b) Equivalent circuit used for fitting Point 1 and Point 2 data. c,d) Bode modulus and phase plots.

	R_{el}	CPE_{pat}		R_{pat}	CPE_{dl}		R_{CT}	Total χ^2
	$k\Omega$	Y^0 ($nS*s$)	N	$k\Omega$	Y^0 ($\mu S*s$)	N	$M\Omega$	
Point 1	28.5	8.46	0.698	235	2.71	0.25	1.88	0.015
Point 2	23.7	16.8	0.672	173	6.94	0.25	56.6	0.005

Table 17 Parameters used for EIS data fittings in Figure 107.

III.4.4 Discussion

The design of the 4E and CB setups has been successfully validated on an actual archaeological artifact (coin 587202), and the 4E has been further tested on a total of four artifacts (coins 587202, 579666, 579679 and A3). Spectra taken with both setups are comparable, with a 2x scale factor in impedance

value due to the doubled contact area for the 4E, and the doubled path into the gel as well. Both the systems allow for the EIS investigation on heavily corroded archaeological metals, which are completely covered by thick insulating patinas. The same analysis could not be achieved by standard non-invasive means due to the thick *patina*, showing that external wiring of the sample metallic bulk fails in absence of an invasive action (such as abrasion due to clamping). Both 4E and CB thus avoid the need for macroscopically invasive means for wiring the metallic bulk of the sample. The 4E achieves this result without requiring any preparation or damage to the sample, while the CB asks for a minimally invasive sample preparation, which may also lead to localised corrosion afterwards. Considering this and the slightly better performance in terms of measurements stability and setup handling, the 4E has to be considered as preferable over the CB.

Specifically, EIS spectra taken with the 4E are reproducible and stable, free of noise even at low frequency and showing an OCP consistently near 0 V (± 10 mV), as its symmetric design imposes. Compared to the other two-cell system proposed in literature [86–88], the 4E symmetric design avoids current dispersion inside patina layers. Additionally, the 4E system is easy to replicate, only requiring two small Teflon cells and four short Pt wires. Once crafted, the same system can be used for long time.

The jellified electrolyte guarantees an adequate conductivity, displaying a resistance of ca. 10 k Ω . Moreover, it proved to be stable across multiple measurements, even across different samples, and its preparation is fast. It is also costless and simple, requiring only mineral water, agar and formate. The gel-electrode approach ensured minimal invasivity thanks to electrolyte retention.

What has been observed on coins 579666 and A3 hints that archaeological patinas can in some case interact with the gel, due to their complex structure, the presence of latent corrosion activity and possibly to the presence of open porosity. The kind of interaction depends on the actual sample and its state of conservation, and can be both reversible and not reversible.

In particular, irreversible modifications have been observed only in presence of bronze disease. It has to be noted that bronze disease is a self-catalytic phenomenon, so some irreversible change experienced by coin A3 can be due to its spontaneous evolution. Bronze disease is triggered by any form of humidity, and the proposed 4E setup is designed to reduce sample exposure to the liquid electrolyte to a minimum. Any level of invasiveness in the present case seems not to depend on the specific system used, but rather on the technique itself or to the natural evolution of the sample.

It must be underlined that irreversible changes have been recorded only on samples with an active corrosion. Yet, the behaviour shown by such samples over time can be a valuable diagnostic information. To exploit this, the results shown here suggest to always performing a series of

measurements instead of a single one, at specific time distance across a limited amount of time, in order to reveal the trend, but limiting invasiveness to the least. Using the 4E setup, stabilisation times for the E_{OCP} on real archaeological artifacts has been observed to be short, within a few minutes, allowing for the implementation of such analytical strategy.

The small contact area of the gel half-cells (5 mm diameter) used allowed for multiple measurements in different spots over the same sample area. Results show that samples slightly change even just few millimetres apart, unveiling the potential of 4E-EIS as a mapping technique. For instance, it could be used for the ROI selection for subsequent FIB cross-sectioning. It must be kept in mind that 4E-EIS contextually analyse one spot on both the surfaces in contact with the two gel semi-cells. Still, by moving just one of the two semi-cells across the surface of the sample, a relative mapping of such surface may be obtained in an adequate amount of time to not cause alteration phenomena due to prolonged contact with the gel.

Preliminary data fitting has been obtained on coin 579679 as proof-of-concept and for the good performance of the system. Further work is needed to achieve an advanced extraction of information from EIS spectra of other coins. Given the reproducibility and the low-frequency stability of the spectra obtained, 4E can be applied to the evaluation of the performance of conservation treatments, as long as a direct comparison with the same sample prior to the treatment is available. An advanced extraction of information from EIS spectra, such as highlighting the presence of mass transport phenomena or achieve a quantification for R_{CT} , requires a fitting process through an equivalent circuit (EC). Each EIS spectrum can be fitted by a great number of ECs, because an EC is merely a mathematical expression while EIS data fitting with ECs is an analytical problem for which the unicity of the solution is not guaranteed. Moreover, finding a physical explanation for a specific EC is tricky and interpretative. For these reason, EIS data fitting must be approached with critical thinking, starting from a base hypothesis generated from the observation of spectra and precedent knowledge of the sample, and then refining the EC by iterative fitting, targeted addition or removal of equivalent elements, and so on. In addition, the management of the iterative process for the optimisation of the parameters of the equivalent elements must not be underestimated, because many different numerical solutions may exist even just at this level.

In this panorama, EIS data of archaeological copper-based items add even more complexity, introducing many non-ideality due to roughness of the surface, overlapping of multiple mechanisms, etc. This results in the vast use in the literature of Constant Phase Elements (CPEs), a generalised form of capacitor whose mathematical expression has been created to adapt to various forms of non-ideal behaviours [79]. CPE helps in finding suitable ECs for the complex spectra of archaeological metals,

however it is not as easy to find proper physical explanations for such strong deviations from an ideal capacitor.

It is outside of the scope of the present work to solve the issue related to EIS data fitting. Nonetheless, this work demonstrates how it is finally possible to perform EIS on archaeological metals without invasive actions, using a simple setup that guarantees reliable and reproducible measurements, thus allowing to analyse multiple objects and creating a large EIS dataset. The setup proposed even allows for investigation the same objects on multiple near spots, in a mapping-like fashion. Having a large amount of quality data represent the first step towards a widespread use of EIS in Heritage Science.

III.5 Evaluation of protocols for the reproduction of archaeological *patinas*

Here, two artificial aging protocols were tested with the goal of setting a procedure for the rapid production of substrates that reproduce the state of conservation of archaeological items. The samples were aged with two different processes: one electrochemical, and another mimicking the protocol of a counterfeiter. The aged samples were characterised by means of micro-Raman spectroscopy and SEM-EDS and their similarity to real artifacts was carefully evaluated.

III.5.1 Results

III.5.1.1 Visual inspection

After the exposure to hot coals, counterfeiter's-like samples (CF0) have shown a uniform and matte black patination, with a limited tendency to flaking. When flaking happened, the black layer revealed a strong red sublayer. This patina looked as flat as the starting sample, retaining the surface roughness of the original substrate (Figure 108 a).

Patina has become quite cohesive and not flaking even by application of a consistent frictional stress already after 15 days (CF1). Concretions have started appearing after 45 days (CF2), progressively increasing their presence after 120 (CF3) and 150 days (CF4). This is accompanied by an increase in the roughness of the surface. At the CF2 step, there is also the appearance of sparse small green grains, coherent with the growing *patina*. No significant differences have been observed for the two alloy types (B555 and B774). At the end of the aging process, the samples surface well resembled a real archaeological *patina* in the overall aesthetics as well as its surface texture.

On the other hand, electrochemically aged samples (B555-EL) present dark green *patina*. Even though the degree of surface coverage is high, it still looked incomplete, as part of the metal substrate is still visible. The degree of surface coverage presents a gradient along the axis of immersion in the aging solution.

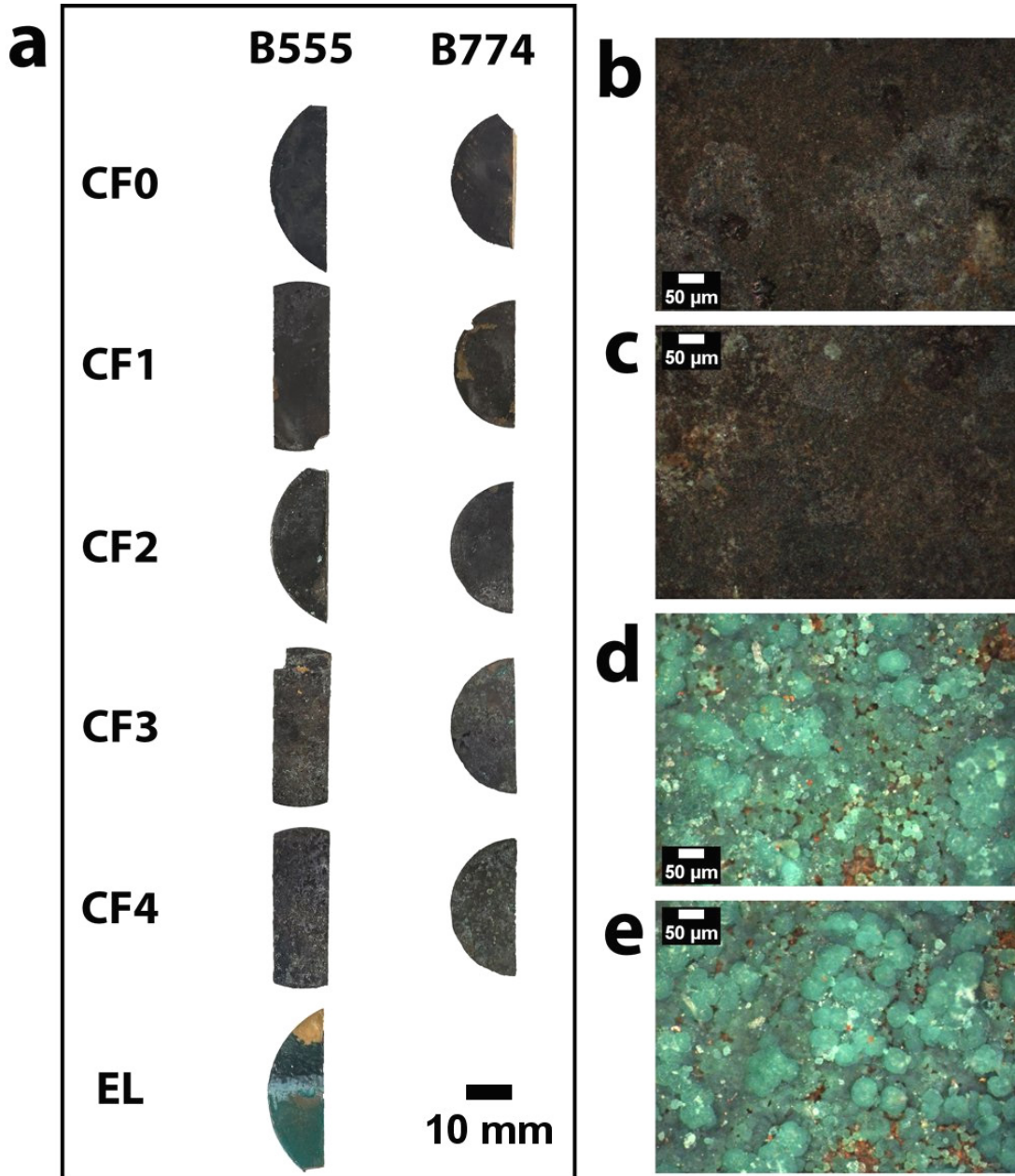


Figure 108 a) Optical photographs of one aged sample per aging time. b-e) Optical micrographs (10x original magnification, dark field) of the surface of a B774-CF4 (b,c) and B555-EL (d,e). Coin samples were cut before the starting of the aging process.

Microscopic analysis of the surface of CF samples has revealed a compact surface, with dark red to black shades, white veiling and occasional greens spots. The surface of EL samples, instead, are covered by green globular grains of various size, which do not fully cover the underlying reddish layer.

III.5.1.2 Microscopic and Spectroscopic Characterization

The observation of cross-sections of the CF samples have revealed that the first harsh aging step, obtained by placing metal samples on hot coals, has resulted in the rapid formation of a *patina* layer in

the range of 10 μm . The colour of this layer presents different shades of blue-grey in bright field (Figure 109 a), which is characteristics of copper oxide compounds, and a reddish one in dark field. The layer is characterised by high porosity, which is more evident at the interface with the bulk metal. In certain spots (Figure 109 b), the patina is partially detached. The presence of metallic grains inside the altered layer has also been observed, most likely induced by the fast corrosion process to which the sample has been subjected. Nonetheless, the *patina* looks well developed across the cross-section.

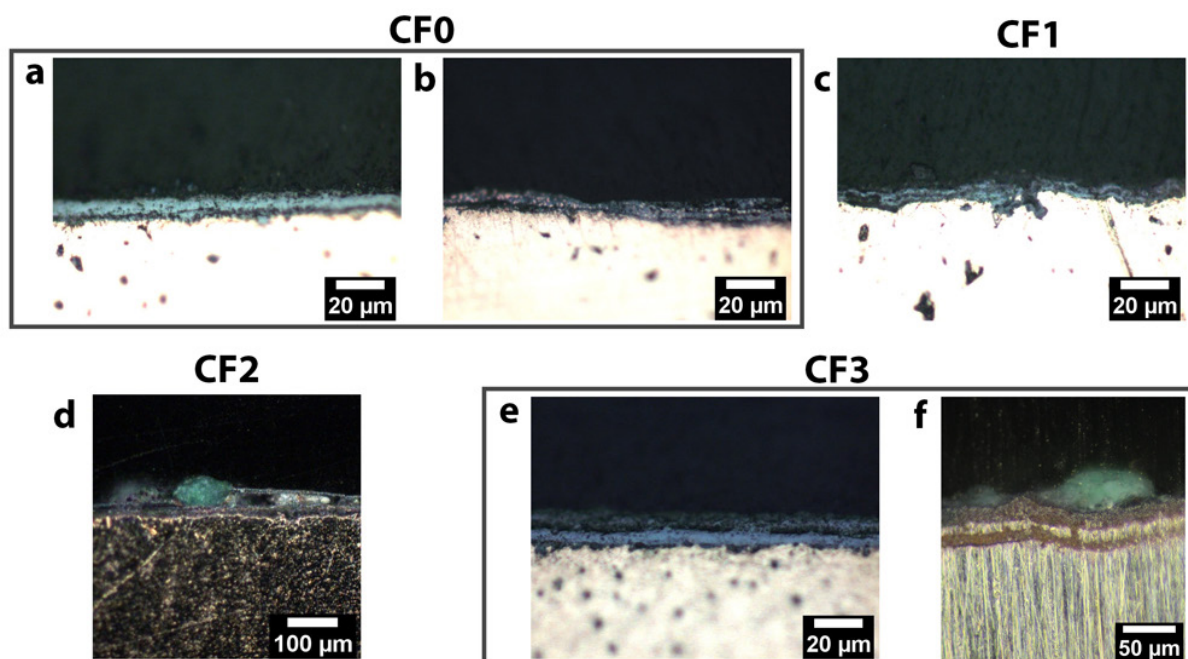


Figure 109 Optical micrographs of cross-sections of representative aged samples, ordered by aging time. All images are in bright field, except for (d) that is in dark field.

Conditions remain mostly unchanged after 16 and 45 days of aging, except for the emergence of few large round-shaped grains of vivid green colour at 45 days (Figure 109 c,d). A significant evolution is observed after 120 days of aging within soil. The inner blue-grey patina looks more compact, and the establishment of an external layer made by mixed blue and greenish small grains is observed (Figure 109 e). As visible in Figure 109 f, the presence of metallic grains or even layers, whose inclusion inside patina has most likely originated during the harsh treatment with hot coals, is still visible in some cases after the further ageing.

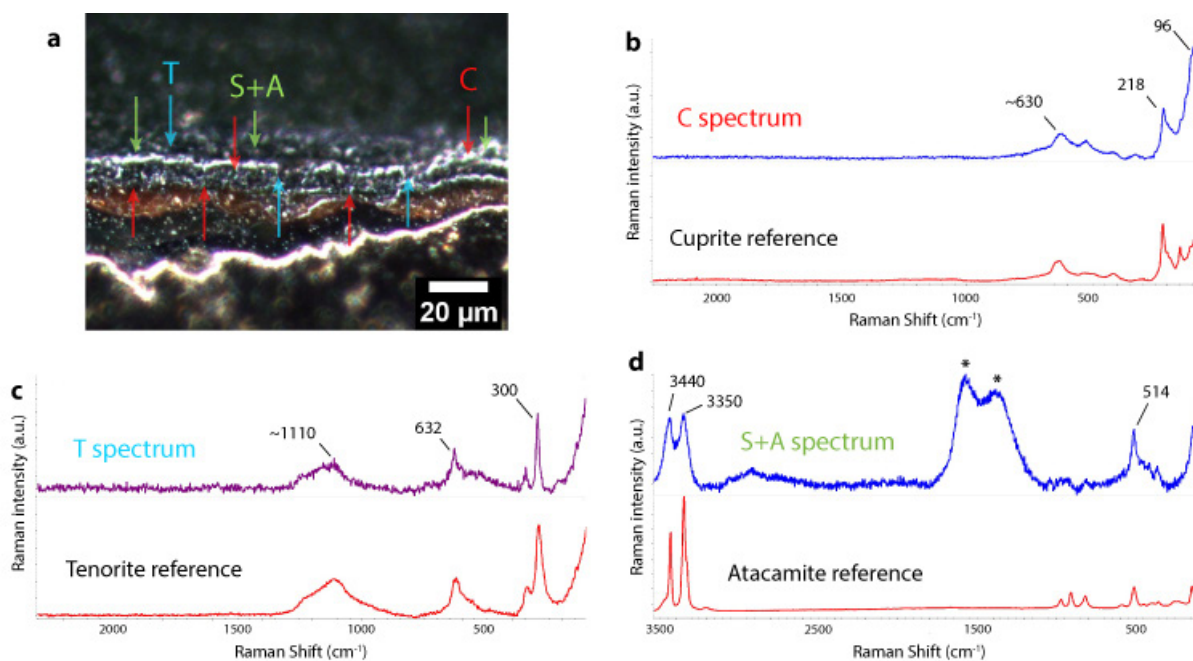


Figure 110 Representative area on a B555-CF4 cross-section. a) Optical micrograph of the area in dark field, original magnification 50x. b,c,d) Representative Raman spectra of the four main patina compounds identified: cuprite (spectrum b, spots in which it was found are marked with “C” and red arrows on (a)), tenorite (spectrum c, “T” light blue arrows), amorphous carbon and atacamite (spectrum d, “S+A” green arrows). All spectra are compared with reference data. Asterisks in (d) indicates amorphous carbon peaks.

Micro-Raman investigation has permitted the identification of the primary corrosion products involved. As shown in Figure 110, the main patina component can be attributed to cuprite, together with a lower amount of tenorite, which is present inside cuprite porosity. Malachite has not been found in any of the CF samples. The externally growing layer is still characterised by the presence of cuprite, together with a significant quantity of amorphous carbon, most likely linked to the presence of incorporated matter soil (Figure 110 d) and to the presence of ash from the hot coals. Finally, the presence of copper hydroxychlorides has been assessed in the external layer (Figure 110 d) and in the spherical inclusions (Figure 111), confirming the presence of bronze disease. Most likely, hydroxychlorides are more in the form of anatacamite rather than atacamite (which is reported as reference), given the shaper peak at 514 cm^{-1} and the characteristic shape of the OH-stretching region around 3400 cm^{-1} [89]. However, the presence of polymorphs of hydroxychlorides cannot be excluded.

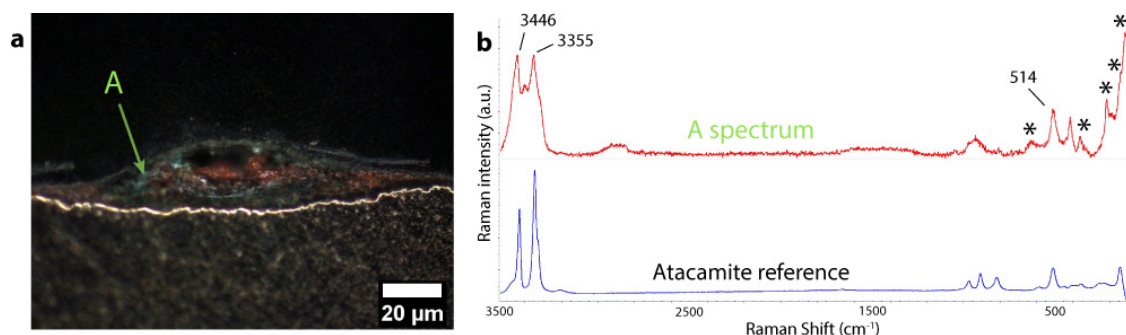


Figure 111 a) Optical micrograph in dark field of a globular inclusion. b) Raman spectrum of the point indicated in (a), compared with atacamite reference. Contributions from cuprite are marked with *.

It is possible that other compounds formed by the corrosion of secondary alloying elements are also present. Most likely, their small size and low concentration have hindered their identification by spectroscopic means.

A certain degree of variability has been observed in different replicas with the same aging time in terms of *patina* thickness and local detachments. However, their microstructure and composition, as well as the overall aesthetics are congruent across different replicas. The variability is independent from the composition of the base alloy. Indeed, no significant differences have been observed for the two alloy types.

The cross-section of an electrochemically aged sample has revealed a deep patination, with a global thickness of around 50 μm. The *patina* is well stratified, with a light blue-grey/red layer (in bright/dark field, respectively) which follows the original surface morphology, and a dark green layer grown at the top of it (Figure 112 a,b,c,d). Raman data have clearly revealed that the inner layer is constituted by cuprite, while the outside layer is malachite (Figure 112 e,f,g). Figure 112 d shows a weak signal that can be tentatively associated with traces of tenorite present at the interface with the bulk metal, but its identification is uncertain. Cuprite layer shows a marked macro-porosity. The as-described *patina* looks continuous and homogeneous in thickness and composition across the cross-section.

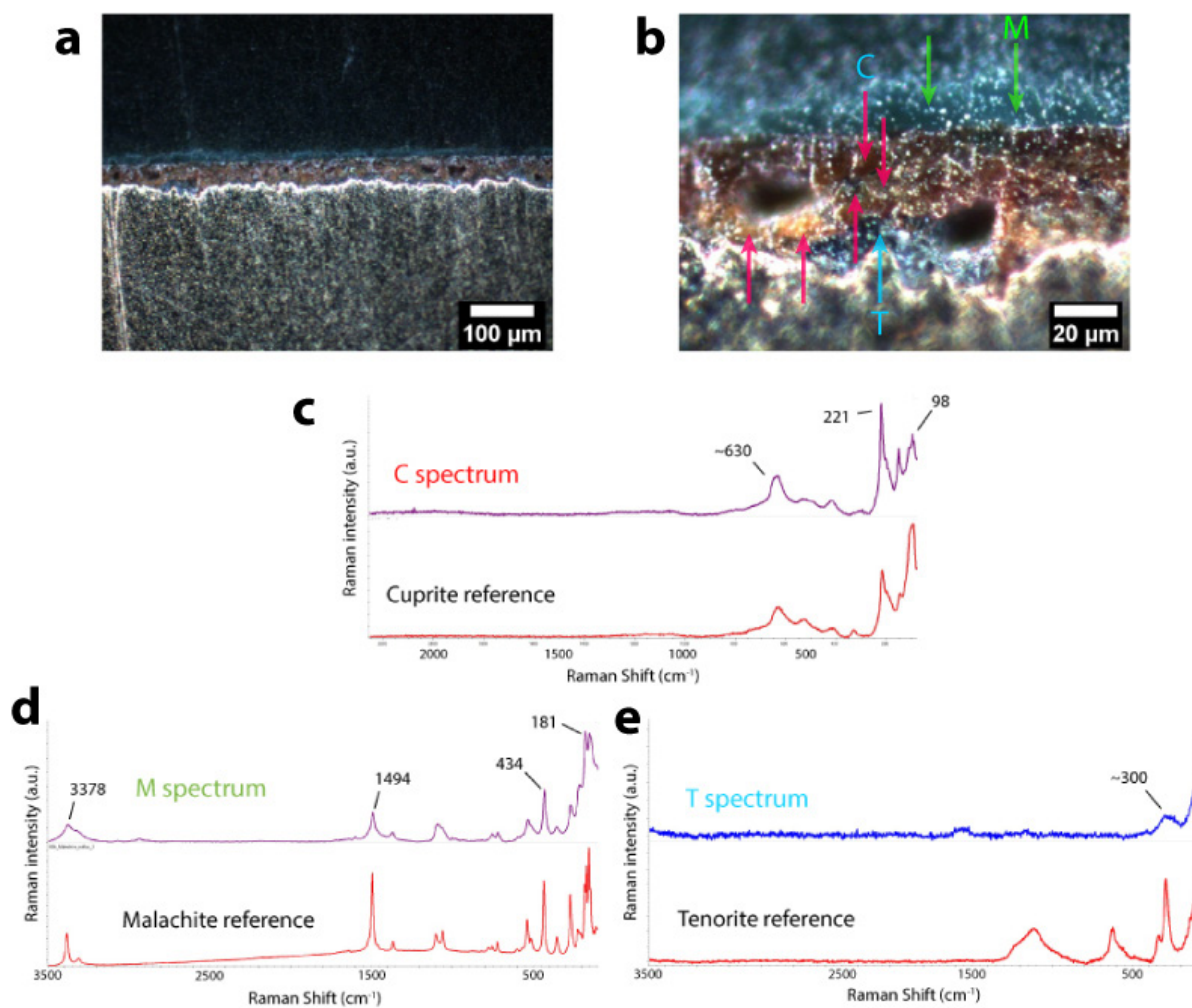


Figure 112 a,b) Dark field optical micrographs of representative areas on the cross-section of a B555-EL. c,d,e) Representative Raman spectra of the three main patina compounds identified: cuprite (spectrum c, spots in which it was found are marked with “C” and red arrows on (b)), malachite (spectrum d, “M” green arrows), tenorite (spectrum e, “T” light blue arrows). All spectra are compared with reference data.

III.5.1.3 SEM-EDS investigation

In the artificially aged samples, SEM-EDS has highlighted the insurgence of phenomena that are distinctive of archaeological *patinas*. This is the case of the tin-enrichment and decuprification phenomena which has been observed already after the first aging step for CF samples. In fact, in Figure 113, a localisation of Sn can be observed in the first altered layers, close to the bulk alloy. There, Cu has been preferentially attached, leaching outside of the original surface to grow on its outer part as oxides. Interestingly, the same behaviour is shown by both the alloys (Figure 113 a,b).

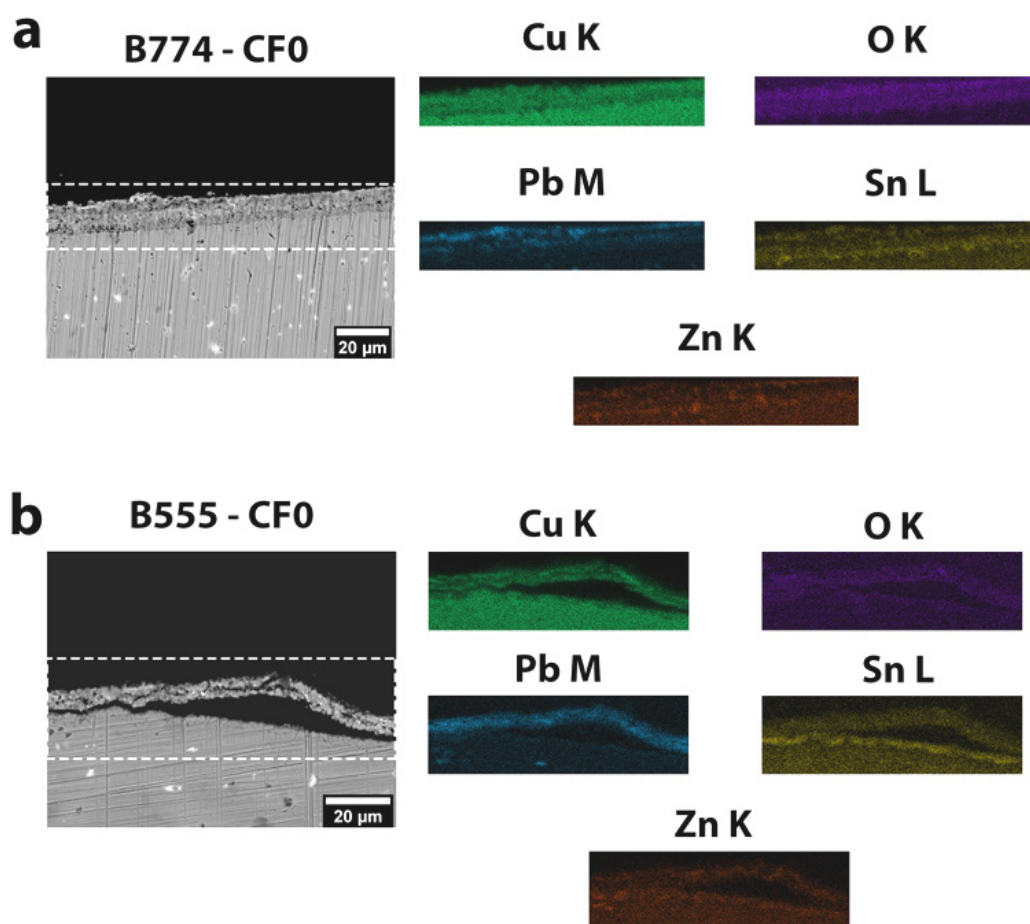


Figure 113 SEM-EDS data of two CF-aged samples: a) B774-CF0 and b) B555-CF0.

Figure 114 a, instead, shows a localised corrosion product linked to bronze disease. As expected, it is mainly composed by Cl compounds. Actually, Cl has been found also inside the *patina* of CF1 samples, indicating that the bronze disease has started propagating earlier, although macroscopic evidence for it have only appeared starting from CF2 samples. The EDS maps, additionally, have highlighted a lower concentration of Zn in the inner *patina* layer, suggesting the onset of a dezincification process. Moreover, the outermost *patina* layer is enriched with P and Ca, supporting the observation that along the aging process, the *patina* grows outwards by embedding material from the nearby environment, as commonly seen in metallic objects which have past centuries in a burial environment..

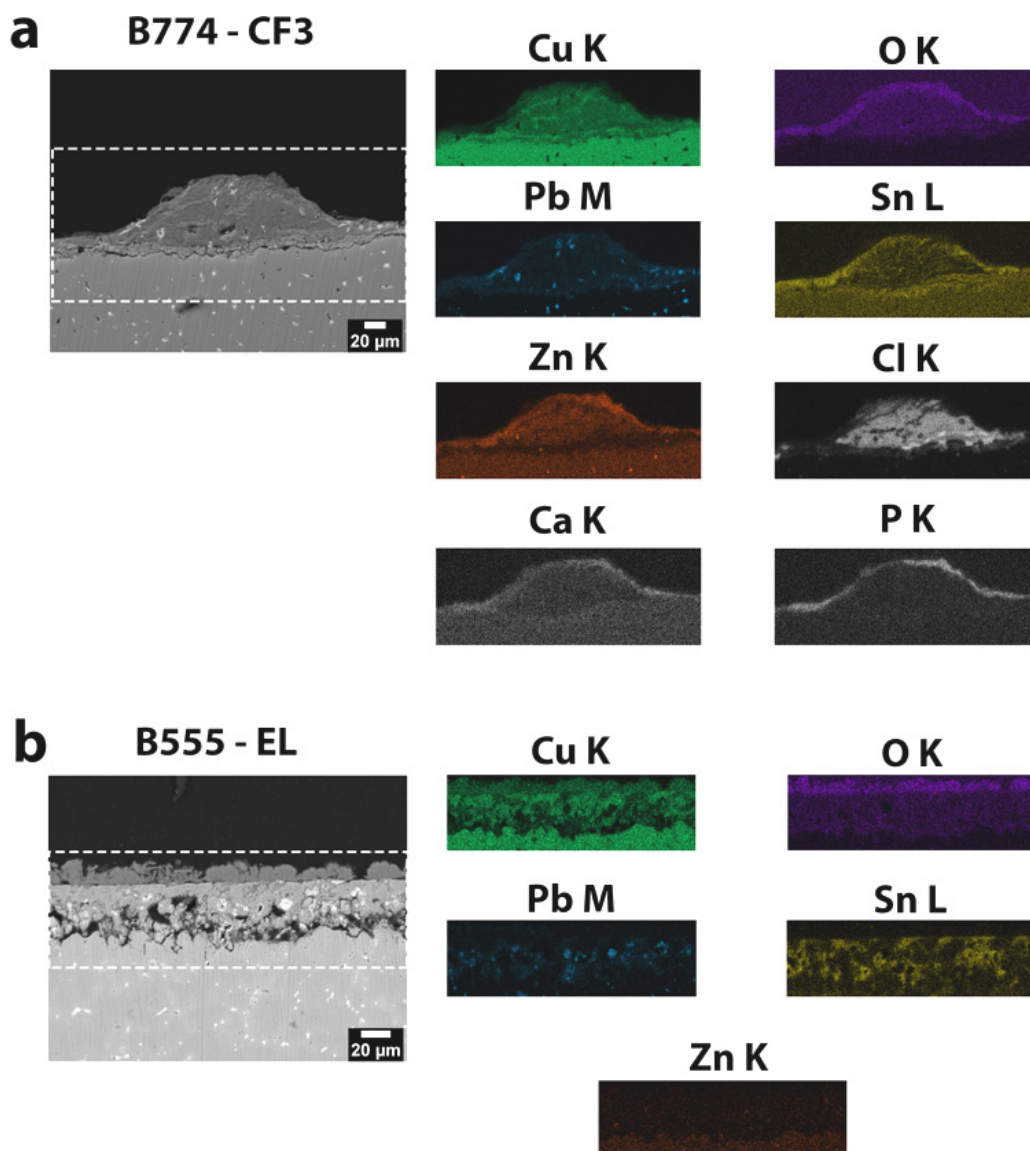


Figure 114 SEM-EDS maps of a) B774-CF0 and b) B555-EL.

Finally, SEM-EDS on the cross-section of an electrochemically aged sample (Figure 114 b) allowed to clearly observe the separation between the primary, inward growing patina, and the secondary patina, formed by nucleation of malachite on the original surface of the sample. The primary patina is formed by well separated Cu, Pb and Sn corrosion products. Looking in detail at the Sn distribution map, it is evident how Sn does not leach in the environment after being oxidised, but remains in place as corrosion by-product. For this reason, its distribution keeps trace of the shape of the original surface of the sample. This is perfectly in line with the mechanism of Type I *patina* formation [24]. Sn also appears enriched in this *patina* layer. Cu, instead, have leached in the local environment to subsequently re-precipitate or nucleate as malachite on the top of the corroded sample surface. The different degree of oxidation (in particular, between cuprite in the primary inner layer, and malachite in the secondary outside layer) is clearly remarked also by the O distribution map.

III.5.2 Discussion

The preliminary aging step of the CF protocol produces a strong attack on the metal substrate, rapidly forming a first patination of consistent thickness, made by cuprite and tenorite. Microscopically, such *patina* is characterised by a certain degree of porosity, while macroscopically has a dull colour and present some tendency to flake. During the accelerated aging in soil, the existing *patina* gradually compact, while a new layer grows outward, embedding soil components during the process. Most likely, it is this soil component to grant to the aged mock-up a considerable resemblance to real samples.

From a microchemical point of view, the main difference with the most common type of archaeological *patinas* is the absence of malachite. Tenorite is present instead, which is typical for artifacts that have been burned or came in contact with fire [90]. The occurrence of hydroxychlorides and of a high Chlorides concentration inside patina proves that CF samples are affected by bronze disease. Nonetheless, the occurrence of green outbreaks on the surface of the sample, linked to bronze disease by-products, is very limited even after 150 days of burial aging. Given the presence of active but slowly evolving bronze disease, such samples can be ideal for the testing of long-term stabilisation from chlorine attack.

No significant differences have been spotted in the behaviour of the two different alloys used. A slight heterogeneity has been registered within a single sample and between various replicas of the same kind. On one hand, this increases the likelihood of mock-ups with real archaeological samples, which are highly heterogeneous on a small scale. On the other hand, this is something to take into account when using them as testing substrate for protective treatments.

It can also be interesting to try to tune the output of the CF aging, acting on the local environment in the soil. For instance, one can push the environmental conditions in the soil towards a more malachite-friendly environment, by modifying the solution used for periodic watering and eliminating the chloride component, in favour of carbonates.

As last note, the extensive presence of residual metallic grains (even an entire layer) inside some portion of the patina can be addressed to the first fast oxidation by contact with hot coals. Such feature survives the aging in soil, and can be classified as a hint to the counterfeiting process. The same applies to the traces of tenorite found in the CF samples. More in general, having an analytical benchmark of the result of a counterfeiting process may also be useful in the future as a weapon in the fight against the illicit trade in counterfeit goods, or as a negative support for authentication.

The electrochemically aged sample perfectly mimics the chemical composition of an archaeological *patina*, with its well-defined cuprite-malachite layering as primary-secondary *patina* layers, respectively. This suggests that the aging environment has been properly selected. Consequently, EL aged samples can be used for studying the chemical interaction with the patina of specific environments, treatments or chemicals.

An aspect to improve for the EL aging protocol is the continuity and compactness of the *patina* layer achieved, which are important requirements for the application to electrochemical studies. In fact, the presence of uncovered metallic areas short-circuits the system, making impossible to evaluate the insulating component of the system with EIS, for instance. The globular morphology of malachite grains is typical for electrochemically grown phase, which subdue to a fast nucleation and growth of many small nuclei. The fast *patina* growth suggests that the aging process can be further prolonged, in order to increase *patina* coverage. Next tests will focus on this. It is conceivable that, by maintaining a constant potential, the patina growth rate will present a non-linear behaviour, decreasing as together with the increase coverage of the metal surface. It will therefore be necessary to find the ideal trade-off between the final output and the total ageing time.

The efficiency of this methodology can be further improved by increasing the number of working electrodes (mock-ups) in parallel. In fact, the process is scalable to a large number of ageing samples in parallel, provided that the cell, and especially the counter electrode, are properly scaled in size.

Overall, the results of the two ageing processes are both of high value, considering the wide diversity of their outputs. Both the aging protocols determine the insurgence of typical phenomenon of natural corrosion, such as decuprification, tin-enrichment and dezincification. On one side, EL *patinas* more closely embody the chemical conditions of a classic malachite *patina*, which is highly common archaeological artifacts. CF *patinas*, instead, well represents complex cases of bronze disease from burial conditions, as well as compact cuprite/tenorite *patinas* typical of burned objects. Moreover, the aesthetic resemblance with a real archaeological object is high, which is a positive feature for its use on the evaluation of the aesthetic impact of novel treatments.

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Chapter IV Conclusions

In this concluding chapter, the key scientific findings and noteworthy contributions stemming from this thesis will be considered. By focusing on the implications for archaeology and the conservation domain, the chapter aims to synthesize the overarching significance of this research.

Commencing with artifacts in post-excavation conditions, this study demonstrates the pivotal role of employing μ XCT scanning on archaeological copper-based coins before any invasive cleaning procedures. This approach proves to be crucial in enhancing numismatic investigations, preventing the irreversible loss of information and expediting the identification process.

After being cleaned from dirt and soil, metallic artifacts require investigation to understand their past and ensure preservation for the future. Here, it is demonstrated how FIB trenching enables the extraction of spatial and depth-resolved information, thanks to an optimised protocol that allows to investigate features as deep as 150 μ m inside thick corrosion patinas.

The use of LA-ICP-MS for the study of corrosion layers in ancient metals is reported herein for the first time. The various working modalities of this technique (1D, 2D and 3D) are assessed, revealing a high potential for the determination of main elements distribution inside and between the various layers composing the corrosion patina, as well as the bulk alloy.

Thanks to the decisive contribution of SPEM, the phenomenon of metallic silver whiskering is, for the first time, ascertained as corrosion product on a heritage object and, more in general, on an object subject to a burial environment. This previously unreported observation, complemented by FIB-SEM-EDS and lab-based XPS analyses, reveals a new feature to look for to better understand the original conservation environment of silver-bearing samples, which in the specific case points to the exposition to a source of sulphur. Furthermore, the possibility to couple SPEM with micro-invasive sample preparation techniques, as has been done here with laser ablation, foresees potential implementations in terms of achieving spatial and depth-resolved information on patina and alloy chemistry, overcoming the intrinsic limitations of SPEM applied to insulated substrates.

As regards the diagnostics of latent corrosion activity, the design of two new EIS cell setups is proposed and validated for the use on real archaeological items. Both cell designs, one based on a carbon-brush electrode and the other on a symmetric four-electrode scheme, provide quality and reliable EIS data, enriched by mapping-like capabilities. The four-electrode scheme demonstrates particularly suitability for the scope, thanks to its complete non-invasiveness.

Additionally, this work also proposes a new strategy for the preparation of archaeological replica samples. Two distinct protocols for the production of archaeological replica mock-ups have been tested: the first, an electrochemically-based protocol, proves to be faster and more reproducible, achieving a patination with a good chemical correspondence to real archaeological items, and well replicating the classical cuprite/malachite layered system; the second, based on the receipt of a counterfeiter, attains a better aesthetic and microstructural result, with a well-developed and compact patination and the diffused presence of copper chlorides, replicating instead the conditions of quiescent bronze disease.

The results achieved throughout the PhD project have manifold implications on the world of archaeometry and diagnostics, as well as on the restoration and conservation practice.

In first place, the achievement of spatial and depth-resolved information by micro-invasive means with FIB, SPEM and LA-ICP-MS is game-changing in the context of archaeological metals, given that up to today their invasive analysis is still considered as mandatory, leading to the sacrifice of many object for the positive goal of preserving many others.

On another side, EIS analysis is an essential tool in corrosion and protection studies, especially for the development of new protective treatments. The establishment and validation of a new way to perform such kinds of measurements on archaeological items, which solves the issues linked to invasiveness and data quality, represents a significant achievement in the field of Cultural Heritage. This will allow to conduct EIS experiments on small archaeological items in a more straightforward and reproducible manner, fostering the acquisition of large quantity of good-quality data, possibly easing the process of in-situ monitoring of conservation conditions.

The successful reproduction of various kind of archaeological patinas, moreover, positively impact the development and testing of various type of treatments, from cleaning to chlorine stabilisation, up to protection.

The research contained in this thesis can have beneficial implications also on the archaeological practice. The large throughput of the μ XCT-based methodology proposed can enable the study of thousands of artifacts, in particular coins, which have been up to now neglected due to lack of manpower and resources. The benefits of this methodology extend to restoration and digitization, making its widespread adoption in the management of archaeological findings highly advisable.

Furthermore, the possibility to achieve archaeometallurgical information from small-sized objects by micro-invasive means, as shown here with FIB, can also allow to achieve a deeper knowledge on coins and similar items, without the need to sacrifice the artifacts or part of them to invasive sampling.

On the other side, the experience gained on counterfeiting procedures and the potential showed by LA-ICP-MS for authentication studies can support the action of archaeologists against falsification and illicit trafficking of ancient objects.

Outside of the Heritage Science field, the new insights brought by this work on silver whiskering and its occurrence in burial environments can contribute to the understanding of this phenomenon, whose thermodynamics is still unclear.

More in general, the approach followed throughout the PhD project clearly shows that the integration of advanced analytical techniques in the field of Heritage Science is a fruitful path to follow. Moreover, it is fundamental, in the design of the research, to allow for an intense dialogue between the hard science-oriented partners and the other stakeholders of this field. As highlighted in this research, a positive impact on real practises can only be achieved by taking directly into account what are the such practises adopted on-field, and directly working side-by-side with conservators, curators, archaeologists and all the relevant figures involved in the management of Cultural Heritage.

Other than what has been reported so far in this chapter, the work reported herein also revealed several limitations and highlighted many possible developments for this research.

In particular, the deep-trenching protocol developed stretches the potentiality of Ga⁺-FIB to its limit, in terms of machine time-output quality balance. The coming of Plasma and Laser-FIB in the next future promises access to next-generation performance, allowing for a further consistent optimization of the process. The present study and the forthcoming technological advancement can pave the way for a more widespread use of FIB in metallic heritage studies. Moreover, here only EDS has been used as analytical technique for the investigation of FIB cross-sections, but many more can be adopted and future work will aim at addressing this point.

On the other hand, the presence of such metallic conductive phases embodied by silver whiskers may have an impact on further degradation processes and, consequently, on the long-term conservation of the item. This aspect is something to be investigated more in-depth in future work, as is the occurrence of whiskering on other artifacts, by exploiting the two diagnostic features identified.

For what concern EIS, the interpretation of data is still an open challenge today. This is something crucial to address in the next future, in order to allow a more widespread use of this technique even by the hands of conservators, something that today is still unfeasible. The collection of large quantity of quality data, thanks to the proposed approach, can represent the first step towards the solution of this issue, and current work is aiming towards this achievement.

In summary, this PhD project has achieved many relevant results towards a new way of studying and preserving archaeological metals, more respectful of their nature as unique heritage objects. The highest challenge will be then transferring these results to the whole Heritage Science community, including archaeologists, conservators and all the figures involved in the management of our common heritage, in order to grant to the latter a long existence for future generations to enjoy.

Appendix A Preliminary investigation for a diagnostic-informed protective treatment

A.1 Materials and Methods

A.1.1 Oxalic acid tests

The interaction between pure chemicals and oxalic acid in highly acid conditions was tested by adding 10 g/L of Cu_2O and $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ into two distinct 0.15 M oxalic acid water solutions (pH ca. 1), each in a 4 mL vial. The vials were shaken daily. After one week, each system was poured on a petri dish and left drying at 30° C for few hours. Optical microscopy and Micro-Raman Spectroscopy were performed directly on the dried material.

The interaction between oxalic acid and patina compounds in milder conditions was tested by immersing the cross-section of a B555-E5 and a B774-EL sample in a 0.15 M oxalic acid water solution, adjusted to pH 4 by addition of a 0.15 M NaOH solution 1:1 v/v. pH 4 was selected as a trade-off in order to limit the corrosive effect that acid solutions have on the bulk alloy, while partially retaining the chemical reactivity of the oxalic acid towards copper corrosion products. It must be noted that, at this pH value, some acid attack it is still expected to happen (see the Pourbaix diagram of Cu in water solution in **Figure 12** for ref.).

Cross-sections preparation and sample description were previously reported in par. II.6.4. Cross-sections were carefully rinsed with Milli-Q water after exposure to the oxalic acid solution and before proceeding with microscopic analysis.

A.1.2 Optical and Micro-Raman investigations

Optical images and Raman spectra were collected using a Thermo Fisher DXR™3 Raman Microscope (Thermo Fisher Scientific) equipped with 10x, 50x and 100x objectives, reaching a spatial resolution of 1 μm and a confocal depth of 2 μm . The acquisition of Raman spectra was made by employing as

excitation source a 532 nm laser (power between 0.2 mW and 2 mW) in continuous wave mode. All the spectra were collected in the spectral range 3550-78 cm^{-1} . Acquisition time and accumulations were optimised for each sample (varied between 0.5 and 2 seconds of acquisition time, with 50 to 200 accumulations). The spectra analysis was performed operating with OMNIC Software supplied by the instrument manufacturer, and they were automatically corrected for fluorescence by the software using a polynomial curve fitting. Reference spectra were taken on KBr pellets of pure compounds on the same instrument and with similar acquisition parameters.

A.2 Results

A.2.1 Effect of Oxalic acid on Cuprite and Malachite

After one week of immersion of synthetic cuprite and malachite powders in oxalic acid solution, a visual inspection has revealed that cuprite had slightly changed its colour toward a darker tone, while in both system a milky supernatant suspension was present.

Optical microscopy of the dried cuprite solution has revealed the widespread presence of a phase with a light green appearance in dark field (Figure 115). Micro-Raman spectroscopy has revealed a diffused presence of copper oxalate together with cuprite, which is still widely present (Figure 115 c).

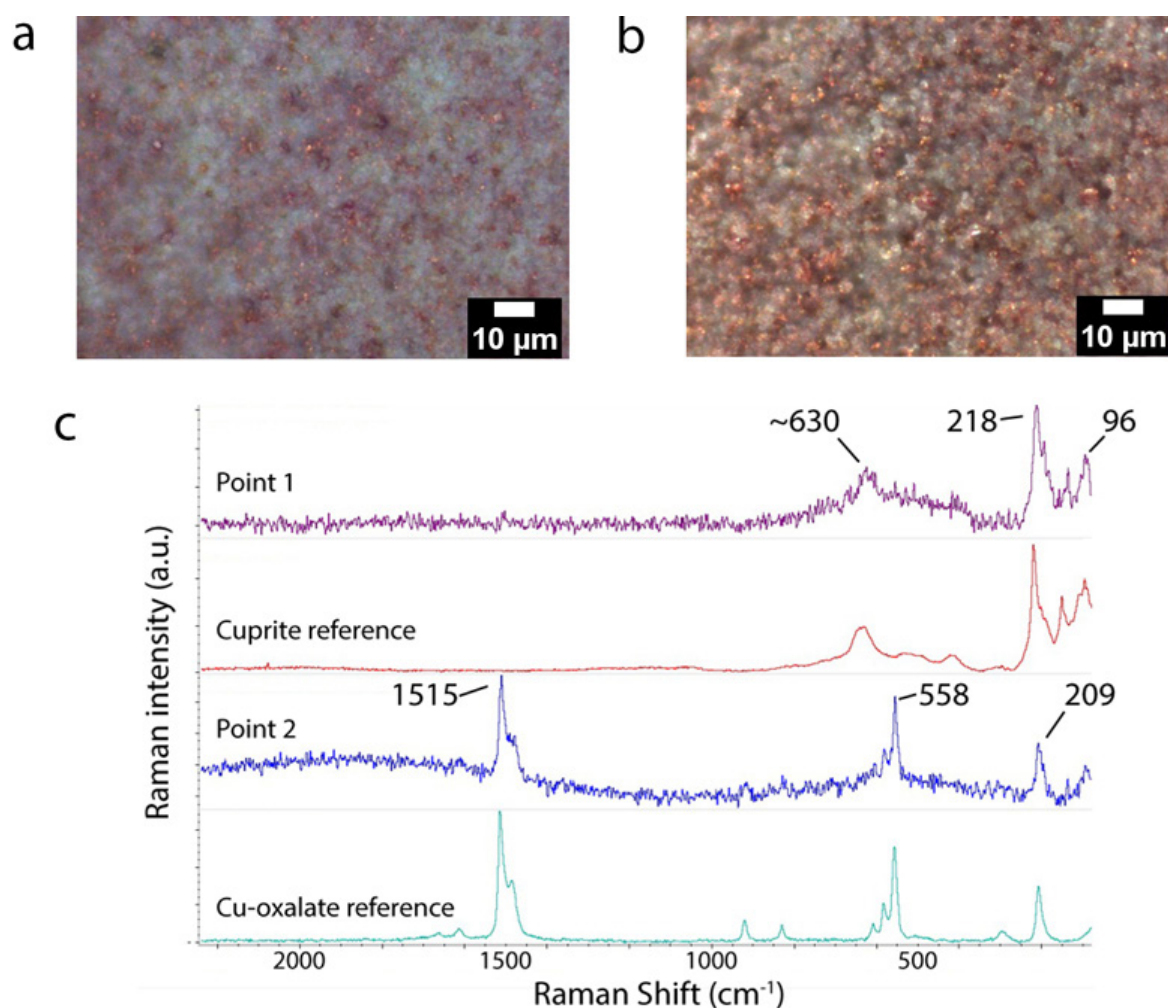


Figure 115 Optical images in dark (a) and bright (b) field (original magnification 50x). c) Purple and blue lines: Raman spectra acquired on two different points of the dried cuprite sample (50x). Red and green lines: reference spectra for cuprite and copper oxalate, respectively. Main peaks are labelled.

Malachite grains appeared as light blue (in dark field) grains of larger size than cuprite ones (Figure 116 a,b). Under higher magnification, they looked covered by a light green layer (Figure 116 c,d). The green tone is more prominent in the smaller grains that fill the space between larger ones. While Micro-Raman spectroscopy has detected both copper oxalate and malachite in spots with more vivid colour, while only oxalate has been detected on the small-sized grey grains (Figure 116 e).

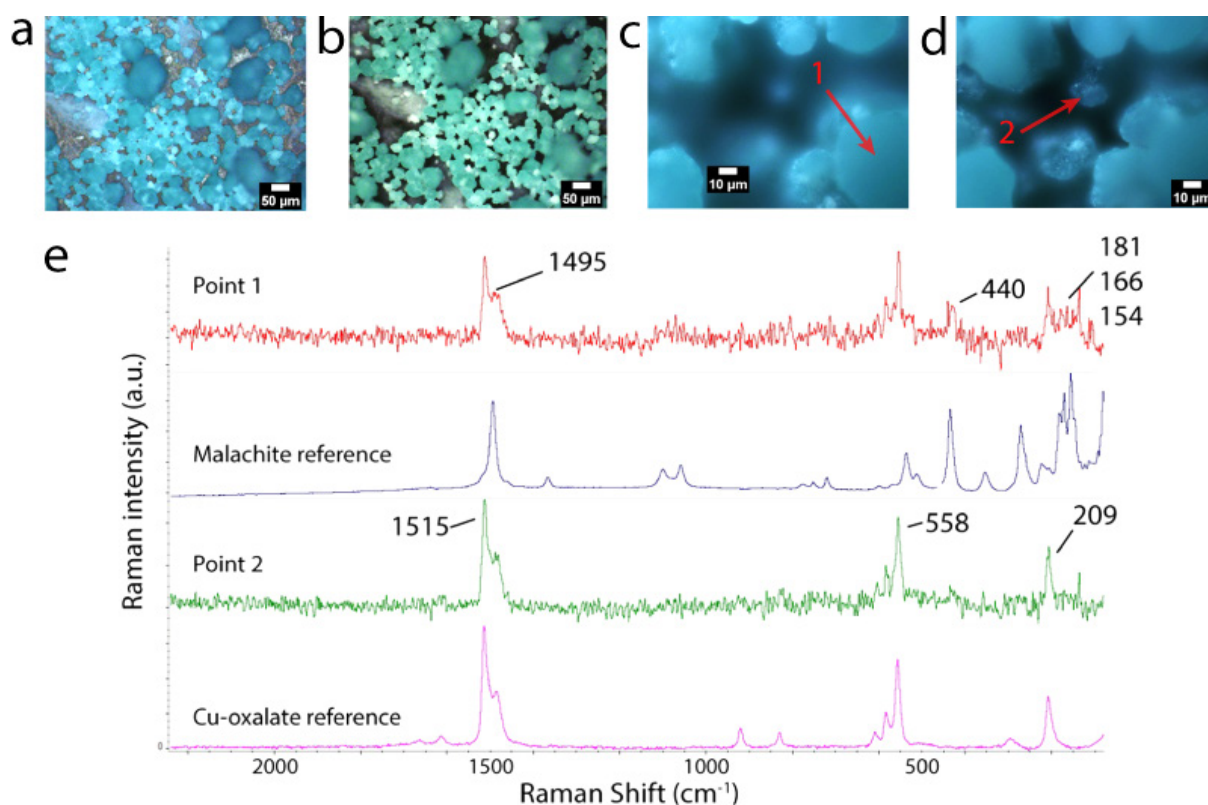


Figure 116 a,b) Optical images at 10x of original magnification in dark and bright field, respectively. c,d) Optical images at 50x of original magnification in dark field of the same area, by varying the focus position. e) Red line: Raman spectrum acquired on a large grain, with more vivid colour (50x). Green line: Raman spectrum acquired on a smaller, darker and greyish grain (10x). Black and purple lines: reference spectra for malachite and copper oxalate, respectively. Main peaks are labelled.

A.2.2 Immersion test of artificially aged samples

Two cross-sections of aged mock-ups (one CF and one EL samples), previously analysed in section III.5, have been immersed in an oxalic acid solution (pH 4) for one day. Even if an accurate evaluation of the interaction and depth of penetration of the solution needs to be performed on whole samples and then assessed on cross-section taken from them, this test has been designed as an early attempt for investigating the direct interaction *in-situ* between an oxalic acid solution and corrosion products mimicking the composition of archaeological *patinas*, i.e. corrosion products grown from - and fixed on - a surface, rather than powders dispersed in a liquid medium as in the test reported in the previous paragraph.

As can be observed by the Raman spectra and the vivid blue appearance of patina layers (Figure 117), copper oxalates have formed over both samples, in the same place where cuprite and malachite were previously present. The occurrence of oxalates is confined to patina layers, indicating that it comes from

the *in-situ* conversion of patina compounds. Additionally, the bulk alloy shows the typical appearance of acid attack.

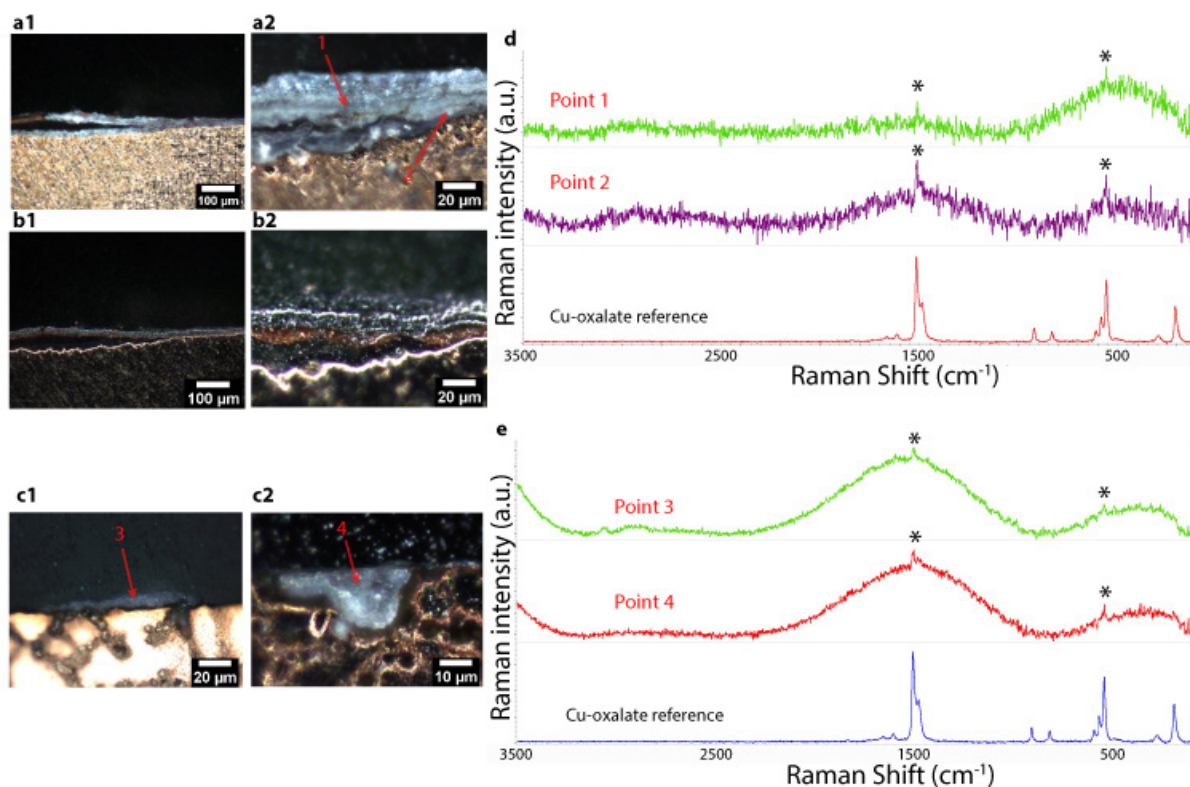


Figure 117 Optical images in (a) and (b) are from a B555-CF4 sample, after and before the application of the treatment, respectively. Images in (b) are from a B555-EL sample, after treatment application. All images are in dark field, except (c1). Original magnification: 10x (a1, b1), 50x (a2, b2, c1), 100x (c2). (d,e) Raman spectra taken on the points indicated on images (a2), (c1) and (c2). Peaks from Cu-oxalate are labelled with *.

A.3 Discussion

Adding to what has been already investigated in literature [1–7], the tests reported in this appendix are early investigations on the interaction between oxalic acid solutions and corrosion products typical for archaeological copper-based objects, and many other test regarding chemical compounds, concentrations, pH and type of samples have to be performed in order to derive complete conclusions. Nevertheless, the direct immersion of pure powders shows that cuprite and malachite do not dissolve in oxalic acid, even in highly acid conditions (pH 1). Regardless, small amounts of copper oxalates are formed. At the same time, the formation of copper oxalates from the *in-situ* conversion of cuprite and malachite, grown as corrosion products on artificially aged samples, seems to takes place even in partially neutralised conditions (pH 4). The newly formed copper oxalates appear to be compact. However, it is necessary to investigate more thoroughly the quantitative effectiveness and homogeneity

of the conversion reaction over a large surface area, and to ascertain the porosity plugging obtained by subsequent cross-section analysis. Moreover, the contact between the partially neutralised oxalic acid solution and the metallic samples also generates some drawbacks. The first is the acid attack of the metallic bulk, which is normally avoided when using oxalic-based biological treatments [8,9]. The second is the colour shift towards a blueish tone. In order to overcome both these limitations, next attempts will point towards the strict confinement of oxalates conversion on the surface of the sample at the nano-scale, using for instance smart-release nano-carriers. Another route under consideration is extending the field of investigation to other dicarboxylic acids, which could guarantee lower reactivity and milder pH conditions, and thus greater possibilities of reaction control.

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Scientific Contributions

List of publications

- 1) A. Artesani, F. Abate, R. Lamuraglia, M.A. Baldo, F. Menegazzo, A. Traviglia, “Integrated Imaging And Spectroscopic Analysis Of Painted Fresco Surfaces Using Terahertz Time-Domain Technique”, *Heritage*. 6 (2023) 5202–5212.
- 2) F. Abate, M. De Bernardin, M. Stratigaki, G. Franceschin, F. Albertin, M. Bettuzzi, R. Brancaccio, A. Bressan, M.P. Morigi, S. Daniele, A. Traviglia, “X-Ray Computed Microtomography: A Non-Invasive And Time-Efficient Method For Identifying And Screening Roman Copper-Based Coins”, *Journal Of Cultural Heritage*. 66 (2024) 436–443.
- 3) F. Abate, M. Leoncini, S. Lauciello, G. Franceschin, N.M.E. Stucchi, M.A. Baldo, A. Toma, A. Traviglia, “FIB deep-trenching strategy for the micro-invasive investigation of highly corroded copper-based samples”, *in preparation* (2024).
- 4) F. Abate, R. Zanini, E. Tartaglia, C. Zanardi, M.A. Baldo, A. Traviglia, “LA-ICP-MS for the investigation of corrosion *patinas* in archaeological findings”, *in preparation* (2024).
- 5) F. Abate, M. Moglianetti, M. Stratigaki, F. De Boni, M. Amati, L. Gregoratti, M. Prato, M.A. Baldo, A. Traviglia, “SPEM for ancient metals: identification of a new form of corrosion and exploration of new methodological synergies”, *in preparation* (2024).
- 6) F. Abate, E. Verlato, S. Daniele, M.A. Baldo, A. Traviglia, “Design and validation of EIS setup for archaeological samples”, *in preparation* (2024).
- 7) F. Abate, E. Tartaglia, E. Verlato, M.A. Baldo, A. Traviglia, “Efficient artificial aging protocols for the reproduction of archaeological copper-based *patinas*”, *in preparation* (2024).

Contributions to International Conferences

- 1) F. Abate, G. Franceschin, S. Daniele, A. Traviglia, Presenting Author: F. Abate, “The Evolving Perspective On The Study Of Ancient Bronze Coins”, Oral Presentation, SCI2021 – XXVII Congresso Nazionale della Società Chimica Italiana (Online, 2021)
- 2) F. Abate, G. Franceschin, L. Pasquale, M. Prato, S. Daniele, A. Traviglia, Presenting Author: F. Abate, “XRF Mapping And FIB-SEM: A Fruitful Cooperation For The Investigation Of Archaeological Copper-Based Artefacts”, Poster, MA-XRF Scanning in Conservation, Art and Archaeology 2022 (Delft (NL), 2022).
- 3) F. Abate, M. De Bernardin, M. Stratigaki, G. Franceschin, F. Albertin, M. Bettuzzi, R. Brancaccio, A. Bressan, M.P. Morigi, S. Daniele, And A. Traviglia, Presenting Author: F. Abate, “Renewing Archaeological Practice With Modern Technology: μ XCT For The Facile Screening Of Excavated Copper Coins”, Oral Presentation. TECHNART 2023 - International Conference on Analytical Techniques in Art and Cultural Heritage (Lisbon (PT), 2023).

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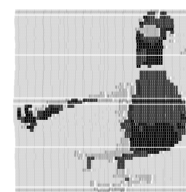
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