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DOTTORATO DI RICERCA IN
SCIENZE DELL'INGEGNERIA

CICLO XXVIII

COORDINATORE Prof. Stefano Trillo

AN ARCHEOMETALLURGICAL APPROACH TO DATING, AUTHENTICATION AND CONSERVATION OF COPPER-BASED ARTEFACTS

Settore Scientifico Disciplinare ING-IND/21

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TO MY BELOVED FAMILY
for making everything possible

Contents

Preface

This doctoral thesis is the result of three years of full-time study, including courses and research activities at the University of Ferrara, Italy, from January 2013 to December 2015. The experimental work was carried out at the Engineering Department (ENDIF) in Ferrara and Professor Gian Luca Garagnani was the supervisor.

The aim of my PhD work was the systematic archaeometallurgical investigation on copper-based artefacts for conservation, preservation, authentication and dating purposes.

The research was subdivided into separate projects and led to four publications, which represent the main part of this doctoral thesis. The manuscripts are:

I. C. Soffritti, E. Fabbri, M. Merlin, G.L. Garagnani, C. Monticelli, "On the degradation factors of an archaeological bronze bowl belonging to a private collection", *Applied Surface Science* 313 (2014), 762–770.

II. C. Soffritti, E. Fabbri, A. Fortini, M. Merlin, G.L. Garagnani, "Fakes in African art: study of a reliquary figure (*Mbulu-Ngulu*) from Gabon", *La Metallurgia Italiana* 4 (2015), 9–13.

III. E. Fabbri, C. Soffritti, M. Merlin, G.L. Garagnani, "An attempt to dating two Benin plaques by quantitative analyses and lead isotope measurements", submitted to *Material Chemistry and Physics*.

IV. A. Balbo, C. Chiavari, C. Martini, F. Zanotto, A. Frignani, E. Fabbri, E. Bernardi, M.C. Bignozzi, C. Monticelli, "Characterization of gilded bronze corrosion behaviour exposed during exposures to simulated outdoor environment", *Proceedings of the XI Giornate Nazionali sulla Corrosione e Protezione*, 2015, Ferrara, Italy.

Part of the research activities was also devoted to the supervision of the following B.S. and M.S. theses:

1. Maria Anna Ciavarella (2013), "Analisi del degrado e ipotesi di intervento di bio-restauro su monumenti esposti agli agenti atmosferici: il caso studio del monumento funerario alla memoria di Gaetano Simoli (Certosa di Bologna, 1895)". Supervisors: G.L. Garagnani, M. Leis, C. Vaccaro, E. Fabbri, C. Soffritti.

2. Manuela Lombardo (2014), “Ambiente urbano e stato di conservazione di arredi in bronzo: valutazione dello stato di conservazione delle statue “Cavallo” di Mario Piva e “Vittoria del Piave” di Arrigo Minerbi”. Supervisors: G.L. Garagnani, C. Vaccaro, E. Fabbri, C. Soffritti.

3. Giorgio Forlani (2015), “Analisi metallurgiche e microstrutturali di monete romane provenienti da Alberone di Ro”. Supervisors: G.L. Garagnani, E. Fabbri, C. Soffritti.

4. Giulia Monari (2015), “Ipotesi ricostruttive dell’estrazione mineraria cobaltifera di Punta Corna e del Vallone del Veil. Supervisors: G.L. Garagnani, C. Vaccaro, C. Soffritti, E. Fabbri,.

Acknowledgements

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All my colleagues at the Engineering Department, administrative and technical staff, for creating a positive work environment.

Abstract

It is well-known that archaeometallurgy is an interdisciplinary field of archaeometry, dealing with the investigation of all aspects of the production, use and consumption of metals from around 8000 B.C.E. to the present. Therefore, it takes into account several different disciplines, including archaeometry, metallurgy, geology, art, history and so on. The main purpose of archeometallurgy is to obtain information about the characterisation of artistic and ancient objects and about their conservation and authentication.

However, despite the large amount of literature on these topics, further researches and innovations must be achieved especially towards conservation and authentication issues.

It is also noteworthy that any artistic object is almost unique, so it is very difficult to find the good compromise between conservation and systematic investigation on Cultural Heritage.

Moreover, the authentication is certainly a strong necessity in the market of artistic object. In addition, it is well-known that the direct dating of metals is not possible and the authentication is one of the most challenges in the archaeometallurgical field.

The demand of corrosion inhibitors which specific features, such as high protective efficiency and low environmental impact, is also reputed essential and it is increased during last years.

For this reason, the results reported in this thesis could be inspired for future researches and interesting detailed studies.

The aim of this doctoral thesis is the research of the better methodology to investigate each artefact together with the evaluation of a non-conventionally techniques' effectiveness to dating contemporary metallic objects. Moreover, further tests in field of efficiency and environmentally-friendly corrosion inhibitor is reported.

The main results of these separate research studies are summarized as follows:

∴ Because of a direct metal dating is not possible, the metallic artefacts are generally dating by only artistic and stylistic investigations; however, these could lead to an uncertain authentication assumption. The well-known lead isotopes technique which allows the measurements of mineral age, such as meteorites and terrestrial rocks, is considered and a different method to calculate the amount of ^{210}Pb is proposed. The measurement is reported in form of ratio between ^{210}Pb and ^{204}Pb, the only one that is a non-radiogenic isotope and it can be used like an index of total lead amount in the sample. The ^{210}Pb is usually ignored for the geological dating because of its relatively short-lived (around 22 years). However, the same feature is particularly useful in process with time-scale lower than 100 years. In archaeometallurgy field, if an amount of ^{210}Pb is detected in studied samples, it is likely that the object was produced in the last 100 years;

conversely, the absence of ^{210}Pb could indicate that the artefacts are older than a century. For this reason, a non-conventionally techniques' to dating contemporary metallic artworks is evaluated in order to convey a simple and fast dating technique which could be a usable tool in the authentication field of contemporary Cultural Heritage.

∴ The gilded bronze corrosion behaviour was investigated during both wet & dry and dropping exposure to concentrated acid rain (simulating conditions of stagnant rain or direct runoff, respectively), before and after silane coating application (PropS-SH). It is important to note that the protective coating PropP-SH is both not harmful for environment and humans and it is effective about the protection of bronze from corrosion. Moreover, electrochemical tests were performed by a special contact probe for non-destructive *in situ* measurements in order to get a deeper knowledge of the protective action of PropS-SH, In the conservation field of Cultural Heritage, it is very important to assess the corrosion processes directly and for long period of time by this type of measurements, allowing to evaluate in real time the possible changes or damage of metal surface and to choose the better restoration procedure.

Sommario

È ben noto che l'archeometallurgia si occupa dello studio interdisciplinare di tutti gli aspetti che riguardano la produzione, l'uso e l'utilizzo dei metalli fin dall'inizio dei tempi. È quindi una materia che prende in considerazione molte discipline, tra cui l'archeometria, la metallurgia, la geologia, l'arte, la storia e molte altre. Lo scopo primario è quello di ottenere il maggior numero di informazioni in merito alla caratterizzazione degli oggetti, alla loro conservazione e alla loro possibile autenticità.

Sebbene tali aspetti siano stati ampiamente discussi in letteratura, ancora molte ricerche devono essere portate avanti in alcuni settori specifici, in particolare nel campo della conservazione e dell'autenticità delle opere d'arte in lega metallica.

È inoltre utile sottolineare che ogni oggetto d'arte è pressoché unico ed è quindi molto importante, e al tempo stesso molto complesso, trovare il giusto compromesso tra conservazione e studio sistematico dell'opera.

Un ulteriore tema fortemente sentito nel campo del mercato dell'arte è quello dell'autenticazione delle opere. È ben noto, infatti, che datare i materiali metallici in maniera diretta non è possibile e quindi, in campo archeometallurgico, l'autenticazione è sicuramente una delle sfide maggiori e più sentite.

Inoltre, una tematica che negli ultimi anni sta suscitando grande interesse nella comunità accademica è la continua ricerca di inibitori di corrosione innovativi, che siano al tempo stesso efficaci e non dannosi per la salute e l'ambiente.

Per questo motivo, i risultati presentati in questo elaborato possono fornire alcuni spunti interessanti per approfondimenti e ricerche future.

Alla luce di tali considerazioni, lo scopo di questa tesi di dottorato è pertanto la ricerca delle tecniche di studio più adatte ad indagare ciascun'opera nella sua unicità, unitamente a valutare l'efficacia di una tecnica non convenzionale per la datazione di opere d'arte contemporanee in lega metallica e ad ulteriori prove in campo di inibitori di corrosione efficaci ed eco-compatibili.

I risultati principali di queste tematiche affrontate sono riportate di seguito:

∴ L'impossibilità di datare direttamente le opere d'arte prodotte in lega metallica comporta che esse siano collocate in determinati periodi storici e/o artistici principalmente mediante valutazioni prettamente stilistiche, che in alcuni casi possono essere poco affidabili. La tecnica dell'analisi degli isotopi del piombo, che consente principalmente di localizzare i giacimenti di provenienza dei minerali e di datare meteoriti e rocce, è stata considerata ed un differente metodo di calcolo del piombo-210 (^{210}Pb) è stato proposto. Nello specifico tale valore è stato ricavato dal rapporto tra il piombo-210 stesso (210Pb) e il piombo-204 (^{204}Pb), unico isotopo che non deriva dal decadimento di altri elementi e perciò viene utilizzato come indice per

calcolare la quantità di piombo totale nel sistema. Il ^{210}Pb ha un tempo di dimezzamento molto breve (circa 22 anni) perciò non è utile nel campo delle datazioni geologiche, ma al tempo stesso tale caratteristica gli permette di essere un utile indice in processi con scale temporali inferiori, o di poco superiori, a 100 anni. Per questo motivo, se una quantità di ^{210}Pb viene rilevata nell'opera indagata è molto probabile che essa sia stata prodotta negli ultimi 100 anni; al contrario la sua assenza può indicare che l'opera ha più di un secolo di vita. Per tali motivi, un differente approccio alla datazione di opere d'arte è stato valutato al fine di indagare una tecnica che possa essere uno strumento veloce, semplice ed utilizzabile nell'autenticazione di opere contemporanee in lega metallica.

∴ In uno dei lavori è stato studiato il comportamento a corrosione di un bronzo dorato sottoposto ad un trattamento protettivo mediante un composto organico (PropS-SH). I campioni sono stati sottoposti ad invecchiamento accelerato sia in condizioni che simulano l'esposizione a pioggia acida stagnante (*wet&dry*) che in condizioni che simulano l'esposizione a pioggia battente (*dropping*). In particolare, il composto utilizzato oltre a non essere nocivo per la salute e l'ambiente, ha evidenziato una buona capacità di protezione anche in condizioni aggressive. Inoltre per valutarne l'efficacia, le misure elettrochimiche sono state eseguite mediante una speciale sonda a contatto per misure *in situ* non distruttive. La possibilità di valutare i processi di degrado direttamente e continuativamente su opere d'arte esposte all'aperto è di sicuro una tematica molto importante nell'ambito della conservazione dei Beni Culturali. Ciò consente, infatti, di monitorare in tempo reale gli eventuali cambiamenti e/o danneggiamenti delle opere, consentendo un rapido intervento di conservazione e restauro.

Introduction

The objective of this thesis work is the systematic study of copper-based artefacts in order to obtain a deeper knowledge about characterisation, conservation, preservation, authentication and dating of bronzes and brasses. To accomplish this, the following scheme has been adopted:

PART 1 is a literature survey intended to give the reader sufficient background on the theories at the base of archaeometallurgy. In particular, an *excursus* through different microstructures which may observe in ancient artefacts, as well as a list of the several corrosion compounds formed in specific environments is reported. A brief history of the Achaemenid Empire, of Benin Kingdom and of Kota population is also described in order to frame the features of the cultures that have created beautiful objects, the main characters of my thesis. Moreover, the problem of fakes and forgeries in art together with the several methods to authenticate the artefacts is presented. In addition, the effectiveness of protective treatment for the conservation of Cultural Heritage exposed in outdoor environment is also highlighted.
Eventually, the summary and the main conclusions from the articles are reported in this part.

PART 2 contains the results of the work as a collection of four articles. The papers are presented in the form they were submitted for publication or printed. The manuscripts included in this section are:

I. C. Soffritti, E. Fabbri, M. Merlin, G.L. Garagnani, C. Monticelli, "On the degradation factors of an archaeological bronze bowl belonging to a private collection", *Applied Surface Science* 313 (2014), 762–770.

II. C. Soffritti, E. Fabbri, A. Fortini, M. Merlin, G.L. Garagnani, "Fakes in African art: study of a reliquary figure (*Mbulu-Ngulu*) from Gabon", *La Metallurgia Italiana* 4 (2015), 9–13.

III. E. Fabbri, C. Soffritti, M. Merlin, G.L. Garagnani, "An attempt to dating two Benin plaques by quantitative analyses and lead isotope measurements", submitted to *Material Chemistry and Physics.*

IV. A. Balbo, C. Chiavari, C. Martini, F. Zanotto, A. Frignani, E. Fabbri, E. Bernardi, M.C. Bignozzi, C. Monticelli, "Characterization of gilded bronze corrosion behaviour exposed during exposures to simulated outdoor environment", *Proceedings of the XI Giornate Nazionali sulla Corrosione e Protezione*, 2015, Paper n°36, Ferrara, Italy.

Part 1

Chapter 1

Theoretical background

1.1 Copper-based artefacts: bronze and brass

Copper has played a crucial role in human development (Scott D.A., 2002) and it is an essential element in our lives because of its ductility and high thermal and electrical conductivity.

The use of native copper began around the 8th millennium B.C.E. Much of the native copper was first extracted by Anatolian and Mesopotamian cultures and subsequently subjected to annealing and hammering treatments with the aim of realising small ornaments and useful weapons (Muhly J.D., 1986; Scott D.A., 2002). Certainly, metal objects played a significant role in the most post-Neolithic societies, as reflected in the denominations for major archaeological periods (Copper Age, Bronze Age and Iron Age).

Some of early alloys were probably derived from the accidental smelting of copper ores with the arsenic during the 6th millennium B.C.E.; whereas tin intentionally added to copper was dated from 4th millennium B.C.E. and began universal during the Bronze Age (since 3200 B.C.E.).

Conversely, discover and use of brass (copper-zinc alloy) was restricted in early usage because of the temperature needed to smelt zinc overstep the boiling point of the metal. In northern Iraq, some of the most ancient brasses dated around 1300 B.C.E. were discovered; however, only during the Roman period, the brass became an important alloy and it was widely used to produce coinage.

Thus, given this extremely short *excursus* it should be noted that bronze is one of the most employed alloys over the past four thousand years (Scott D.A., 2010).

The following briefly describes the bronze and brass phase diagrams in order to appreciate the microstructural and mechanical properties of these alloys. Information about melting point, crystallization and any other phenomena linked to state transitions could be also acquired through phase diagrams perusal.

Figure 1.1 collects the copper-tin equilibrium diagram (left hand) and the two versions of the low-tin side diagrams (centre and right hand), which were drawn by Hanson *et al.* in 1951 (1951). In particular, in the centre of Figure 1.1, it is reported the diagram for bronzes which are fully annealed; in the right hand, diagram for usual sand-cast condition is shown. For our purposes, we can consider only restricted part of the diagrams because ancient bronzes are characterised by low percentage of tin, roughly 12 %wt. maximum. These charts are very useful in helping to explain the ancient metallurgy in order to obtain information about, for example, the complete solubility of the tin in copper or the existence of intermetallic compounds such as delta phase. The latter shall be important because it tends to be very hard with no ductility. For the annealed and casting diagrams it can be noted that the region of alpha and delta eutectoid phase is larger than one of the equilibrium diagram. This means that a low-tin alloy is very difficult to be workable because of its hardness and brittleness. The brittle nature of this type of alloy can be overcome by reducing tin content or by quenching to hold the alloy of higher temperature. Moreover, it is noteworthy that the mechanical properties of the alloys can change appreciably with the increase of tin content; for example, the elongation or the reduction in overall thickness are affected by a specific limit in tin content (18%wt.) (Scott D.A., 2010).

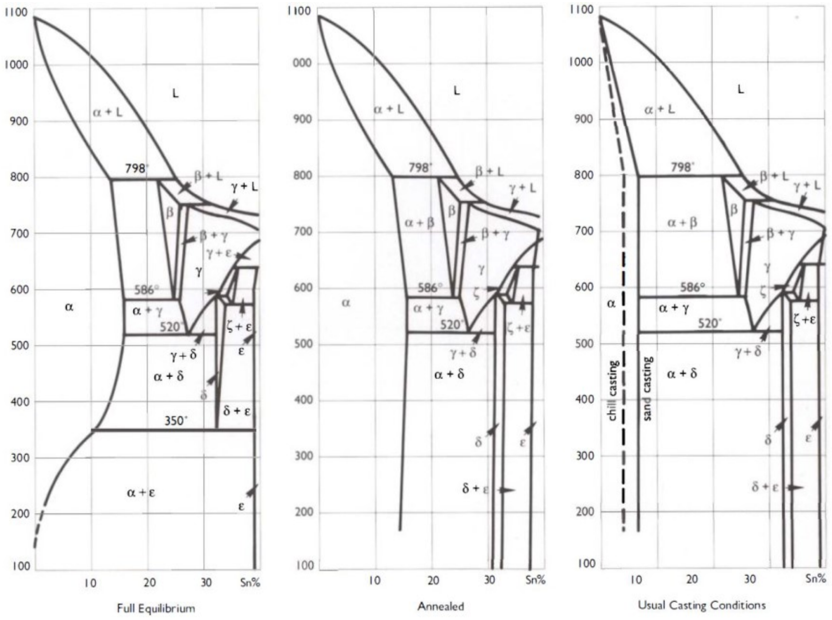


Fig. 1.1 – Part of the copper-tin diagram under different condition (Scott D.A., 1991).

The copper-zinc phase diagram is entirety reported (Fig. 1.2). It can be noted a wide alpha phase region, where copper and zinc are soluble in each other. Most of ancient brasses have compositions that are included in this region of the diagram. At room temperature, the zinc solubility threshold is 28%wt. and its maximum is around 400°C. Beyond 28%wt. of zinc content, phase beta starts to precipitate and the brasses are obviously named alpha-beta.

These types of brasses are common in historic objects and they are characterised by different colour and mechanical properties from alpha brasses. In fact, it is important to note that, since XVI century A.D., brass was produced by the reduction of zinc ore at around 1000°C and the diffusion in metallic copper (cementation process). This technique was then completely abandoned in the middle of XIX century A.D. (Bourgarit D. *et al.*, 2010). Brasses containing zinc below 28 wt.% were very common in ancient time because this amount is the threshold for the cementation process (Craddock P.T., 1985; Pollard M. *et al.*, 1996; Craddock P.T., 2009).

In the past, it is well-known that the mechanical features are affected by the zinc content; in particular, the values of tensile strength progressively decrease with the zinc percentage. Since to ancient times, it is noteworthy that although brasses are essentially copper and zinc alloys, other alloy elements such as lead, iron and arsenic, are contained in the alloy. Both presence and content are responsible of different materials properties (Vilarinho C. *et al.*, 2005); for example, lead is often added to brass in order to improve its machinability, whereas aluminium is employed to promote the castability of the objects.

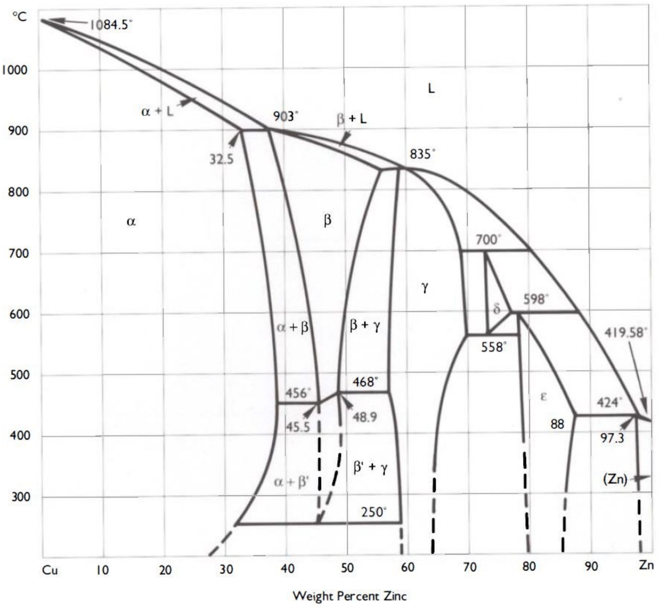


Fig. 1.2 – Copper-zinc phase diagram.

1.1.1 Ancient Persian bronzes: The Achaemenid Empire

The Achaemenid Empire is the earliest and largest of the known ‘World Empires’ (Kuhrt A., 2007). It developed in south Iran, our Persia. In particular, it covered a vast area from Pakistan in the East, to Egypt in the West and from Aral Sea in the North to the Indian Ocean in the South.

Achaemenid term is derived from the eponymous founder of the ruling dynasty Achaemene and it is the name of members which ruled the Empire for more than 200 years. However, the historical information about the first centuries of Persian history (between 1000 and 600 B.C.E.) is inadequately (Curtis J. *et al.*, 2010).

The expansion of the Empire began around 550 B.C.E. with the reign of Cyrus the Great and it was brought to an end by the conquests of Alexander of Macedon and the death of the last Achaemenid Emperor, Darius III (330 B.C.E.).

The initial production of native copper in the Empire began in late 8th millennium B.C.E. and carried on with the smelting of copper ores since the Bronze Age (3200-1400 B.C.E.) and thereafter during the Achaemenid Empire period.

This was a great stylistic time and the metallurgical knowledge of the civilization led to the production of beautiful objects. In particular, as reported by classical Greek descriptions a great variety of metals, such as gold, silver and bronze, were commonly used by Persian aristocracy (Curtis J. *et al.*, 2005). Personal adornments and every types of furniture were made by precious metals and were symbols of oriental luxury.

In particular, the characterisation of a particular Persian bowl, named *phiale*, is reported in one of the papers of this thesis. In Achaemenid culture, bowls formed an important part of the standardized banqueting service since it is well- known that wine-drinking action played a meaningful role in Persian society. In fact, beautiful bowls or cups were clearly perceived as elite status and were indication of elite

drinking behaviours (Dusinberre E.R.M., 2015). In particular, the *phiale* is a bowl used to the libation ritual in which a liquid, such as wine or milk or olive oil, is offered to a god or in memory of ancestors. Most of these metalwares were made by hammering or raising sheet metal, adding decoration in *repoussé* and outlining the details by chasing. These features highlight the deeper knowledge of Achaemenid blacksmiths in metallurgical field.
For these reasons, archaeometallurgical investigations of such gorgeous artefacts can provide further useful information about the technological level reached in mining and metallurgy and can afford historical evidence concerning metalworking trades. In turn, archaeometallurgical studies enabled to throw light on the economy of the Achaemenid Empire, the technological capabilities of its craftsmen as well as their cultural relations (Oudbashi O. *et al.*, 2012).

1.1.2 Brass casting from Benin Kingdom and Kota population (West Africa)

The Kingdom of Benin (Nigeria) was renowned for centuries in Europe as one the major powers in West Africa. Thanks to its geographical location and Portuguese commercial routes, the Empire developed flourishing trade relations with Portugal and achieved its maximum splendour until XIX century A.D. When the British tried to expand their own trade in the XIX century A.D., the Benin people rebelled against the conquerors. For this reason, in 1897 A.D. the British sent an expedition in order to capture the king of Benin (named Oba), destroyed his palace and took away large quantities of Cultural Heritage, including works in wood, ivory and especially brass. A large number of these artefacts, being produced to decorated the pillars of the royal palace, were in high demand by European collectors (Schrenk J., 1994).
For this reason, in the last thirty years, the proliferation of fakes in Benin arts is dramatically increased (Plankensteiner B., 2008) and it is necessary to establish scientific methodologies in order to provide the authentication of the artefacts.

The same problem about intensification of fakes in private collections or in museums is occurred for the Kota artefacts. This peaceful population lived in the eastern part of Gabon (Africa) as long as, in the early of XX century A.D., Christian missionaries arrived in their lands and converted many of them. As a result, many of artefacts associated with their traditional religion were destroyed or buried and the few objects that escaped from this destruction became in high demand by European collectors.
In particular, this community is known for the realisation of metallic reliquary figures, which were set on wooden supports and called *Mbulu-Ngulu* or *Bwéte*. It should be noted that the first samples of these sculptures arrived in France and Germany during the last quarter of the XIX century A.D.
These artefacts are the symbolic representation of a human abstract figure whose head is bigger than the rest of the body. These abstract figures were used to protect and demarcate the bones of family ancestors, which were preserved in containers made of bark (Shakarov A. *et al.*, 2015).
Pablo Picasso was strongly influence by African sculpture between 1906 and 1909. In particular, several sketches of *Mbulu-Ngulu* seem to have inspired his proto-Cubist notions and his idea of the abstraction of the human figure (Karmel P., 2003).
This is another further reason for the increase of *Mbulu-Ngulu* requests and the resulting proliferation of fakes which enrich the art market.

Therefore, it is important to highlight that interdisciplinary investigations must be used with higher frequencies in order to provide a useful help aimed to unmask forgeries and fakes, also for modern and contemporary Cultural Heritage.

1.2 Archaeometry and Archaeometallurgy

So-called Archaeometry is used to describe the discipline concerning the quantitative characterisation of objects produced in the past. It was created through the marriage of physical and historical science in 1958, year of the founding of the homonymous journal (Rehren *et al.*, 2008).
As a matter of fact, the general aim is to understand the problems related to the nature and the production of ancient artefacts with a particular focus on improving preservation and conservation techniques. (Artioli G., 2010).

One of the many other sub-disciplines of archaeometry is archaeometallurgy. It is certainly the earliest manifestations of archeometric research, using science-based approaches to address cultural-historical questions. In particular, archaeometallurgy deals with the investigation of all aspects of the production, use and consumption of metals from around 8000 B.C.E. to the present (Killick D. *et al.*, 2012).
Modern archaeometry and archaeometallurgy are rapidly growing and constantly changing disciplines. Studies of metal objects and the manufacturing methods was dated back to the beginning of XIX century; in particular, the first real quantitative analysis of a Roman coin was carried out by Klaproth M.H. in 1815 (1815). For over a century, many relevant authors were interested to the study of composition and identification of ancient alloys, such as bronze, silver and iron.
In the 1930s and for the rest of the century, systematic analyses were carried out to understand the nature of metals and ores in order to perform provenance determination (Noddack I. *et al.*, 1934; Snoek W. *et al.*,1999; Desaulty A.M. *et al.*, 2008; Cattin F. *et al.*, 2011).

In the last fifty years, a large number of works was dealt with the analyses of corrosion products, named patina, in order to understand their growth and evolution in different environments. Moreover, the relationship between this information and the structure of the alloys (e.g. burial, atmosphere, water) (Fitzgerald K.P., 1998; Krätschmer A., 2002; Fitzgerald K.P., 2006; Ingo G.M., 2006; Piccardo P., 2007; Angelini E., 2007; Bernard M.C., 2009), as well as the eventual aggressive or protective effect on the artefacts were also assessed (Tennent N.H., 1981; Schweizer F., 1994; Robbiola L., 1998). At the same time, a growing number of works was carried out on several protective treatments with the purpose of finding out the most innovative techniques to preserve the artistic objects (Brunoro G. *et al.*, 2003; Muresan L. *et al.*, 2007; Dermaj A. *et al.*, 2007; Marušić K. *et al.*, 2009; Abu-Baker A. *et al.*, 2013).

Archeometallurgy can be summarised by using the cycle working process of metal artefacts, as shown in Fig. 1.3. In particular, the various stages of the working operations from the primary production of metal (that is mining, beneficiation and smelting), through the manufacturing of artefacts to the conservation of objects and their deposition in museums are reported (After Ottaway, 1994; Rehren *et al.*, 2008; Heeb J. *et al.*, 2014).

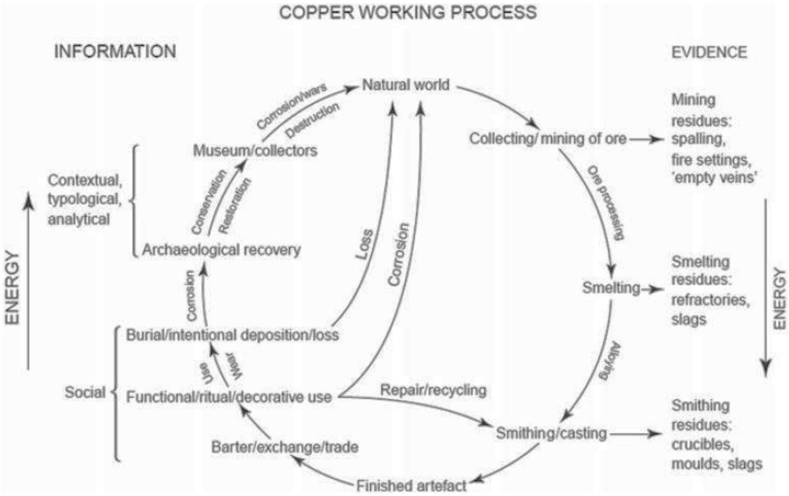


Fig. 1.3 – The copper worked process proposed by (Heeb J. *et al.*, 2014) after Ottaway B., 1994.

1.2.1 Microstructure analyses and patina investigations of copper-based artefacts

Production and working of metal is controlled by some parameters: technical knowledge, the employment of artefacts and cultural traditions.

It is noteworthy that metal objects can be used by humans in the following ways: 1) decorative (jewellery and other accessories), 2) military (weapons and armours) and 3) utilitarian (coinage, tools etc.). It is clear that different exploit may involve specific metal properties, such as hardness, malleability, colour and so on.

A better understanding of the metallurgical knowledge of the societies or the civilisations which produced a specific object is one of the main reasons to analyse metal artefacts. For example, it is very important to understand if a specific metal property is selectively exploited on purpose.

Reconstructing the techniques used to work metals by studying microstructure, physico-chemical properties and the nature of the surface patina is one of the main purposes of archaeometallurgy.

Metal analyses of artefacts are the bedrocks for identifying production technique, geological origin, improvement of civilisations knowledge and any trade of objects.

The fundamental aims of archaeometallurgy are:

∴ Classify objects by materials types in order to identify their original composition and current condition with a particular attention to the interaction which occurs at the interface metal/patina;

∴ Reconstruct metallurgical practice from casting and surface decoration (e.g. gilded);

∴ Compare different objects to identify similarities and differences (e.g. in composition or technique) in order to form groups and extended database;

∴ Find the most suitable conservation method to preserve or in some cases to restore metal objects.

Metallography is certainly an essential component of metallurgical studies in order to obtain information about fabrication technology. It can be also a fundamental supply as regards the authenticity of artefacts (Scott D.A., 2010; Scott D.A. 2013). More specifically, the microstructural components, the corrosion rate and, obviously, the metallurgical practice can be investigated by metallography technique. Several data can be gain but, on the other hand, it is also important to highlight that the removal of a small sample from the analysed objects is necessary in order to observe and examine the microstructure.

In particular, the metallographic examination can provide several microstructure features that can be identified (a few of them are indicated below):

∴ The presence of different phases, any pores or non-metallic inclusions (e.g. in general, many inclusions become elongated along the working direction because of non-recrystallization at the temperatures at which the metals were cast);

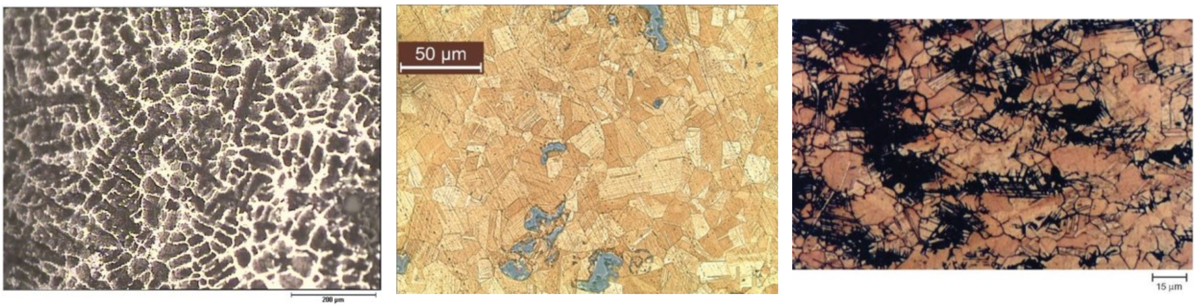
∴ The type of microstructure (dendrites or grains) highlights the employed fabrication technology (by cast or by hammering/annealing treatments, respectively);

∴ The presence of any surface coating;

∴ The presence and the distribution of corrosion products and their interaction with metal base (e.g. cracking, pitting etc.).

It is important to highlight that the microstructure of the alloys is influenced by the condition of crystallisation and by the metallurgical technique used to produce the object.

In particular, it is well-known that the typical as-cast structure is characterised by dendrites (Fig. 1.4a); whereas if this cast structure was then subjected to a full annealing, equi-axed grains are visible in microstructure (Fig. 1.4b). In general, the microstructure of ancient objects realised by alternate hammering and annealing steps is mainly consisted of thermal twin grains and slip lines (Fig. 1.4b and 1.4c), resulting from plastic deformation.



(a) (b) (c)

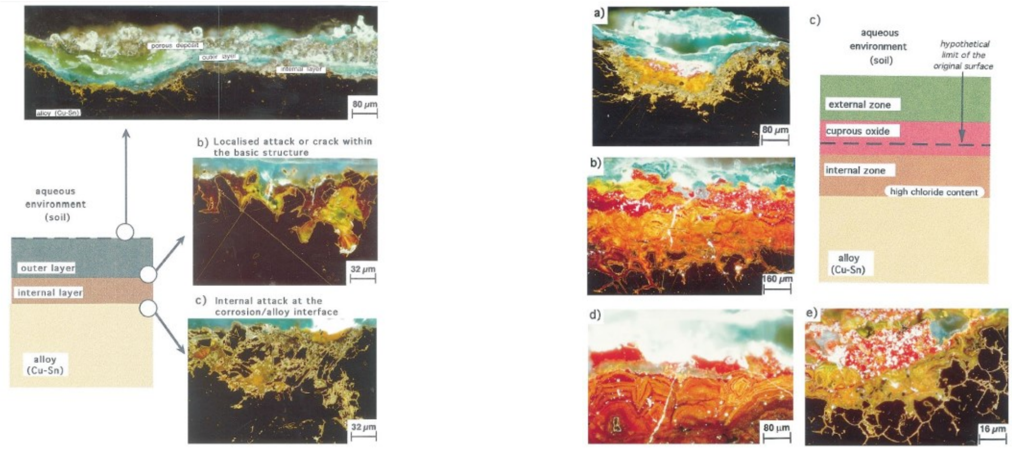
Fig. 1.4 – Different microstructure of ancient copper-based artefacts: (a) dendrites, (b) grains with twinned bands, (c) grains and slip lines, image reported in (ASM Handbook Vol. 9, 2004).

Moreover, information about metallurgical knowledge of the civilisations studied is also obtained by the compositional investigations of the alloys. In particular, X-ray fluorescence spectrometry (XRF) is the less intrusive method because it is possible to perform the analyses directly *in situ*. Another useful method is scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) that can provide fast semi-quantitative analyses (e.g. phase or non-metallic inclusion identification). Instead, specific quantitative analyses of the alloy composition could be carry out by inductively coupled plasma mass spectrometry (ICP-MS).

In addition to the systematic studies of the alloys and their microstructure, it is very important for the scientists to control and stop the deterioration processes of metal artefacts in order to protect and preserve the historic objects (Robbiola L. *et al.,* 1998).
As a matter of fact, the corrosion products are a typical consequence of the natural ageing of the metal object, also known as "weathering", because of the interaction with a particular environment (Piccardo P. *et al.*, 2013).
The patina is therefore the effect of some chemical reactions that are correlated with the alloy composition, the integrity rate of the surface, the type of the environment, its severity and the time of permanence of the artefact in its.
In fact, the grain boundaries are the most unstable zones of the alloy structure because of the disorganisation of the atoms and the corrosion compounds could go through the microstructure easily.
It is clear that the chemical characteristics and the structure of these surface layers are very different depending on the environment typology. In particular, several authors were studied the artistic copper-based artefacts exposed for a long periods of time in different environments, such as soil (Tylecote R.F., 1979; Robbiola L. *et al.*, 1998; Sandu I. *et al.*, 2008; He L. *et al.*, 2011), atmosphere (Graedel T.E. *et al.*, 1987a; Graedel T.E. *et al.*, 1987b; Hayez V. *et al.*, 2004; Fitzgerald K.P. *et al.*, 2006; Chiavari C. *et al.*, 2007), water or sea water (Pearson C., 1987; Hannington M.D., 1993; Angelini E. *et al.*, 2013). A briefly *excursus* through the corrosion products developed in specific environments are reported below.

1.2.2 Burial environment

Burial is a common event in the life of most copper-based artefacts and the corrosion depends on multiple factors that can be classified as endogenous (nature of alloy, method of manufacture, shape and dimension) and exogenous (soil composition, porosity, humidity, conductivity, depth of burial) (Quaranta M. *et al.*, 2008). These factors invariably lead to the formation of layered surface patinas which, according to many studies, may be generally characterised by essentially two types of structures, often present on the same artefact (Wadsak M., *et al.*, 2000; Robbiola L. *et al.*, 2006). As shown in Fig. 1.5, in Type I patinas, the original shape of the object and its original surface can be still identified, while in Type II patinas the original surface cannot be appreciated anymore, due to either macroscopic deposits of pits and crevices or losses due to localised or intense generalised metal dissolution (Robbiola L. *et al.*, 2006). In particular, Type I structure is characterised by two layers and it is mainly due to oxidation together with decuprification process. On the other hand, Type II structure is characterised by three layers and it is caused by an aggressive attack. The presence of chloride at the internal layer/alloy interface is representative of this type of structure.
In general, the characteristics of corrosion layers are strictly dependent on the interaction between the soil mineral and the alloy. A distinctive feature of most copper-based artefacts is the formation of a cuprite crust (Cu_2O) that is adjacent to the metal and overlaid with malachite ($Cu_2(CO_3)(OH)_2$). As regard the presence of chloride or any other compound layers, it is due to the specific characteristic of the burial environment or to the possible flow of groundwater (Scott D.A., 2002).



(a) (b)

Fig. 1.5 – Types of corrosion structures: (a) Type I ("even" surface) and (b) Type II ("coarse" surface) (Robbiola L. *et al.*, 2006).

1.2.3 Ooutdoor and indoor environment

As regard the copper-based artefacts exposed in atmosphere environment, it is necessary to make a distinction between outdoor and indoor exposure. In particular, rainfall and air pollutants in urban environment are the main problems for outdoor objects; conversely, a museum is a typical indoor environment and in general it can be considered safe for the heritage. Instead, the large presence of visitors involves the massive concentration of organic pollutants that can be very dangerous for the artefacts (Bernard M.C. *et al.*, 2009).

The outdoor corrosion events are much less complex than burial circumstance and it is often possible to assess the corrosion rate of the copper alloys. The corrosion products reveal several compounds which are depending on the condition of atmospheric exposure and also on the surface orientation of the artefact (Robbiola L. *et al.*, 1993). Moreover, the water can be the result from of precipitation or condensation at the object surface and it could play a crucial role in the corrosion process.

During the past two centuries, the chemistry of air pollutants' precipitation is dramatically changed because of industrial activities (Strandberg H., 1998; Scott D.A., 2002). Before this period, thin layer of cuprite (Cu_2O) with small quantities of sulphate and carbonate slowly overlaid the exposed surface. Nowadays, the sulphur-containing contaminants are increased in the atmosphere and alterations are observed in several works (Strandberg H., 1996; Strandberg H., 1998); in particular, the typical colouring of the patinas is generally changed in different shades of green or brown and black.

In general, the development of corrosion patina on exposed objects is characterised by the formation of two layers. Cuprite (Cu_2O) is the initial corrosion product and it is in direct contact with the alloy, whereas above green compounds typically consist of sulphur-containing contaminants, such as brochantite ($Cu_4(OH)_6SO_4$) and antlerite ($Cu_3(OH)_4SO_4$), or chlorine-containing species in strictly correlation with the local atmospheric compositions (Robbiola L. *et al.*, 1993; Fitzgerald K.P. *et al.*, 2006).

An interesting schematic representation of the outdoor formation patina was proposed by Robbiola L. *et al.* (1993), which explained by few steps the interaction between atmospheric compounds, precipitation and metal objects. It is noteworthy that in the representation of Fig. 1.6, a distinction between surfaces directly washed by rainwater and surfaces which are not exposed to rainfalls is reported. This distinction highlights that the surface washed by rainwater is exposed to leaching of soluble copper compounds (Graedel T.E., 1987b; Robbiola L. *et al.*, 1993).

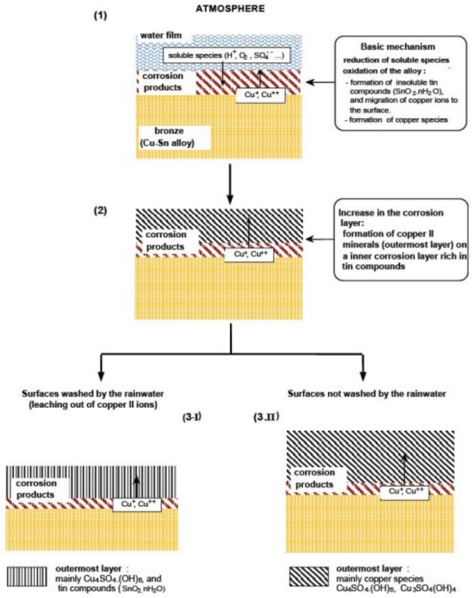


Fig. 1.6 – Schematic representation of the outdoor corrosion processes (Robbiola L. *et al.*, 1993).

The development of alteration products on metallic surface objects could be caused by the intrinsic characteristic of indoor environment and probably due to pollutants, relative humidity and temperature (Scott D.A. 2002).

The principal problems associated with the conservation are: 1) the particulate matter could be deposited on the surface artefacts and 2) the formation of localised higher humidity that reacts with the dusts. These situations, coupled with the presence of sulphate, chloride or any other ions, may induce an accelerate corrosion process.

Moreover, display cases, cabinet and furnishing in museums may significantly increase the levels of organic contaminants. In addition to these compounds, many other pollutants are often present in indoor environment.

Standard ISO 11844:2008 (Corrosion of metals and alloys – Classification of low corrosivity of indoor atmosphere) specifies the most important contaminants, such as SO_2, NO_2, O_3, organic acids and so on, in indoor environment.

As a result of several typologies of pollutants, the effect of corrosion process in this type of environment is more difficult to predict compared to outdoor environment (Tidblad J., 2013).

For these reasons, a constant monitoring techniques is essential to indoor air research. Several works were performed on the assessment of the particulate matter deposition and the corrosion rate in indoor environments (Brimblecombe P., 1990; Lobnig R.E. *et al.*, 1993; Sjögren L. *et al.*, 2007), even if the main objective was to establish parameters for every contaminants and their threshold in order to help conservators in restoration work (Watt J. *et al.*, 2009).

1.2.4 Marine environment

The degradation of copper-based artefacts in seawater is caused by a complex and intense chemical and biological activity. The most common components of seawater are water itself, chloride, sodium and many other ions in addition to carbonates and silicates. Moreover, marine life, algae and so on, can lead to encrust with concretions the surface objects. Because of this complex environment, it is possible to observe different corrosion forms: 1) generalised corrosion of the surface, 2) galvanic corrosion favoured by high conductivity of seawater, 3) pitting or crevice corrosion, 4) corrosion induced by seawater flow, 5) stress corrosion, 6) erosion-corrosion, 7) fatigue corrosion and 8) corrosion caused by organisms (Scott D.A., 2002; Memet J.B., 2007).

Generalised concretions could appear on copper-based artefacts discovered in seawater, which could be linked to the interaction with the marine soil. To sum, the corrosion products on copper-based artefacts are mainly consisted of cuprous chloride and cupric hydroxyl chlorides, which occur both in the surface corrosion products and deep down in crevices inside the residual metal. Moreover, because of sulphide ions in polluted marine environments, such as estuaries, some copper sulphides from covellite (CuS) to chalcocite (Cu_2S) are generally produced (Pearson C., 1987).

1.3 Dating and Authentication: the problem of fakes and forgeries

Authenticity is a relative concept and its definition could be different for archaeologists, scientists or art historians. In fact, for someone the objects must be materially original, but for many other groups of academics, the authenticity is an idea of links between the original parts and the appearance that must be preserved. Thus many artefacts contain few original parts; however, they are considered original because those few original pieces could be rebuilt to original specifications (Craddock P.T, 2009).

Authentication of artefacts still remains an important scientific challenge that requires both methodology and criteria and it could be strictly linked with the dating studies, because many scientific methodologies are enable to dating the artefacts and to provide if they are fakes.

The authentication is probably the most complex survey because the forgery or imitation of art objects dates back more than three thousand years. It occurred in all ancient civilizations and continues until the present (Zacharias N. *et al.*, 2011).

In fact, forged artefacts can be classified as (Oddy W.A., 2004):

∴ Copies that are the same of the original objects;

∴ Copies that are similar to the original objects;

∴ Original objects which have been altered to make them more valuable;

∴ Forgeries made in the past.

For this reason, to unmask a fake interdisciplinary investigations are necessary, which take into account archeometry, art, history and many other disciplines.
In particular, the scientific detention of forgeries can be occurred by the investigation of: 1) the materials of manufacture, 2) the alteration products (corrosion compounds or weathering layers), 3) the structure and the production technique and 4) the age of the object.
It is important to realise that any artistic objects cannot be authenticated by only one of the scientific investigation mentioned above, for example only by the analysis of the material compositions or the corrosion products layers; but it is essential that every aspect relating to the authentication of the object is taken into account.

1.3.1 Microstructural and chemical analyses as dating indicators

The scientific approach to dating objects is based on all constituents and impurities of the metals, which could be undergone to a gradual alteration or weathering with the time. Alterations such as changes in chemical composition, radioactive decay, leaching and so on, could give information about the ageing of the objects. It is important to note that, in general, fake materials are not aged.
Moreover, microstructural and chemical analyses together with absolute dating techniques of the alloys could give a useful help in order to provide the authenticity of the artefacts.
The real problem is that direct dating of metal objects is not possible and it is necessary to find a different way in order to obtain information about the production period.
The examination of the internal structure of the alloys can give important information about the production method and it is possible to identify a fake if the manufacture techniques are not comparable with those used in the assigned manufacturing period of the object (Pernicka E. *et al.*, 2008).
In particular, this investigation is based on the characterisation of the materials (composition, manufacturing, microstructure and alteration or patinas) in order to verify the original features of the objects.

Observing the microstructure of the samples, it is possible to knowledge the methods used to produce the artefacts. For example, the difference between ancient and modern metalworking practice concerns the introduction of rolling sheet in post medieval Europe and therefore the microstructure is completely changed. After this revolution, the metal objects start to be realised by as-cast processes followed by multiple cycles of hammering and annealing in order to obtain a specific form.
Moreover, the elements occurring into the metals could be indicator of the production period, the provenance or cultural links. In fact, metal objects from some specific places or periods can be characterised by distinctive compositions, in particular some element patterns are often indicator for the fabrication in specific periods or centuries (Craddock P.T, 2009; Pernicka E. *et al.*, 2009).
As already mentioned, the zinc content in brasses was considered by several authors as a criterion for identifying modern fakes (Pollard M. *et al.*, 1996; Craddock P.T., 2009). Brass was produced by the reduction of zinc ore at around 1000°C and the diffusion in metallic copper (cementation process), from the antiquity to XVI century A.D and it was completely abandoned in the middle of XIX century A.D. (Bourgarit D *et al.*, 2010). With this process it is possible to produce brass with an upper limit of 28 wt.%; therefore, an exceed of zinc content could be an indicator of a modern artefact.

Main role is also played by the trace elements because they come into the metal as natural impurities, such as iron, nickel, bismuth and so on. They are also intentionally added in order to improve the features of the alloys, like aluminium, phosphorous and silicon. In particular, some intentional added elements are in general not part of modern alloys or they are used in totally different amounts.
Aluminium is the typical example: this element was known as a metal since 1827 and became available in the industrial production at the end of XIX century, after some technical innovations (Tylecote R.F., 2002; Pernicka E. *et al.*, 2009). In particular, it is added in small concentrations to the alloys in order to promote castability, to reduce zinc evaporation and to improve the mechanical resistance of the metal. Thus, the detection of this element could be another sign of a modern fake object (Vilarinho C. *et al.*, 2003).

An additional problem, equally important, is referred to any intentional alterations of the metal surface in order to make the object more ancient.
The investigation of the corrosion products could not provide a specific dating of the artefacts, but could give important information about the ongoing processes between environment and metal surface. In fact, the composition and the structure of the layers could convey evidence regarding to authenticity or intentional alteration of the surface (Pernicka E. *et al.*, 2009). As described in *Sections 1.2.2, 1.2.3, 1.2.4*, specific corrosion compounds were produced in particular environments and they were developed by long lasting processes. Thus the reproduction of this genuine corroded layer on the metal surface of a fake object could be very difficult. However, it is important to note that, sometimes, similar corrosion compound could be achieved under laboratory conditions.

1.3.2 Absolute dating methods

Some scientific techniques, named absolute dating methods, could be used in order to figure out if a metal object is original or not. The concept at the base of these methods is the measurement of a physical quantity that is proportional to the time elapsed from a specific starting point in the history of the material (Artioli G., 2010). In particular, these absolute dating techniques for metal objects are: the thermoluminescence analysis (TL) and the lead-210 analysis (^{210}Pb).

The term "luminescence dating" includes several techniques, which mainly refer to the thermoluminescence (stimulated by heat) phenomena and optically stimulated luminescence (OSL – induced by sunlight and now much used for dating archaeological and geological sediments).
All materials contain some parts per millions of radioactive isotopes of elements, such as thorium and uranium. Because of their natural decay, the production of energetic rays (α, β and γ) together with the interaction with an atom of the lattice can cause the removal of an electron. In general, this electron is neutralised by an oppositely charged ion, but in some materials, such as quartz or feldspars (typical compound of ceramics), defects of the lattice could entrap the electron at ambient temperature. Their number steadily increases during time and the entrapped electrons are released from the traps by a heating process, hence the term, thermoluminescence (heat–light). The amount of light emitted is proportional to the number of electrons released, which in turn is proportional to the time that was elapsed since the last time the material was heated (usually when the artefacts were produced) (Craddock P.T., 2009).

In the beginning, thermoluminescence was applied for the analysis of ancient pottery, but other materials are suitable for this dating, such as the cores from lost wax metal castings. In general, the core is constituted of a mixture of clay and charcoal eventually trapped inside the castings and from which it is possible to obtain thermoluminescence dates (Willet F. *et al.*, 1976).
Because the unsullied core of the artefacts is generally removed from the artefact, the authentication and dating could require another type of investigations.

Another absolute dating method, named lead isotopes analysis, is used in archaeological and geological fields in order to provide answers to a number of questions since the late 60s. In particular, lead isotopes may be used as fingerprint of the ore deposits, but could also be applied to ascertain if a metal object is ancient or not.
The analytical technique proposed by Keisch in 1968 (Keisch B., 1968a, Keisch B., 1968b) is based on natural radioactivity of lead isotopes, in particular of ^{210}Pb. The author noted that it is possible to estimate the age of metal objects by determining the concentrations of ^{210}Pb and ^{226}Ra. Keisch B. highlighted that the radioactive equilibrium between these isotopes can be disrupted during the extraction of lead from its ore and a stable situation is restored by the decay of ^{210}Pb (22,3 years). For this reason, if an amount of ^{210}Pb is detected in studied samples, it is likely that the object is produced in the last 100 years; conversely, the absence of ^{210}Pb could indicate that the artefacts is older than a century (Riederer J., 2011).
Whilst some researches were carried out in past on using this technique, no recent studies are established probably because of the difficult and expensive data acquisition method.
For this reason, in one of the papers reported in this thesis, an evaluation of a non-conventionally technique to dating the artefacts using the measurement of some lead isotopes ratio, in particular ^{210}Pb/^{204}Pb, is proposed. In this case, the abundances of lead isotopes were assessed by thermal ionisation mass spectrometry (TIMS) and the results were reported in the form of ratios between different lead isotopes and ^{204}Pb, the only one that is a non-radiogenic isotope.
In fact, the three lead isotopes (^{206}Pb, ^{207}Pb, ^{208}Pb) are formed by the well-known natural decay of uranium and thorium; conversely, the ^{204}Pb may be attributed entirely to common lead and it can be used like an index of lead impurity in the sample (Nier, A. O., 1939; Nier, A. O. *et al.*, 1941).
The assessment of these ratios is widely used to dating minerals, such as meteorites and terrestrial rocks (Patterson C., 1956). However, the intermediate members of the decay (e.g. ^{210}Pb and ^{214}Pb) are usually ignored for these studies because of their relatively short-lived (Dickin A. P., 2005).
Thus, the measurement of ^{210}Pb/^{204}Pb ratio is proposed to dating artefacts. Subsequently the obtained results are compared to extensive quantitative alloy analyses databases, which are presented in literature in order to ascertain if this different dating method could provide usable results.
To conclude, it is therefore deemed necessary to combine all the results obtained by different scientific methods in order to provide the highest number of information about the studied artefacts and their authenticity.

1.4 Effectiveness of protective silane treatment for the conservation of copper-based artefacts

The corrosion processes are the main form of degradation that affects the metallic works of art (Balbo *et al.* 2012). The protection against these processes is the most important action in order to preserve the surface objects and to pass on the preserved artefacts to future generations.

The typical approach to the conservation of bronzes during XIX or first half of XX century was the chemical or electrolytical removal of the patina with sometimes the loss of original surface and associated material (Scott D.A., 2002). Moreover, these severe treatments could cause significant change in appearance of colour surface of the artefacts (Jaeschke H. *et al.*, 1988).

An effective solution for the protection could be the use of corrosion inhibitors as they can reduce several conservation interventions.

In general, a protective coating can be applied on the surface metal in order to prevent the growth of corrosion products and can acts as an insulation from the external environment can be produced by this layer. It is also important that the corrosion treatments should be reversible or should be easily removable and should not modify the material and its surface appearance (Cano E. *et al.*, 2010).

ISO 8044:2015 defines corrosion inhibitors as “chemical substances that decrease the corrosion rate when present in the corrosion system at suitable concentration, without significantly changing the concentration of any other corrosion agent”

Over the last decades, the most used corrosion inhibitor for copper-based alloys was BTA (1,2,3-benzotriazole). A barrier of polymeric complex with copper is formed by this compound, which protects the metal surface in different environments (Dugdale I. *et al.*, 1963). In particular, BTA is able to anchor on the thin film of copper oxide and it is known to be chemically adsorbed on metal in order to retard the reduction of the oxygen (Scott D.A., 2002).

The first application of BTA for conservation of cultural heritage was proposed by H.B. Madsen (H.B. Madsen, 1967) as a treatment for bronze disease in 1967 and became a very popular treatment in the following decades.

However, Brunoro *et al.* (2003) demonstrated that BTA effectiveness is lower in case of bronze than pure copper. Moreover, suspicions about its safety raised because of the toxic effects on flora and fauna (Pillard D.A. *et al.*, 2001; Kim J.W. *et al.*, 2011) and the demand of “safe” inhibitors is increased during the last thirty years (Cano E. *et al.*, 2013).

In particular, some thiadiazole and imidazole derivatives, such as MAT (2-mercapto-5-amino-1,3,4-thiadiazole) and TMI (4-methyl-1-(ρ-tolyl)-imidazole), are considered good substitution of BTA (Muresan L. *et al.*, 2007).

Promising and environmentally-friendly compounds seem to be alkoxysilanes and similar silicon groups. In particular, 3-mercapto-propyl-trimetoxy-silane (PropS-SH) shown interesting protective properties and it is subjected of an intensive research (Zucchi F. *et al.*, 2007; Li Y.S. *et al.*, 2009; Chiavari C. *et al.*, 2013; Peng S. *et al.*, 2014).

The silane coating is usually tested after alkaline degreasing of metal surface on which is applied the compound in the hydrolysed form by immersion (Zhu D. *et al.*, 2004). The compound adsorption is promoted by the specific bonds formation between silane and the cuprous oxide on the metal surface (Zucchi F. *et al.*, 2007; Balbo *et al.*, 2012). This highlights that the effectiveness of PropS-SH is affected by the alloy composition and the patina nature.

Nevertheless, it is noted that PropS-SH is characterised by a much higher inhibiting effectiveness than that other compounds, such as amino derivatives (Zucchi F. *et al.*, 2003). Moreover, several tests are performed by Balbo *et al.* (Balbo A. *et al.*, 2012) on different silane compounds and it is suggested that only PropS-SH is capable to hinder bronze corrosion in chloride solutions.

In order to get a deeper knowledge of the corrosion rate and the effectiveness of PropS-SH towards copper alloys, weathering tests are usually performed in several papers. In general, the artificial exposure is the preferred choice as a method for ageing the metal surface because of the possibility to simulate different outdoor environments, such as the stagnant rain (wet&dry test) or the runoff exposures (dropping test) (Bernardi E. *et al.*, 2009; Chiavari C. *et al.*, 2010).

These tests are enabled to assess the coating features and its performances on metal surfaces. In particular, it is noteworthy that the patina and the protective compounds on the metal surface are markedly influenced by the exposure geometry. For this reason, different corrosion behaviour may occur in sheltered or unsheltered areas with respect to the rainfall because of the presence or not of alterations and alloying element leaching (Chiavari C. *et al.*, 2013).

Moreover, the simulated outdoor condition can provide that PropS-SH is a good inhibiting efficiencies except for runoff conditions in which the silane coating adhesion is weakened (Chiavari C. *et al.,* 2015). Another further weakness of PropS-SH was proposed by Chiavari C. *et al.* (2013); in particular, the authors highlighted that PropS-SH is not able to block the metal release, in particular of zinc and mainly of lead.

In addition to bare bronzes and brasses, gilded bronzes are also subjected of an intensive research because they are often affected by corrosion degradation due to the presence of pores and defects on gilded layer. Because of this unstable system, it is very important to find better restoration and conservation solutions (Mazza B. *et al.,* 1975; Alunno-Rossetti V., *et al.,* 1976; Masi G. *et al.,* 2016).

In recent time, organosilane coatings attracted research attention for their effectiveness on gilded bronzes, which are widely used in historical monuments and in architectural elements.

In particular, PropS-SH applied on gilded layer is able to limit the corrosion degradation, but as in case of bronzes, the silane is not able to block the lead release (Chiavari C. *et al.,* 2015).

Even though, it is important to note that natural exposures are also very important to assess the coating characteristics because it is the only way to take into account all the possible environmental conditions (Chiavari C. *et al.*, 2015).

However, the coating resistance to external stresses, such as temperature, UV radiation or wet/dry cycles (Bierwagen G. *et al.*, 2003; Chiavari C. *et al.*, 2015) together with the investigation of silane compounds behaviour on pre-patinated surface (Chiavari C. *et al.*, 2013) are considered in few works. In particular, Gupta G. *et al.* (2012) reported that the exposure of organic coatings to some particular conditions, like UV radiation, high temperature and moisture could produce chemical structural changes and thermal degradation.

Moreover, UV radiation is responsible of the impairment of silane coating performances but it is also important to highlight that an improvement of the PropS-SH stability is noted by the addition of nanoparticles, such as TiO_2, in order to increase the protectiveness against corrosion (Chiavari C. *et al.*, 2015).

All these results reported briefly in this paragraph suggest that PropS-SH is a very promising compound for the conservation of outdoor Cultural Heritage.

However, it is also important to collect much more data and information in order to assess the influence of external stresses affecting the impairment of coating and to improve its performances.

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Chapter 2

Main Contributions and Impact of the Research

2.1 Overview of the Articles

Article A

Article A presents an investigation of a bronze bowl stylistically consistent with the Achaemenid art (550-330 B.C.E.) in order to determine the cause of the artwork local fragmentation.

Metallographic observations together with corrosion products characterisations were taken into account in order to obtain information about the cause responsible for the damage occurred.

The metallographic analysis showed that the bowl was obtained from a monophasic copper – 11% tin alloy containing iron, sulphur and arsenic traces. The chemical composition of the alloy was determined by scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS). Remarkable shrinkage cavities were visible in the microstructure together with copper-iron sulphide inclusions, residual from incomplete ore smelting. The presence of an inhomogeneous microstructure with both thermal twin bands and slip lines was due to multiple hammering steps followed by partial annealing treatments and consistent with the manufacturing process employed by smiths during Achaemenid Empire.

The corrosion products were characterised by energy dispersive X-ray fluorescence spectrometry (EDXRF), Raman spectroscopy and electron microscopy (SEM+EDS).

A complex corrosion products stratification was detected on both the internal and the external side of the bowl. In particular, the internal patina was characterised by layers of copper oxide and tin oxide covered by copper hydroxycarbonates and soil components. The layer in contact with the metal consists in an apparently continuous tenorite layer intermixed with cassiterite. For kinetic reasons, this oxide is quite rarely present in comparison to cuprite. Its presence was probably connected to a heating treatment before or during burial or to an intentional patination process, applied for aesthetical reasons.

The external patina was less compact and banded than the internal one. The layer in contact with the bronze contained cuprite and it covered a severe intergranular attack that is reputed the cause of the artefact intrinsic brittleness.

On the bowl a very limited chloride contamination was observed and chlorides were never detected in proximity to the metal. These finding and the morphological/compositional characteristics of the patinas permits to classify the internal one as a Type I structure, while the external one as a borderline between a "noble" patina and a disfiguring one.

Article B

Article B deals with the chemical and microstructural characterisation of a reliquary figure stylistically consisted with the art of Kota population, which lived in the eastern of Gabon (Africa), in order to obtain information about the manufacturing technique and to assess the production period by identifying the alloys' chemical composition and microstructure. The artefact is characterised by a carved piece of wood covered on one side with metal sheets, which are fixed onto the support with small metallic nails. The sculpture was subjected to preliminary observation by stereomicroscopy; subsequently, optical microscopy (OM) and scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) analyses were carried out on a fragment and on surface compounds. Lastly, AMS radiocarbon dating of the wooden support allowed further information about the production period to be obtained.

The results showed that the microstructure of the alloy was characterised by the presence of both non-homogeneous grain size and thermal twin bands, which suggested that the artefact was obtained by casting and then subjected to alternate hammering and annealing steps.

SEM/EDS analysis highlighted that the sculpture was produced by a copper-zinc alloy without the addition of alloying elements, i.e. lead. Moreover, no impurities (i.e. arsenic, iron and antimony), which are very common in the ancient alloys, were detected. It is also noteworthy that comparable amounts of copper and zinc could also be found in modern brasses such as the commercial "Yellow Brass" (65 wt.% of copper and 35 wt.% of zinc). Non-metallic inclusions made up of sulphur and selenium was also detected by SEM/EDS; in particular, one reference in literature reported that some South African metallic artefacts were characterised by copper-iron sulphide inclusions containing selenium, residual from incomplete ore reduction.

As regards the greenish and whitish alteration products, which were mainly collected near the nails and in proximity to the overlaid sheets, they were founded to consist of copper carbonate and zinc oxychloride compounds. Moreover, high concentrations of chloride and lead were detected. In particular, since the latter element was totally absent in the alloy it is possible to suppose the patina was not produced by natural corrosive processes.

Finally, the AMS radiocarbon technique allowed to certainly dating the wooden support after 1950 A.D. It is well-known that the demand for these artefacts from Western collectors is grown enormously in recent years, causing the proliferation of fakes and starting from the first decade of the XX century; on the other hand, the practice of recasting damaged copper and brass to recover the precious metal is very common. The obtained results suggest the analysed sculpture was realised by this recent method

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Article C

Article C presents an investigation of two metal plaques belonging to a private collection, stylistically consistent with the Royal art of Benin (Nigeria) in order to characterise the alloys and to evaluate the production period by identifying the alloys' chemical composition and microstructure.

Alloys and patinas were characterised by optical microscopy (OM), scanning electron microscopy (SEM) equipped with an energy dispersive microprobe, X-Ray diffraction spectrometry (XRD), inductively coupled plasma mass spectrometry (ICP-MS) techniques. Lastly, thermal ionisation mass spectrometry (TIMS) was used to assess the abundances of lead isotopes and to attempt a dating by the measurement of ^{210}Pb.

The obtained results highlighted that the compositions of the two plaques are almost the same. They were mainly consisted of a slightly leaded brass alloys with low concentration of tin, nickel iron and manganese. It is in accordance with the composition of the majority of the "Benin bronzes" characterised by a ternary Cu–Zn–Sn alloy together with lead. However, the presence of relatively high concentration of aluminium, cadmium and antimony should be regarded with suspicion about the authentication of the plaques. For example, cadmium generally comes into brasses because of modern technologies of zinc production. In according to literature, Benin brasses from the XIX century contained a cadmium percentage above 0.002 wt.%. The two investigated plaques were characterised by an amount of this element of 0.002 wt.% and 0.004 wt.%, respectively.

The microstructures of both artefacts were constituted of cored alpha solid solution, typical of as-cast brasses and also characterised by the presence of recrystallized non-homogeneous twinned grains in the areas corresponding to surface decoration. This was due to multiple hammering steps followed by partial annealing treatments.

The corrosion products were almost the same on both plaques and the patinas mainly consisted of copper and zinc oxides together with a non-continuous layer of sulphur-containing contaminants and chloride-containing compounds probably due to the interaction with outdoor environment. Nevertheless, the presence of a low corrosion rate and the absence of artificial patination, which raised suspicion in their self, are not enough to state if the original patinas were removed or if the artefacts were preserved.

In the present work, thermal ionisation mass spectrometry (TIMS) was used to assess the lead isotopic abundance contained in the two plaques and to attempt a dating of metallic artefacts by a different method to calculate the amount of ^{210}Pb. The measurement was reported in form of ratio between ^{210}Pb and ^{204}Pb, the only one that is a non-radiogenic isotope and it could be used like an index of total lead amount in the sample. Moreover, the obtained results were compared to those collected by quantitative alloy analyses (SEM/EDS and ICP-MS). Because of ^{210}Pb relatively short-lived (around 22 years), the detection of an amount of this isotope could indicated that the artefact is produced in the last 100 years; conversely, the absence of ^{210}Pb could suggested that the artefacts were older than a century. The collected data could be indicative that the investigated plaques were probably produced shortly before or after 1900 A.D.

Article D

The aim of this paper is to investigate the gilded bronze corrosion behaviour during both wet & dry and dropping exposure to concentrated acid rain (simulating conditions of stagnant rain or direct runoff, respectively).

The morphology and the composition of surface samples were characterised before and after corrosion tests by Scanning Electron Microscopy equipped with Energy Dispersive Spectroscopy (SEM ZEISS MA 15 with Oxford INCA X-Act). In particular, surface sections of the samples were produced by FIB-FEG/SEM (TFEG-SEM FEI Dual Beam Strata 235M System, with ion beam Ga^+) to gather information about the corrosion products at the metal/gold interface.

The corrosion process was monitored by a "contact probe" coupled with EIS technique and the measurements were carried out using a Potentiostat/FRA/Galvanostat (PAR 2273).
The studied materials were typical historical sculpture alloy (Cu, Sn, Zn, Pb) covered or not by a gilding layer produced by the typical Renaissance method. The bronze specimens showed a dendritic microstructure of cored alpha solid solution, typical of as-cast bronzes with Pb globules and Sn- and Sb-rich precipitates in the interdendritic spaces. On the other hand, the gilded bronze showed a complex surface morphology, characterised by uniform compact zones which were close to other regions with a globular morphology. This is probably connected to mercury evaporation and it due to the inefficient mechanical burnishing treatment.
An silane-based compound, 3-mercapto-propyl-tri-methoxy-silane (PropS-SH) was used as a protective treatment on bronze and gilded bronze samples. The samples were then subjected to accelerate ageing in order to assess the corrosion behaviour of the metal and the golden layer.
Localised corrosion products at gilded defects were observed after short exposure times and the damage extent was correlated to the exposure conditions. In particular, a limited number of craters were produced by W&D exposure, instead the dropping condition resulted more aggressive, as it caused several large pits filled by corrosion products SEM/EDS and micro-Raman analyses evidenced the formation of alternating layer of Cu and Sn corrosion products (Cu_2O/SnO_2).
Dropping tests (30 days of TOW) were carried out on gilded bronzes in the absence and in the presence of PropS-SH coating and the corrosion products were totally absent on the gilded bronze covered by the silane film. The sample without the protective layers was characterised by the presence of corrosion products at the bronze/gold interface because of the aggressive environment.
Finally, a special contact probe for non-destructive *in situ* electrochemical measurements was tested in order to monitor the corrosion processes. The results suggested that the performances of R_p and E_{oc} values measured by the three electrode cell are similar to those collected by the contact probe. However, the probe in contact with artificial rain tended to underestimate the corrosion rate when the surface samples were covered by a layer of instable corrosion products. On the other hand, if the environment was characterised by a low corrosion rate (e.g. presence of the protective film), correct measurements of the corrosion process were collected by using the contact probe.

2.2 Scientific Implications

The main conclusions of the research projects were discussed in detail above. However, some of the results reported in this thesis will also have some important scientific implications.

- ∴ The usefulness of an interdisciplinary approach to clarify some general aspects about the manufacturing process and the state of conservation of metal artefacts is highlighted. Most scientific disciplines can contribute to the knowledge of the story of an artistic object. The issue is very important because any lost information in archaeometry is often lost forever. For this reason, all scientists could be aware of the fundamental results that an interdisciplinary study could lead, such as information about the state of conservation or history of the artefact (e.g. manufacturing method, environment of deposition), hypothesis of authentication and so on.

- ∴ Dating metals artefacts still remains an important scientific challenge. Nowadays, the metallic artefacts are generally dating by artistic and stylistic investigations and these could lead to an uncertain authentication assumption. Although a direct metal dating is not possible, employing techniques such as thermoluminesce (TL) and chemical analyses of main and trace alloy elements could enable to obtain information about the production period. In this manuscript, a non-conventionally technique to dating contemporary metallic artworks is evaluated in order to convey a simple and fast dating procedure which could be a usable tool in the authentication field of contemporary Cultural Heritage. In particular, the well-known lead isotopes technique which allows the measurements of mineral age, such as meteorites and terrestrial rocks, is considered and a different method to calculate the amount of ^{210}Pb is evaluated.

∴ The importance of non-destructive *in situ* electrochemical measurements is highlighted. The assessment of the corrosion processes can be monitored directly and for long period by this type of measurements, allowing a deeper knowledge of the effects of the climate change on the conservation of the artefacts surface. This capability is very appreciable to the field of Cultural Heritage, allowing to evaluate in real time the possible changes or damage of metal surface and to choose the better restoration procedure.

∴ The selection of corrosion inhibitors and coatings with high protective efficiency and low environmental impact is reputed increasingly essential. For these reasons, the research of alternative surface treatments for the protection of metal artefacts in different outdoor environments, such as urban, industrial or marine atmospheres is considered very important in the field of conservation of Cultural Heritage.

Part 2

Article I

On the degradation factors of an archaeological bronze bowl belonging to a private collection

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Abstract

A bronze bowl belonging to a private collection, stylistically consistent with the Achaemenid art was investigated to determine the cause of the artwork local fragmentation.
The corrosion products were characterised by energy dispersive X-ray fluorescence spectrometry (EDXRF), Raman spectroscopy and scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS). The last technique was also used to determine the chemical composition of the alloy.
The metallographic analysis showed that the bowl was obtained from a monophasic bronze alloy, containing about 11% tin and other elements in traces. The presence of an inhomogeneous microstructure with both thermal twin bands and slip lines was consistent with multiple hammering steps followed by partial annealing treatments.
On the bowl a very limited chloride contamination was observed and chlorides were never detected in proximity to the metal. These findings and the morphological/compositional characteristics of the patinas permitted to classify that on the internal side of the bowl as a modified Type I morphology, while the patina on the external side of the bowl was less compact, so that it was judged borderline between a "noble" patina and a disfiguring one. On this side, a significant intergranular attack was found, reputed responsible for the fragmentation occurred.

I.1 Introduction

In this work, the metallurgical characteristics and the corrosion conditions of an ancient bronze bowl, probably discovered in the area of ancient Persia and now belonging to a private collection, were investigated. The bowl exhibited a flaring rim (Fig. 1a) and a decoration with 13 lotus buds around a central rosette (Fig. 1b).

It was not possible to trace out the detailed information about the excavation, but the artefact was stylistically consistent with the libation vessel named *phiale*, which was one of the hallmarks of the Achaemenid period. Therefore, it was tentatively dated back to the I century B.C.

The Achaemenid Empire (559–330 B.C.) was one of the most dynamic and historically significant socio-political entities of the first millennium B.C.; it covered a vast area from Pakistan in the East, to Egypt in the West and from Aral Sea in the North to the Indian Ocean in the South [1]. The Iranian Plateau, rich in raw materials, was witness of one of the earliest metallurgy in the world [2].

The initial production of native copper objects began in the late 8th millennium B.C. and carried on with the smelting of copper ores since the Bronze Age (3200–1400 B.C.) and thereafter during the Achaemenid Empire period. This was a period of great stylistic and metallurgical research that led to the production of gorgeous prized objects, such as *rhytà*, swords and *phialai* [3,4]. Archaeometallurgical investigations of such artefacts can provide useful information about the technological level reached in mining and metallurgy and can afford historical evidence concerning metalworking trades. In turn, this may throw light on the economy of the Achaemenid Empire, the technological capabilities of its craftsmen as well as their cultural relations [5].

Corrosion of bronze artefacts in soil depends on multiple factors that can be classified as endogenous (nature of alloy, method of manufacture, shape and dimension) and exogenous (soil composition, porosity, humidity, conductivity, depth of burial) [6,7]. These factors invariably lead to the formation of layered surface patinas which, according to many studies, may be generally characterised by essentially two types of structures, often present on the same artefact [8–10]. In Type I patinas, the original shape of the object and its original surface can be still identified, while in Type II patinas the original surface cannot be appreciated anymore, due to either macroscopic deposits at pits and crevices or losses due to localised or intense generalised metal dissolution [8].

These structures have been rationalised by Robbiola *et al.* [8,9], who show that in low aggressive media the first step of corrosion of Cu/Sn alloys always involves preferential dissolution of tin, the less noble alloying element. Tin is converted into insoluble tin compounds (oxides, hydrated oxides), so that the subsequent oxidation of the underlying copper-enriched substrate is hindered and controlled by mass transport through pores and cracks of the tin oxide layer. This leads to the formation of Type I patinas, characterised by a copper-depleted (with respect to the alloy composition) bilayer structure, with essentially a cuprous oxide inner layer, due to local precipitation of copper oxidised species, and a strong tin enrichment in the outer layer. In dependence of oxygen availability and pH, the cuprous oxide film may be further oxidised to cupric oxide (tenorite) [8,11].

In more aggressive conditions, less insoluble tin corrosion products are formed and copper dissolution is quicker. In this case, Type II patinas are detected, characterised by a three-layer structure. The inner layer exhibits a significant accumulation of chloride ions, together with tin and cuprous oxides and is topped by an intermediate cuprous oxide layer. The external corrosion product layer consists in copper(II) corrosion products, such as $Cu_2(OH)_2CO_3$ (malachite), $Cu_3(CO_3)_2(OH)_2$ (azurite), together with $Cu_2(OH)_3Cl$ (atacamite and paratacamite) [12–14]. Aging of Type I patinas may stimulate the migration of copper species through the tin oxide film and the subsequent growth of this kind of copper(II) corrosion product outer film, over the basic bilayer structure of the patina [8]. Such external layer often incorporates soil components [9].

At high chloride levels in soil, in the inner layer the voluminous growth of cuprous chloride (nantokite) pockets is often detected and although in many cases this compound is detected adjacent to the metal surface in the patina [15,16], different stratifications can be also observed. In particular, nantokite was also found to overlie cuprite or be sandwiched between cuprite layers [13,17,18].

High chloride contamination has shown to induce complete solubilisation of tin and lead corrosion products from bronze, so that tin- and lead-depleted patinas have been detected [13,19]. When the excavated chloride-contaminated objects come into contact with moist air, the oxidising power of the environment increases and a cyclic bronze corrosion process (bronze disease) may start and bring to a quick disfiguring of the bronze artefact. Corrosion progress is instead interrupted if the relative humidity (RH) is reduced below about 40% [17,20].

In this paper, the results of investigations on the alloy microstructure of the studied bronze bowl are presented. Microstructural features are used for determining manufacturing procedures and evaluating their coherence with the possible dating.

The second part of the work dwells on the study of the main corrosion products, the patina stratification and corrosion attack morphology in order to elucidate the corrosion process which led to the detachment of fragments from the bowl bottom.

The characterisation is carried out by optical microscopy (OM), scanning electron microscopy (SEM) equipped with an energy dispersive microprobe, energy dispersive X-ray fluorescence spectrometry (EDXRF) and Raman spectroscopy techniques.

(a) (b)

Fig. 1. Macroscopic images of the bowl: (a) flaring rim and (b) decoration with 13 lotus buds around a central rosette.

I.2 Material and methods

In order to preserve the bowl from further damage, most of the investigations were carried out on three fragments, detached from the artefact. The analysis of their polished surfaces by a ZEISS EVO MA 15 scanning electron microscope (SEM), coupled to energy dispersion spectroscopy (EDS) permitted the evaluation of the alloy composition, while the surface investigation after etching (in $FeCl_3$/HCl hydro–alcoholic solution) by light field (LF) OM and SEM/EDS analyses, carried out according to procedures described in [21,22], clarified the alloy microstructure.

The portable energy dispersive X-ray fluorescence (EDXRF) spectrometer ARTAX 200 was used to determine the chemical composition of the surface corrosion products on both the external and the internal side of the bowl. The system is equipped with an air cooled X-ray tube working at maximum 50 kV and 1.5 mA. In this case, the tube was operated at 30 kV and 1.3 mA, with a measuring time of 90 s. The spot diameter at the measurement point is about 1 mm. The detector is a Peltier-cooled Si-Drift (area 10 mm^2, energy resolution < 159 eV for Mn-Kα at 10 kcps, 0.65 mm collimator). During each EDXRF measurement a Helium gas flow was used to detect the light elements starting from Na (Z = 11) to Ar (Z = 18).

Raman spectra of the surface corrosion products were collected by a spectrometer HORIBA Jovin Yvon LabRam HR800 equipped by a He–Ne laser (= 632.81 nm) under low laser powers ($P_{output} \leq 5$ mW) to avoid sample degradation. For a more complete characterisation of the surface patinas, this technique was applied on both the internal and the external side of all fragments. The patina stratigraphy was investigated on the cross sections of a fragment embedded in cold mounting resin to avoid the alteration of the corrosion products. First, the patina stratigraphy was studied by dark field OM (DF-OM) and SEM/EDS, according to the procedures described in [23]. Therein, Piccardo highlighted that the DF-OM technique allows one to differentiate the main corrosion products of copper alloys colorimetrically, with a higher sensitivity than that reached by the more classical light source. Afterwards, the nature of the corrosion products exhibiting different colours was assessed by Raman spectroscopy.

I.3 Results and discussion

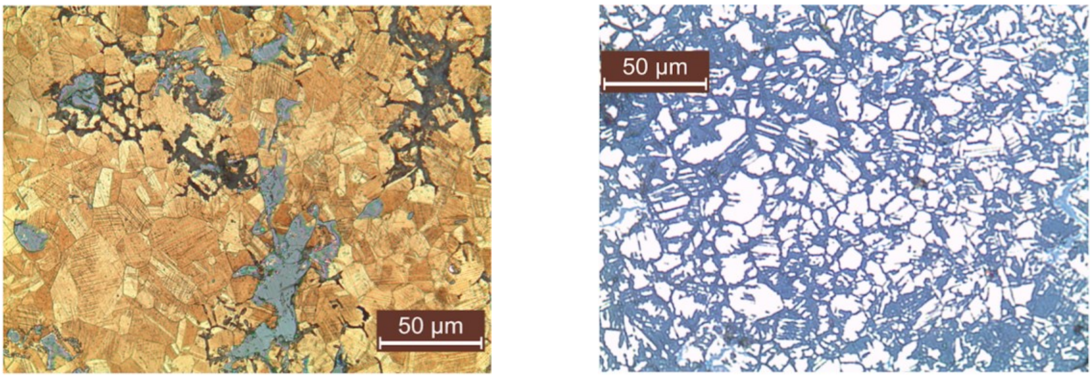
I.3.1 Alloy microstructure and chemical composition

Fig. 2 shows the microstructure of the chemically etched alloy. The presence of both thermal twin bands and slip lines is consistent with the manufacturing process typical of most Achaemenid metalwares. In fact, at that time, the vessels were usually made by hammering or rising sheet metal, adding decoration in *repoussé*, outlining the details by chasing and finishing with a burnish which sometimes left a slightly fluted surface [1,24]. The observed twinned microstructure is due to the forming of a cast bronze ingot into a sheet metal vessel by alternate hammering and annealing steps. Since mechanical working caused the sheet metal to work-harden, annealing heat treatments (usually between 500 ◦C to 800 ◦C for copper alloys) were applied at intervals, in order to restore workability and toughness to the metal [5,25,26]. Fig. 2a shows the presence of a non-homogeneous grain size and residual slip lines which are likely due to incomplete annealing, carried out for a too short time or at a too low temperature, so permitting only partial recovery and reduction of the structural defects. A more prolonged annealing treatment performed within the correct temperature interval would produce recrystallization and a consequent regular microstructure, with equiaxed grain [27]. In Fig. 2a shrinkage cavities and elongated inclusions are also visible. The inclusions were better investigated by SEM (Fig. 3a). In particular, SEM-EDS analysis showed that they mainly consisted of copper–iron sulphides, residual from incomplete ore reduction (Fig. 3b).

Table 1: Average composition of the alloy (measured by EDS, weight %) on wide areas (1.0 × 0.5 mm^2) of the core metal on fragments 1 and 2 (fragments from the base of the artefacts, Fig. 2a and b).

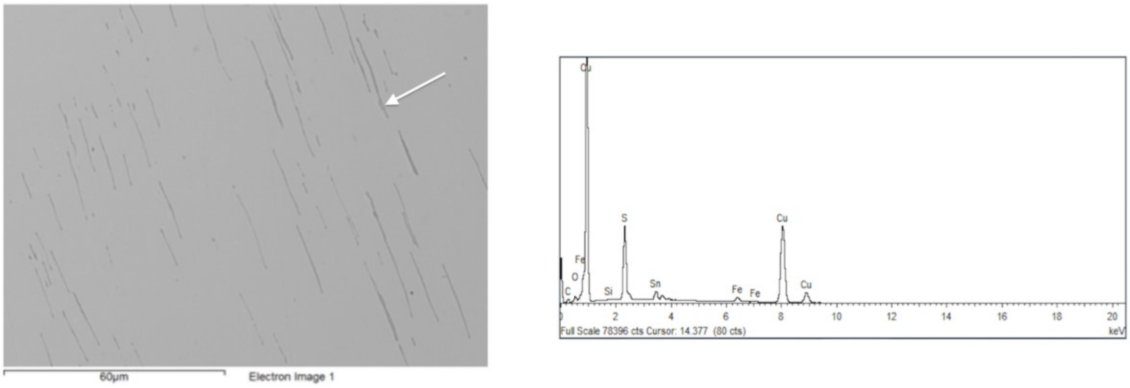
Fragment	**O**	**S**	**Fe**	**Cu**	**As**	**Sn**
1	1.26	0.28	0.13	87.31	0.23	10.79
2	1.15	0.43	0.13	86.84	0.41	11.04

The alloy composition, estimated by SEM-EDS analysis, is reported in Table 1. It can be noted that the alloy contains copper (≈87 wt.%), tin (≈11 wt.%) and small amounts of iron (≈0.13 wt.%), sulphur (≈0.36 wt.%) and arsenic (≈0.32 wt.%). Iron, sulphur and arsenic might be the result of poor smelting and refining techniques, with arsenic representing a common copper ore impurity. As regards the tin content, the measured value is in the range of complete solid solubility of tin in copper. Moreover, it is lower than the limit of 14% by weight typical of annealed tin–bronzes.



(a) (b)

Fig. 2. Optical images on: (a) details of shrinkage cavities and non-metallic inclusions on the chemically etched surface; (b) intergranular corrosion attack on the polished surface.



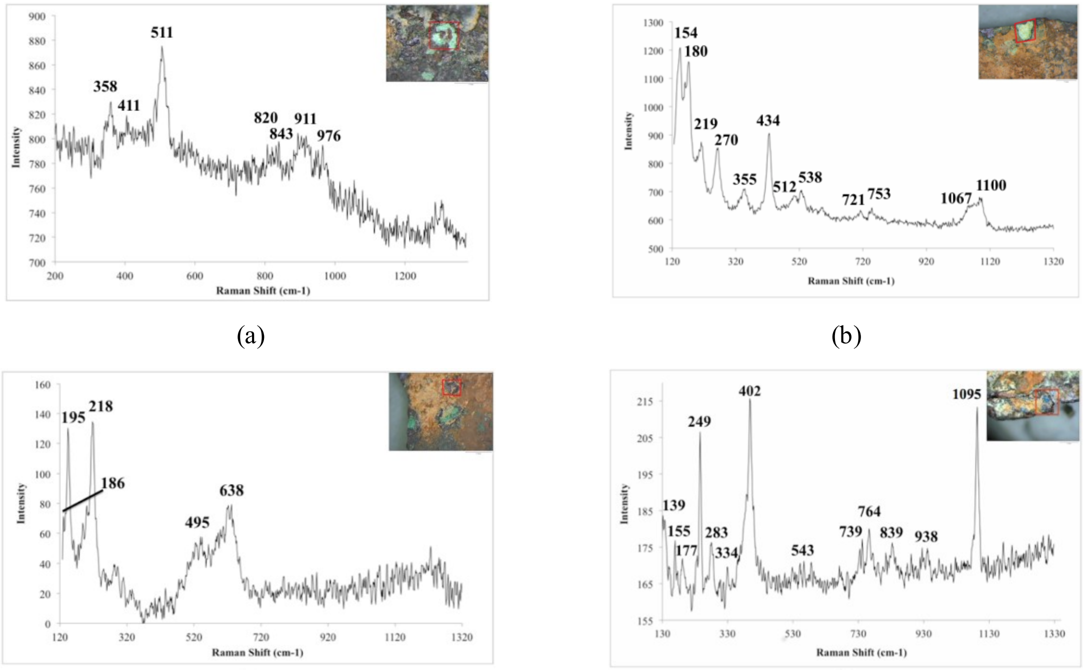
(a) (b)

Fig. 3. SEM backscattered electron image of the elongated inclusions (indicated by white arrow) (a), together with the corresponding EDS spectrum (b).

I.3.2 Characterisation of the corrosion phenomena

The polished external surface of the bowl (as revealed by fragment analysis) clearly shows that corrosion preferentially attacks the grain boundaries (Fig. 2b). The corrosion process is also often localised on twin borders and slip lines, resulting from plastic deformation. These forms of corrosion are typical of ancient artefacts and are often considered determinant factors for authentication purposes [9].

EDXRF spectra were carried out systematically on the small islets of light green corrosion products visible on the bowl surface and spot-like on other surface regions of both the internal and the external side of the bowl. They always evidenced small amounts of silicon, calcium and iron, coming from the burial environment, and copper, tin and lead deriving from the alloy. Sulphur, which could have both an endogenous (from inclusions) and exogenous (from soil) source, was also often detected. A small chlorine amount was only found by EDXRF spectroscopy in a few light green corrosion products and was not uniformly distributed on the artwork surface. Fig. 4a shows an example of chlorine-containing islet with the corresponding Raman spectrum, which is clearly indicative of the presence of natural atacamite ($Cu_2Cl(OH)_3$). In fact, the most intense spectrum bands occur at about 511 cm^{-1}, but peaks are also observed at 976, 911, 843, 820, 411 and 358 cm^{-1} [28–31]. It is not uncommon to see isolated patches of atacamite on archaeological bronze artefacts. This compound is often reputed a dangerous compound which may be indicative of cyclic corrosion processes [13,19]. On the contrary, a continuous layer of atacamite directly adjacent to the metal surface is a typical artificial patination product [20].



(a) (b)

(c) (d)

Fig. 4. Raman spectra obtained on the external bowl surface, in correspondence of (a) the rare chloride-containing light green or (b) chloride-free pale green or (c) reddish purple or (d) deep blue corrosion products. In each figure, an inset exhibits the corrosion product area where the spectrum was recorded. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Most pale green patches on the bowl did not correspond to chlorine-containing corrosion products. As an example, all peaks of the Raman spectrum in Fig. 4b, obtained in correspondence of the green spot shown in the inset, are connected to the presence of malachite (1100, 1067, 753, 721, 538, 512, 434, 355, 270, 219, 180, 154 cm^{-1} [28,29,32–34]). This copper hydroxycarbonate ($Cu_2(CO_3)(OH)_2$) is quite commonly found as a corrosion product of copper alloys after long burial periods in soils. It is also a minor constituent of the surface patinas when the same alloys are exposed outdoors [35,36].
On the external side of the bowl, under the orange soil encrustations, many reddish-purple areas emerge. They exhibit a Raman spectrum corresponding to cuprite (Fig. 4c) [28–31]. In particular, the most intense band occurs at about 218 cm^{-1}; peaks are also observed at 195 and 186 cm^{-1} [30] and a broader band with several maxima appears between 400 and 700 cm^{-1} [31]. Cuprite may exhibit a range of colours from dark yellow to reddish to dark brown depending on several factors, such as impurities, particle size and nonstoichiometric composition. Unexpectedly, this compound was not detected on the internal side of the bowl.

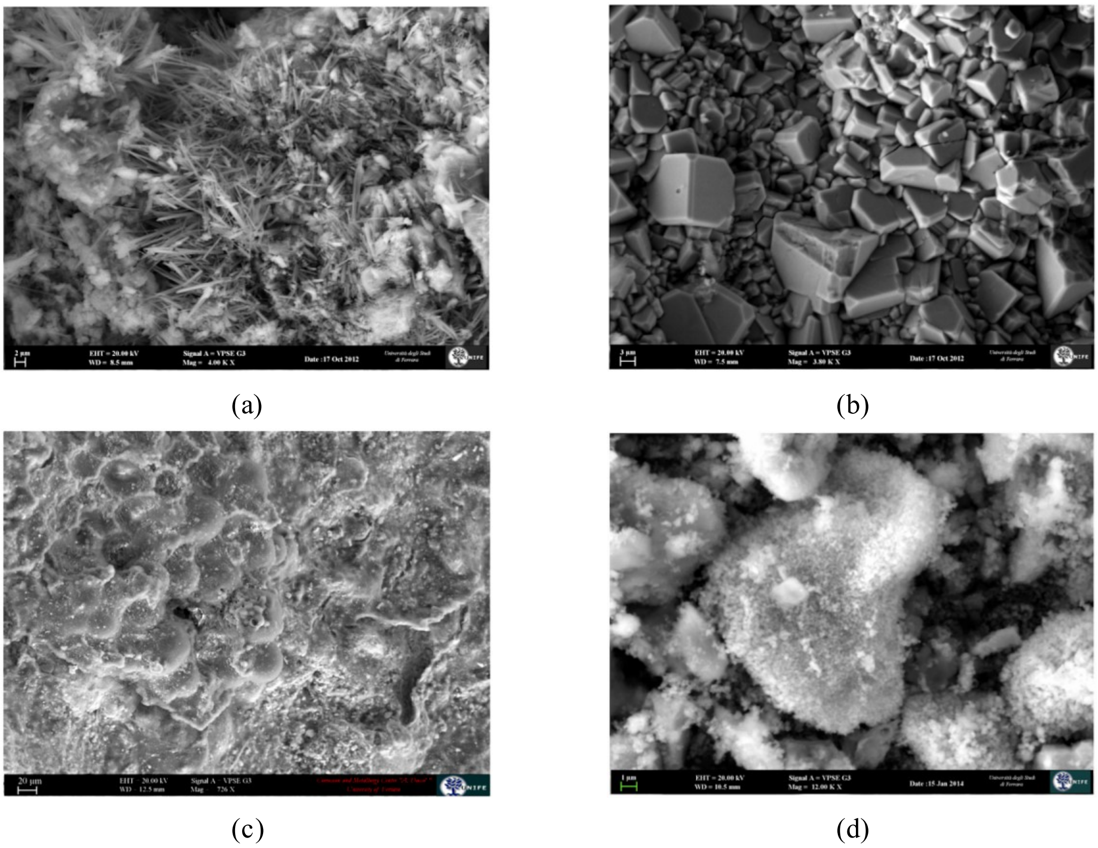

(a) (b) (c) (d)

Fig. 5. Representative SEM images of the morphology of surface corrosion products: (a) malachite, (b) cuprite, (c) azurite and (d) atacamite.

Raman spectroscopy performed on rare small deep blue patches revealed the presence of azurite ($Cu_3(CO_3)_2(OH)_2$, Fig. 4d). The most intense spectrum band occurs at about 402 cm^{-1}; peaks are also observed at 1098, 938, 839, 764, 739, 543, 334, 283, 249, 177, 155 and 139 cm^{-1} [28]. Azurite is a rather uncommon corrosion product, since in the presence of moisture it may be converted into malachite through loss of carbon dioxide. However, discrete crystals or patches of azurite are reported to be found in association with malachite and cuprite [35].

The morphology of these corrosion products was evaluated by SEM. Malachite has a monoclinic crystal structure, which commonly forms different types of aggregates, such as fibrous, reniform and globular, rod-shaped, curved and fibrous crystals [35]. Fig. 5a shows that, in the case of the Achaemenid bowl, malachite is present in the form of silky fibrous aggregates. Cuprite usually presents octahedral crystals, sometimes with modified cubic crystal edges, as actually shown in Fig. 5b. Azurite is present in the form of globular aggregates (Fig. 5c), while atacamite (Fig. 5d) consists mainly of anhedral products.

The stratigraphy of the surface patina on the external side of the bowl is shown in the DF-OM micrograph of Fig. 6. Its thickness is higher than 150 μm and on the basis of Raman spectroscopy and SEM-EDS analysis it was possible to investigate its compositional evolution from the inner layer/alloy interface to the layer close to the burial environment. In the inner reddish layer (indicated by letter A), Raman spectroscopy essentially evidences cuprite, likely admixed with cassiterite (SnO_2). The latter compound is suggested by the presence of a small peak at 580 cm^{-1} superimposed on the typical cuprite spectrum. In fact, it is well known that bulk Raman vibrations of cassiterite (crystal size > 10 nm) occur at 842, 776, 635, 475 cm^{-1}, but in nanometric SnO_2 (crystal size < 2.5 nm) bulk vibrations are hidden by surface mode at 580 cm^{-1}, as pointed out by many researchers [47–49]. Very insoluble corrosion products, such as cassiterite, often present nano instead of micro-crystallinity. In fact, after the compound nucleation, dissolved soluble tin cations are reduced to so low levels, that the subsequent crystal growth undergoes mass transport control and can become too slow to keep in step with nucleation [50]. Over this inner cuprite/cassiterite layer, a pure cuprite layer follows (indicated by letter B), topped by a malachite layer (indicated by letter C), once more intermixed with cassiterite, as suggested by a peak at 580 cm^{-1}. In fact, though the formation of quite insoluble cassiterite-rich layers, bronze corrosion is not blocked, because the resulting surface patina is defective and discontinuous at a microscopic level so permitting the slow diffusion of copper ions toward the external more oxidising environment where these ions are converted into the observed copper(II) basic carbonate (e.g. malachite) top layer, intermixed with soil components. The micrograph of Fig. 6 also shows that beneath the patina a marked intergranular attack is present, as already noticed in Fig. 2b.

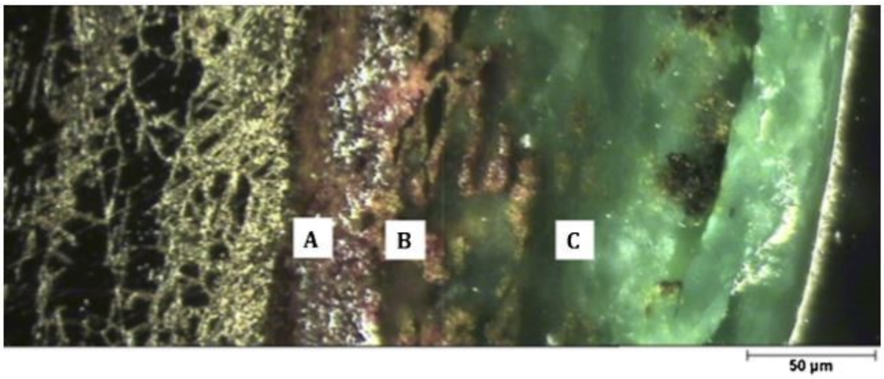


Fig. 6. DF-OM micrograph of the cross section of the corrosion patina, observed on the external side of the bowl. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The SEM-EDS mapping of the same portion of surface film is reported in Fig. 7 and clearly evidences its complex structure. In fact, it shows the presence of many sulphur-containing inclusions (ghost sulphide inclusions [8], Fig. 7d), inside the corrosion layers. They are remnant of the alloy corrosion and permit to evidence the corrosion product volume taking the place of the original corroded metal, which was comprised within the two dotted lines reported in the figure. The elemental maps well evidence the banded structure of the patina, where a cuprite film (indicated by letter B, in analogy with Fig. 6) lies between two tin oxide-enriched layers, (indicated by letter A and C). Alternated SnO_2/Cu_2O layers have already been detected in tin bronzes [7,37]. According to some authors [7,37] these structures are connected to interdiffusion of metal ions and soil components partially dissolved in groundwater and are referred as Liesegang phenomena [38], while according to others [39] they may be also connected to environmental changes in burial conditions such as seasonal temperature fluctuations, rainfall fluctuations and change in soil corrosivity. Fig. 7 also shows that the external malachite layer is partially intermixed with the outer tin rich layer but also exceeds it, growing beyond the ghost sulphide inclusions zone. No chloride ions are detected inside the patina.

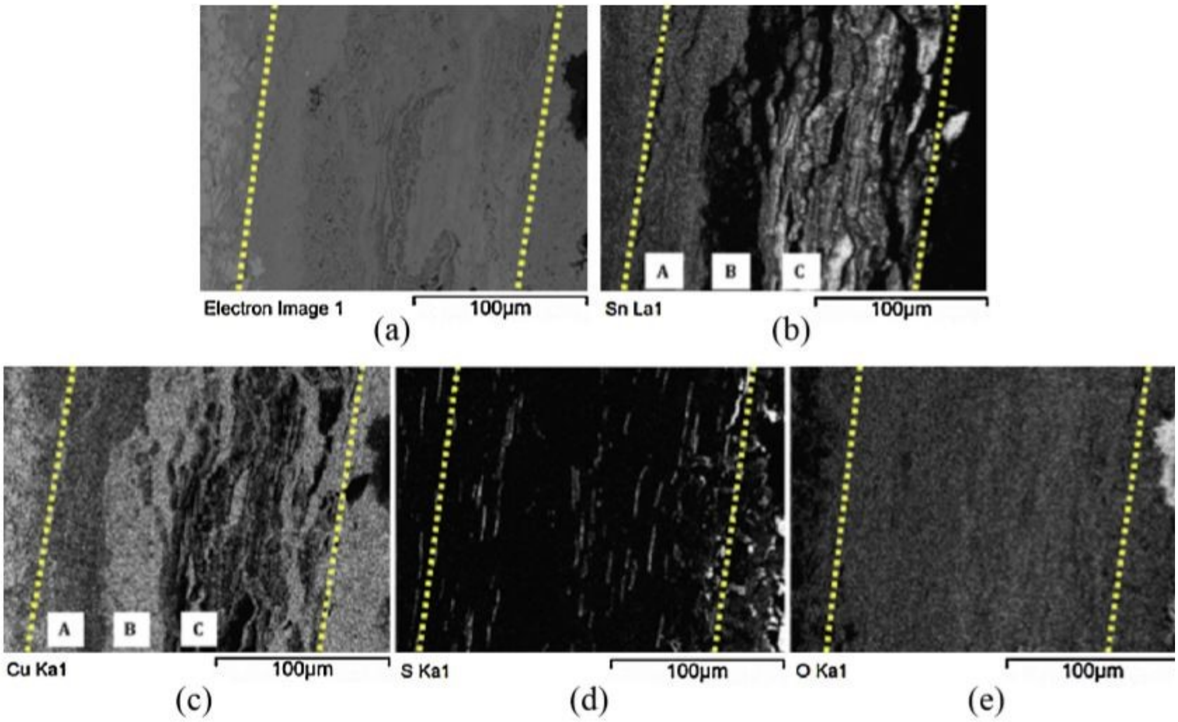


Fig. 7. SEM image and X-ray maps of elemental distribution on the patina cross section, in correspondence of the external surface of the bowl (yellow dashed line = limit of the original surface on the basis of the ghost sulphide inclusions; letters refer to layers in Fig. 6). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

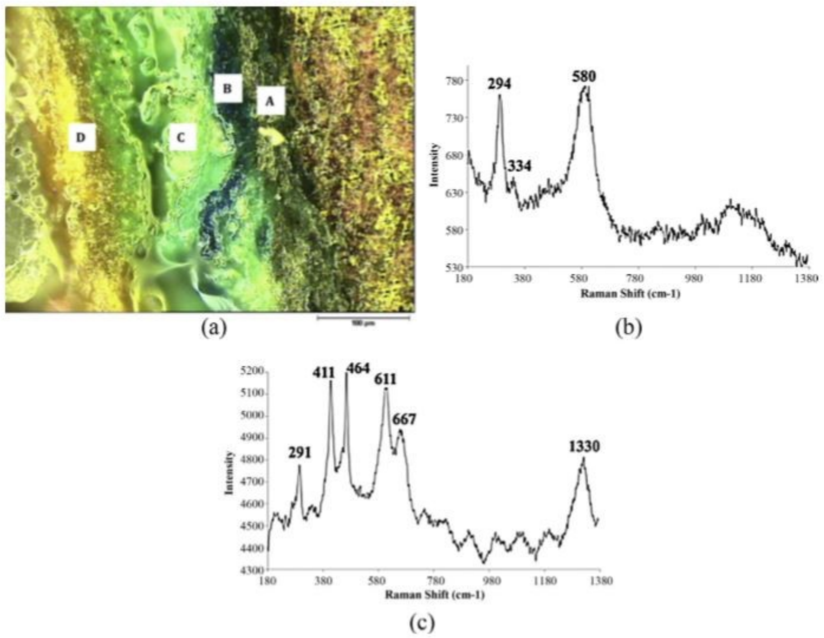
The stratigraphy of the surface crust on the other (internal) bowl side is shown in the DF-OM micrograph of Fig. 8a. This surface layer is more than 200 μm thick and on the basis of Raman spectroscopy it appears to consist of (starting from the metal surface): tenorite (CuO, 294 and 334 cm^{-1} [30]) and cassiterite (SnO_2) (layer A, Fig. 8b), azurite (layer B, $Cu_3(CO_3)_2(OH)_2$), malachite (layer C), hematite (Fe_2O_3 [28]), magnetite (Fe_3O_4 [28]) and quartz (SiO_2) (layer D, Fig. 8c). The compounds in Fig. 8c are connected to soil contamination. As already found by Raman analysis of the internal surface of the bowl, no cuprite was detected in cross section.

The absence of cuprite in the patina covering the internal side of the bowl and its substitution by a continuous tenorite layer is rather surprising. Even if the Pourbaix diagram predicts tenorite stability in a wide potential/pH region, for kinetic reasons this oxide is quite rarely present in comparison to cuprite. Its presence is usually connected to a heating treatment before or during burial or to an intentional patination process, applied for aesthetical reasons. However, a thermal process (between 400 ◦C and 600 ◦C [35]) would induce the oxide formation on both sides of the bowl and for this reason it can be excluded as a cause of tenorite formation. As concerns intentional patination of archaeological artefacts many relevant studies can be found in the literature. In Mesopotamia as early as the third millennium B.C. or in Egypt during the second millennium B.C., polychromy was used by metal craftsmen in order to create metal artefacts characterised by a combination of colours [40,41]. Several researches investigated the black patination of copper-based alloys containing small amounts of gold and silver and demonstrated that surface modification by chemical etching was used to improve the artistic effect [40–43]. Artificial black patinas using sulphur treatment are also documented [44]. These black coloured alloys are called "black bronze", "black copper", Corinthian bronze", shakudo, etc. [40–43]. To our knowledge, only two research studies reported about an artificial black patination treatment of archaeological Cu–Sn alloys. In the first case, tests carried out on an Egyptian bronze also containing lead and arsenic evidenced that in the black patina sulphides and chlorides (clinoatacamite, $Cu_2Cl(OH)_3$) were present [45]. Another study investigated ancient Japanese bronze objects with a similar composition to the previous one which showed likely intentional black patinas. The dark colour was connected to the presence of sulphides and oxides (Cu_2O, CuO and Cu_2S) [46]. However, in the case of the Achaemenid bowl, an intentional patination is likely to be excluded, because the alloy does not contain any gold and silver and the black patina does not exhibit a surface cuprous sulphide layer. Moreover, an intentional patination would likely cover the whole surface of the artefact.

So, formation of a black tenorite film by an intentional patination or by a heat treatment has to be excluded. The only reason why it could occur is a local pH increase, which has interested only the internal side of the bowl. Therefore, the formation of a black tenorite layer on the internal side only of the vessel is tentatively ascribed to the antique everyday usage of the vessel, likely involving the prolonged contact with alkaline beverages, such as herbal infusions [35].

Fig. 9 collects the SEM-EDS mapping of the cross section of the patina on the internal side of the bowl (in a region close to that shown in Fig. 8). It confirms the stratigraphy highlighted by Raman Spectroscopy. In particular, the oxygen distribution permits to define the boundary between the alloy and the surface patina (red line) and clearly evidences the presence of a thin inner copper (and tin) oxide layer adjacent to a thick tin (and copper) oxide film. A large crust of malachite/soil components forms the outer patina layer. Again no chlorides are detected therein. On this side of the bowl no strong intergranular attack is evident.

In general, the absence of chlorides in proximity of the metal and the presence of inner tin-rich oxide films, suggest to interpret both the internal and the external patinas, as modified Type I morphologies, where the modification is connected to the overall presence of an outer soil-contaminated malachite layer. In the case of the patina on the external side, a severe intergranular corrosion attack is present beneath, also included by Robbiola *et al.* [8] within the possible modifications of Type I patinas. However, the fairly good conservation state of the bowl, embrittled by the intergranular attack itself and the banded less compact structure of the external patina may suggest to classify it, as borderline between a "noble" patina and a disfiguring one.



(a) (b)

(c)

Fig. 9. (a) DF-OM micrograph of the patina cross section in correspondence of the internal side of the bowl; ((b) and (c)) representative Raman spectra of the layers indicated by letters A and C, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

I.4 Conclusions

A bronze bowl belonging to a private collection, stylistically consistent with the Achaemenid art and tentatively dated back to the I century B.C., exhibited a brittle behaviour and underwent a partial fragmentation. In this study, the chemical composition and microstructure of the alloy and the corrosion phenomena affecting the artefact were investigated in order to assess the reason for the damage occurred. The results show that:

∴ The alloy was a monophasic copper–11% tin alloy containing iron, sulphur and arsenic traces. The microstructure was characterised by remarkable shrinkage cavities and copper-iron sulphide inclusions, residual from incomplete ore smelting. Moreover, it exhibited the presence of both thermal twin bands and slip lines, consistent with the manufacturing process employed by the blacksmiths during the Achaemenid Empire.

∴ On both the internal and the external side of the bowl a complex corrosion product stratification was detected. In particular, the patinas were characterised by an inner copper oxide/tin oxide layer (with some banding phenomena in the external patina) covered by copper hydroxycarbonates and topped by soil components. No chlorides were detected in proximity of the metal.

- ∴ In the external patina, the layer in contact with bronze contained cuprite, while in the internal patina this layer consisted in an apparently continuous tenorite layer (intermixed with cassiterite).
- ∴ The external patina was less compact and banded. It covered a severe intergranular attack, that was reputed the cause of the artefact intrinsic brittleness.
- ∴ The compositional and morphological characteristics of the patinas suggest to classify the internal one as a Type I structure, while the external one as borderline between a "noble" patina and a disfiguring one.

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Article II

Fakes in African art: study of a reliquary figure (*Mbulu-Ngulu*) from Gabon

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Abstract

The aim of the present work is the chemical and microstructural characterisation of a reliquary figure, stylistically consistent with the art of the Kota population, which lived in the eastern part of Gabon (Africa). The artefact was subjected to preliminary observation by stereomicroscopy, and then optical microscopy (OM) and scanning electron microscopy (SEM) analyses are carried out on a fragment and on surface compounds. Lastly, AMS radiocarbon dating of the wooden support allowed further information about the production period to be obtained.
The results show that the artefact was produced by a Cu-Zn alloy and contains non-metallic impurities made up of S and Se. The greenish and whitish surface compounds, which are mainly collected near the nails and in proximity to the overlaid sheets, are probably only partly related to natural corrosive processes. Finally, radiocarbon dating established that the wooden support certainly dates after 1950.

II.1. Introduction

The proliferation of fakes in African arts has grown enormously in recent years, with a particular explosion since the 1950s, due to an increase in demand by collectors, which created new fields of activities for African foundries. In fact, in the 1980s the quantity of antiquities on sale increased further and today many replicas of tourist souvenirs and fanciful copies of traditional forms enrich the art market.

The official definition of authenticity for African artefacts consists of two inseparable conditions: any object created for a traditional purpose and by a traditional artist may be considered authentic [1].

It is rather difficult to determine if an African artefact is original or a copy because literature is characterised by incomplete information about the African arts and the production of artefacts by artists [2]. The studies of African artefacts are somewhat incomplete since there is no correlation between the style used in these works, the materials used to produce them and the geological context of the extraction zone.

Archaeometric analyses are essential to determine the state of conservation of the objects as well as to evaluate the production period in order to establish the authenticity of the artefacts.

The aim of the present work is the characterisation of a sculpture, stylistically consistent with the art of the Kota population, which lived in the eastern part of Gabon (Africa). This community is known for the realisation of metallic reliquary figures, which were set on wooden supports and called *Mbulu-Ngulu* or *Bwéte*. It should be noted that the first samples of these sculptures arrived in France and Germany during the last quarter of the 19th century. Reliquary artefacts should, however, be more ancient given that the local copper mines had already been exploited to obtain metal for the coating of artefacts [3].

Unfortunately, the majority of researchers have relied solely on stylistic analyses of the ornaments, which decorate the surface of the objects. More extensive investigations on the chemical composition of the alloy of the artefacts, in conjunction with a systematic characterisation of original African metallic objects would allow the evaluation of the provenance and the dating of Kota funeral art [4].

The present paper focuses on the investigation of the symbolic representation of a human abstract figure whose head is bigger than the rest of the body. These abstract figures were used to protect and demarcate the bones of family ancestors, which were preserved in containers made of bark.

The artefact consists of a carved piece of wood (42 cm in height, 23 cm wide and 2 cm thick) covered on one side with metal sheets, which were fixed onto the support with small metallic nails. These metal sheets are very thin in order to fix almost perfectly to the carved wood. The following morphological elements of the sculpture are detectable in Fig 1a-c:

∴ The oval face has stylised eyes and nose but the mouth is not depicted. Two metallic plates are nailed onto the surface to represent a cross. In agreement with E.W. Herbert [5] this element has been found starting from the end of the 15th century as a result of the Congolese population's conversion to Catholicism;

∴ Two lateral parts at ear-level which are often considered the representation of a hat;

∴ Two cylindrical pendants placed on the base of the lateral parts, which are the abstract representation of traditional male and female hairstyles;

∴ One half-moon shaped sheet is located above the oval face and harmoniously integrated with the lateral parts;

∴ One rhomboid element that symbolises the body and the legs, placed on a rectangular wooden base;

∴ Another rhomboid element, on the back of the sculpture, stretched along the vertical axis and with a protruding “vein”.


(a) (b) (c)

Fig. 1 – Macroscopic images of the sculpture: front (a), back (b) and side view (c).

II.2 Materials and methods

The sculpture was observed by stereomicroscopy, equipped with a Moticam 2500 – 5 Mp camera, in order to obtain information on the manufacturing technique and to check the state of conservation. The investigations have revealed the presence of some compounds, which are mainly concentrated near the nails and in proximity to the overlaid sheets.
Thereafter, the evaluation of the alloy and the composition of the different colour surface compounds was carried out using a ZEISS EVO MA 15 scanning electron microscope (SEM), coupled with energy dispersion spectroscopy (EDS).
Moreover, a metal fragment of a few millimetres was taken from an unobtrusive area of the sheet. The sample was mounted in conductive resin, polished and submitted to conventional metallographic observation using LEICA MEF4M optical microscopy (OM).
Lastly, a sample of a few grams was collected from the base of the wooden support and subsequently was dated using accelerator mass spectrometry (AMS) at Centro di Datazione e Diagnostica (CEDAD) – University of Salento.

II.3 Results and discussion

II.3.1 Macroscopic investigations

Preliminary macroscopic investigations have yielded a great deal of information about the manufacturing technique as well as the nature of the products located on the surface.
In agreement with some of the literature and private communications expressed in the last few years [4], the parts of the face that are not overlaid by the two metallic sheets (positioned in a cross) consist of a

single plate. These are decorated with "*lamellage*", a technique characterised by various equidistant streaks, which are placed in a slanting or horizontal pattern. These strips are also depicted on the half-moon sheet and on the rhomboid element that symbolises the body and the legs. In the latter two cases, a multitude of pitting embossed using a punch also decorates the surface of the plate [4].
Fig. 2 shows representative images of the rare compounds using stereomicroscopy, which were mainly collected near the nails and in proximity to the sheets. The colouring of these products is clearly green or whitish.

(a) (b)

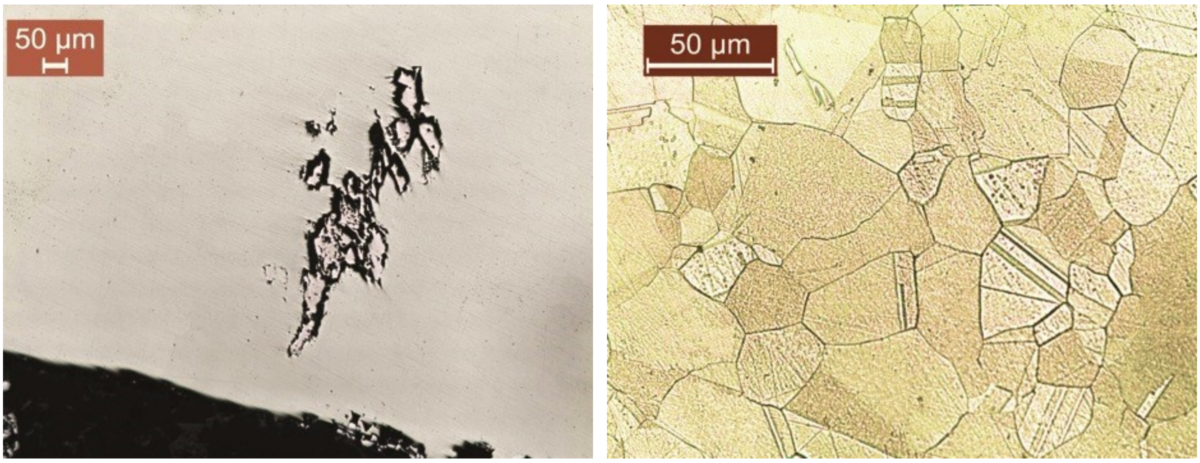
Fig. 2 – Macroscopic images of the different colour compounds that appear on the surface.

II.3.2 Radiocarbon measurement

The AMS radiocarbon dating established that the wooden support is certainly dated after 1950. It is well known that the production of these sculptures ended around the 1930s because of the great number of Catholic missions, which imposed a new social organisation based on Western households [4]. Finally, it should be pointed out that the integrity as well as the total absence of signs due to a wooden support substitution is clearly evident.

II.3.3 Microstructural analysis

After metallographic preparation, the microstructure of the metal fragment taken from the sheet was highlighted. In particular, in Fig. 3a a shrinkage cavity of remarkable dimensions, formed during the alloy solidification, is visible. Fig. 3b also shows the microstructure of the alloy after chemical etching by $FeCl_3$/HCl. The presence of both non-homogeneous grain size and thermal twin bands would suggest that the artefact was obtained by alternate hammering and annealing steps. It should be noted that the variable grain size is probably due to a heterogeneous plastic deformation induced by manual hammering.



(a) (b)

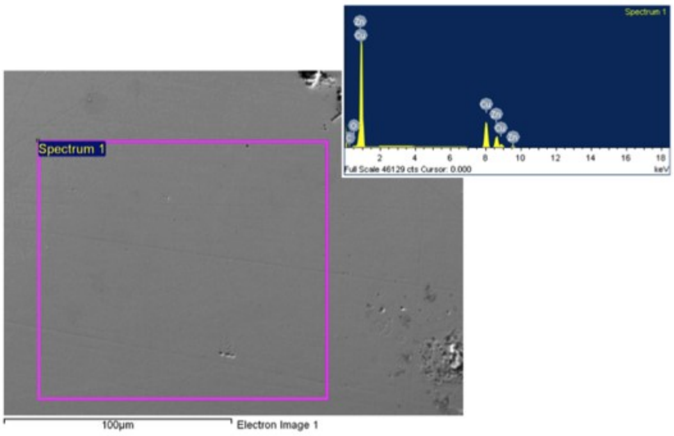
Fig. 3 – Optical images of: (a) a detail of a shrinkage cavity on the polished surface; (b) the microstructure of grains with the presence of thermal twin bands on the chemically etched surface.

II.3.4 Chemical analysis

Fig. 4a shows a SEM image of the alloy together with the corresponding EDS spectrum. SEM-EDS analysis highlights that the artefact was produced by a Cu-Zn alloy, without the addition of alloying elements, i.e. Pb. No impurities (i.e. As, Fe, Sb), which are very common in the ancient alloys, were detected. It should be noted that, comparable amounts of Cu and Zn (Fig. 4b) could also be found in modern brasses such as the commercial "Yellow Brass" which contains 65 wt.% of Cu and 35 wt.% of Zn [7].

Fig. 5a shows a SEM image of rare microscopic inclusions that are visible in the alloy. In particular, SEM-EDS analysis allows the verification of the presence of non-metallic impurities enriched with S and Se. To our knowledge, only one reference reports some South African (Lowveld) metallic artefacts [8], approximately dated from 1000 A.D. to 1980 A.D., which were characterised by many copper-iron sulphide inclusions containing up to 3% Se by weight, residual from incomplete ore reduction.

Over the centuries, the Kota reliquary figures went into stylistic decline and they were characterised by more abstract and grotesque meanings. Moreover, the demand for these artefacts from Western collectors has grown enormously in recent years, causing the proliferation of sculptures without any "funerary" meaning for the purpose of enriching the flourishing art market. Starting from the first decade of the 20th century, the practice of recasting damaged copper and brass to recover the precious metal was very common. In particular, E. Andersson [9] highlighted that many "*Mbulu-Ngulu*" were obtained by recasting ancient alloy which was later mounted in more recent wooden supports (second half of the 20th century). In this regard, because of the perfect realisation of the artefact without the addition of alloying elements or common impurities, the rare Se inclusions and the dating of the wooden support (see § *Radiocarbon measurement*), it is possible to further suppose that the sculpture analysed in this paper was realised by the methods described by Andersson in [9].

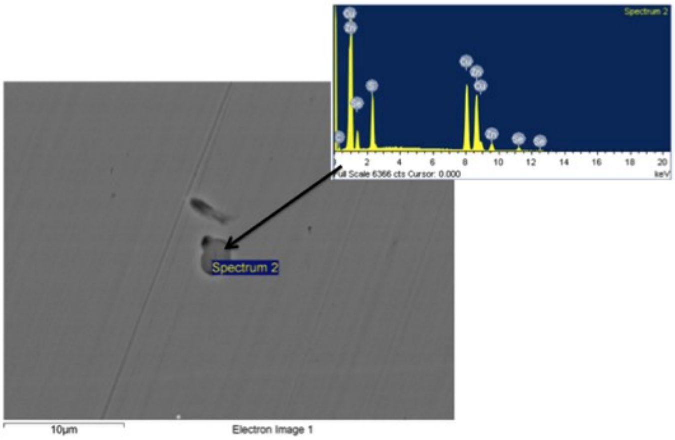


(a)

Element	Weight%	Atomic%
C K	2.44	11.59
O K	0.57	2.03
Cu K	62.65	56.35
Zn K	34.35	30.03
Totals	**100.00**	

(b)

Fig. 4 – SEM backscattered electron image of the alloy indicated by pink square (*Spectrum 1*), together with the corresponding EDS spectrum; (b) average composition of the area in Fig. 4a (measured by EDS). The contents of Cu and Zn are highlighted in Fig. 4b



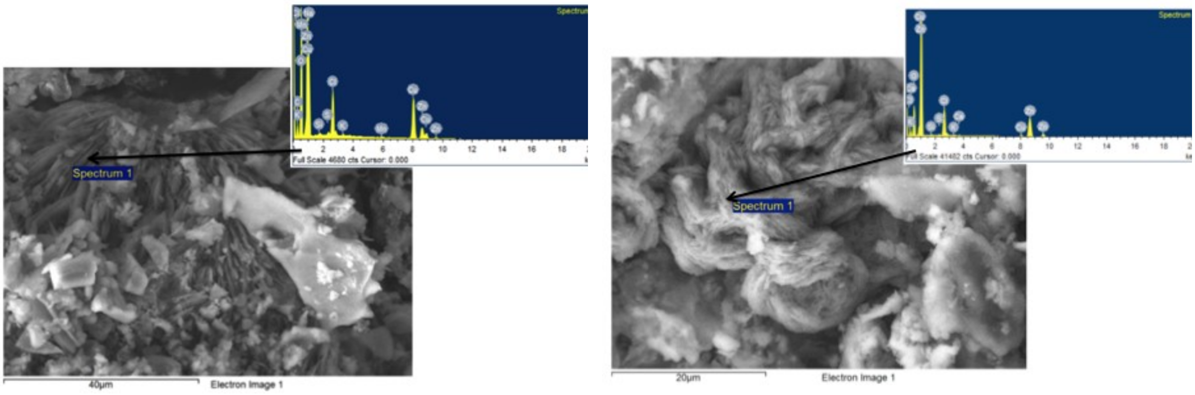
(a)

Element	Weight%	Atomic%
C K	12.17	40.42
S K	9.38	11.66
Cu K	36.53	22.92
Zn K	36.60	22.32
Se K	5.32	2.69
Totals	**100.00**	

(b)

Fig. 5 – SEM backscattered electron image of an inclusion, indicated by a black arrow (*Spectrum 2*), together with the corresponding EDS spectrum; (b) average composition of the analysed point in Fig. 5a (measured by EDS). The contents of S and Se are highlighted in Fig. 5b.

The SEM image of the greenish surface compounds together with the corresponding EDS spectrum is reported in Fig. 6. Because of the small amount of products on the surface, it was not possible to take samples and to carry out specific analyses like XRD or Raman spectroscopy. First of all, the morphologies in Fig. 6a and 6b are very different. It should be noted that the needle-like or lamellar structure shown in Fig. 6a is frequently observed in copper carbonate compounds. This evidence is supported by SEM-EDS analysis. On the contrary, the same technique would suggest that the compounds of Fig. 6b are probably zinc oxychloride.



(a) (b)

Fig. 6 – Representative SEM images of the morphology of surface greenish compounds, together with corresponding EDS spectra.

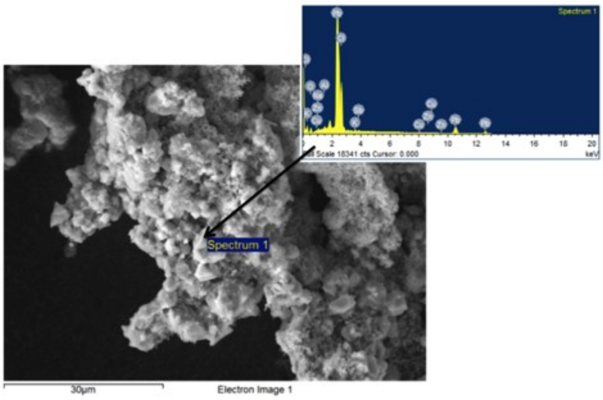


Fig. 7 – Representative SEM image of the morphology of surface whitish compounds, together with corresponding EDS spectrum.

Fig. 7 is a representative SEM image of whitish compounds, which are mainly collected in proximity to the overlaid sheets. The EDS spectrum emphasises high concentrations of Cl and Pb. In particular, the latter element is totally absent in the alloy and it is possible that it is not produced by natural corrosive processes.

II.4 Concluding observations

The present work has proved the usefulness of an interdisciplinary approach to clarify some general aspects about the manufacturing process and the state of conservation of metal artefacts.
Macroscopic examinations have highlighted a good state of conservation of the sculpture and a manufacturing process consistent with the reliquary Kota art.
Observations by optical microscopy (OM) have established that the sculpture was obtained by a casting and was subsequently subjected to alternate hammering and annealing stages.

SEM-EDS analysis has highlighted that the artefact was produced by a Cu-Zn alloy, with an amount of the latter elements comparable to those that could can be found in modern brasses (i.e. “Yellow Brasses”). The absence of alloying elements and the presence of rare Se inclusions bear witness to an advanced manufacturing process and this suggests that the artefact was obtained by a rather recent recast. Finally, the chemical analyses of greenish and whitish surface compounds lead to the assumption that they are only in part related to natural corrosive processes.

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Article III

An attempt to dating two Benin plaques by quantitative analyses and lead isotope measurements

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Abstract

Two metal plaques belonging to a private collection, stylistically consistent with the Royal art of Benin (Nigeria) were investigated to characterise the alloys and to evaluate the production period.
The characterisations of the alloys and patinas were carried out by optical microscopy (OM), scanning electron microscopy (SEM) equipped with an energy dispersive microprobe, X-Ray diffraction spectrometry (XRD), inductively coupled plasma mass spectrometry (ICP-MS) techniques. Furthermore, thermal ionisation mass spectrometry (TIMS) was used to assess the abundances of lead isotopes and to attempt a dating by the measurement of ^{210}Pb.
Both artefacts were mainly consisted of slightly leaded brass alloys (Cu ≈ 65-70 wt.%, Zn ≈26–29 wt.%, Pb ≈2–3 wt.%) with low concentrations of tin, nickel, iron and manganese. Moreover, the presence of relatively high concentration of aluminium, cadmium and antimony should be regarded with suspicion about the authentication of the plaques.
The microstructures of both artefacts were constituted of cored alpha solid solution, typical of as-cast brasses and also characterised by the presence of recrystallized non-homogeneous twinned grains in the areas corresponding to surface decoration. This was due to multiple hammering steps followed by partial annealing treatments.

The corrosion products were the same on both plaques and the patinas mainly consisted of copper and zinc oxides together with a non-continuous layer of sulphur-containing contaminants and chloride-containing compounds probably due to the interaction with outdoor environment.

An attempt to dating the artefacts using the measurement of ^{210}Pb/^{204}Pb ratio was proposed and the obtained results were compared to those collected by quantitative alloy analyses. Therefore, all the results suggest that both objects are not coherent with the features of ancient Benin plaques.

III.1 Introduction

In this work, two metal plaques belonging to a private collection, stylistically consistent with the Royal art of Benin (Nigeria) were investigated in order to evaluate the production period by identifying the alloys' chemical composition and microstructure.

According to oral tradition, the plaques were first produced in the early XVI century, during the period of Portuguese contact with Benin [1]. As decorations for the halls of the king's palace, the plaques were designed to proclaim and glorify the prestige of the king together with the ceremonial life of the court [2].

In 1897, during punitive expedition against the kingdom of Benin, the British removed many of the plaques and other manufactures from royal palace and a large number of the artefacts were sold in Europe at government auction to dealers, private collectors and museum [3].

During XIX century, objects from Africa have obtained much attention because of the tendency to consider them as ethnographic material useful for comparative insights into earlier phases of mankind's development [4].

For this reason, in the last thirty years, the proliferation of fakes in Benin arts was dramatically increased [5-8] and it was necessary to establish scientific methodologies in order to provide the authentication of artefacts.

Although direct dating of metals was not possible, there was some approaches to figure out if a Benin metal object was original or not: thermoluminescence analysis (TL), lead isotopes analysis (^{210}Pb) and the analysis of trace and main elements [9].

In the beginning, TL was applied for the analysis of ancient pottery, but other materials were suitable for this dating, such as cores from lost wax metal castings. In general, the core is constituted of a mixture of clay and charcoal eventually trapped inside the castings and from which it is possible to obtain TL dates [10].

The clay core of Benin objects was traditionally removed from the reverse side of plaques; therefore, an attempt to date the artefacts by TL is generally impossible [9].

Another dating method, named lead isotopes analysis, was used in archaeological and geological fields in order to provide answers to a number of questions since the late 60s. In particular, lead isotopes may be used as fingerprint of the ore deposits, but could also be applied to ascertain if a metal object is ancient or not.

The first work about dating metals by lead isotopes was proposed by Keisch in 1968 [11, 12], but the experimental procedure was described in details years later, by Pernika *et al.* [13]. The analytical technique is based on natural radioactivity of lead isotopes, in particular of ^{210}Pb, which has a very short life time (22,3 years). Dating assumptions of the metal objects were ascertained by the detection of this isotope; in particular, the absence of it could indicate that the artefact was produced in the last 100 years

[9]. However, it should be noted that the absence of ^{210}Pb is not necessarily the proof of authenticity because an ancient metal could be used to produce a forgery in modern times [11].

Several studies have reported that the analysis of trace and the main elements could be used as a dating tool because of the changes in elemental compositions [9, 14, 15]. In particular, some elements with their presence and amounts could be the fingerprints of specific historical times.

A mean role is played by the trace elements because they came into the metal as natural impurities, such as iron, nickel, bismuth and so on; on the other hand, they were intentionally added in order to in improve the features of the alloys, like aluminium, phosphorous and silicon. In particular, some intentional added elements are in general not part of modern alloys or they were used in totally different amounts. For this reason, the production period of the artefacts could be evaluated by the combination of the results obtained by all these analyses in order to establish the authenticity of the objects.

In this paper, the results of investigations on the alloys microstructures and on the corrosion products of two Benin plaques are presented. In particular, the combination of conventional metallography and chemical analyses were used for determining manufacturing procedures and evaluating the authenticity of the plaques.

Moreover, an attempt to dating the artefacts by employing the measurement of $^{210}Pb/^{204}Pb$ ratio was proposed and the obtained results were compared to those collected by quantitative alloy analyses in order to ascertain the effectiveness of the different authentication method.

The characterisation of the alloys and patinas was carried out by optical microscopy (OM), scanning electron microscopy (SEM) equipped with an energy dispersive microprobe, X-Ray Diffraction spectrometry (XRD), inductively coupled plasma mass spectrometry (ICP-MS) techniques. Furthermore, thermal ionisation mass spectrometry (TIMS) was used to assess the abundances of lead isotopes.

(a) (b)

Fig. 1: Macroscopic images of the two plaques: (a) two figures that are kneeling on sides of a central figure armed with a weapon; (b) king of Benin (Oba) on horseback with three attendants.

III.2 Material and methods

The two investigated plaques are shown in Fig. 1a and 1b; in particular, small static groups arranged around a central figure are portrayed in both artefacts. The first one (Fig. 1a), called *"axe"*, depicts two attendants kneeled on the both sides of a central figure armed with a weapon, whereas in the second one, briefly named as *"horse"*, king of Benin (Oba) on horseback with three attendants are portrayed (Fig. 1b).

Most of the investigations were carried out on four fragments collected from the backside of each plaque. Two fragments from both plaques were mounted in conductive resin in the longitudinal section (observed in the direction of the metal surface), polished and prepared by emery papers, polished down to 1 μm diamond spray. Then the surfaces were etched by $FeCl_3$/HCl, diluted in ethanol and then the samples were submitted to conventional metallographic observation using LEICA MEF4M optical microscopy (OM). The fragments were observed in cross section in order to investigate the stratification of corrosion products and composition of the alloys by using a ZEISS EVO MA 15 scanning electron microscope (SEM), coupled with energy dispersion spectroscopy (EDS) and through Inductively Coupled Plasma Mass Spectrometry (ICP-MS), after acid digestion for major and trace elements. In particular, the elemental composition and distribution of major and trace elements were determined by laser ablation system (LSX-200+, CETAC, USA) coupled to inductively coupled plasma mass spectrometer (ELAN 9000, Perkin Elmer SCIEX, Canada). An LSX-200+ system at 266 nm UV laser (Nd-YAG, solid state, Q-switched) with maximum energy up to 6 mJ/pulse and pulse repetition rate from 1 to 20 Hz with a viewing CCD camera system was used for laser ablation.

The identification of corrosion powders was also carried out by X-Ray Diffraction (XRD) with Cu Kα radiation source, a 40 kV accelerating voltage and a 40 mA filament current. The 2θ scans were collected from 8° to 90° with a 0.02° step size and a 10 s dwell time.

To assess the presence of ^{210}Pb, a standard chemical procedure to separate lead from matrix was set up by an ion-exchange separation technique. The measurements were performed by Finningan Mat 262 multi-collector Thermal Ionization Mass Spectrometer (TIMS) on both standard NIST SRM 981 and on two samples of the plaques in order to correct isotope fractionation. Data acquisition follows a strict procedure: filament is heated for 15 minutes at a rate of 100 mA/minute, then at a rate of 30 mA/minute until filament temperature reaches 1100 °C and a current around of 2200 mA. Subsequently, filament heating is stopped and data acquisition starts after that the signal slowly decreases. The ion beam of each mass number was collected by a fixed Faraday cup. Filament heating time is approximately 30 minutes and data acquisition time is about 35 minutes for each measurement.

III.3 Results and discussion

III.3.1 Alloy compositions

The alloy compositions of the two plaques measured by ICP-MS and by SEM/EDS analyses are reported in Table 1 and in Table 2, respectively. It can be noted that both artefacts were mainly consisted of slightly leaded brass alloys (Cu ≈ 65-70 wt.%, Zn ≈26–29 wt.%, Pb≈2–3 wt.%) with low concentrations of tin, nickel, iron and manganese.

It is well-known that the majority of the “Benin bronzes” were constituted of brass also named gunmetal, a ternary Cu–Zn–Sn alloy together with lead.

From the antiquity to XVI century A.D., brass was produced by the reduction of zinc ore at around 1000°C and the diffusion in metallic copper (cementation process). The process was then completely abandoned in the middle of XIX century A.D. [22]. Several studies on cementation process reported as threshold for ancient brass the limit of 28 wt.% in zinc content [23-25].

For the horse plaque, the amount of zinc is slightly above the limit of 28 wt.%; conversely, for axe plaque, the zinc content is around 25 wt.%. However, in the latter case, it is not possible to provide the authenticity of the object only considering this parameter.

The Benin Kingdom brasses of the late period were characterised by low concentrations of tin and arsenic. Below 5 wt.%, small amounts of lead were generally due to the copper or zinc ores and it was not represented a deliberate addition in the alloy to improve the features of the molten metal [16].

Moreover, a low tin content might be due to the use of tin-containing ores [17] whereas the presence of small amounts of iron and nickel was probably ascribed to poor smelting condition.

The presence of aluminium and manganese was meaningful, since most brasses produced in the XX century were characterised by small amounts of these lithophile elements and should be clear indicators for modern industrial alloys [13, 18]. In particular, aluminium in the range of 0.2–0.7 wt.% was added to promote castability, to reduce zinc evaporation and to improve the mechanical resistance of the alloy [19]. Moreover, the corrosion resistance could be improved by the presence of aluminium and the surface metal tended to become homogeneous and smooth [20].

It can be noted that aluminium was also one of the main components of clayey soils together with iron and silicon [21] and its presence into the alloys could be due to the interaction with the mould wall for as-cast objects.

In the case of studied fragments, the presence of aluminium in the samples, where ICP-MS analysis was made, might be explained by a non-completely removed soil compounds. However, SEM/EDS analysis was carried out on core metal where environmental contamination cannot take place and aluminium was still detected.

For this reason, it is possible to presume that aluminium was added to both alloys on purpose, suggesting that the artefacts were produced in modern time because of the relatively recent addition of aluminium in metal alloys [19].

Table 1: Composition of the alloys (measured by ICP-MS, weight%) of fragments collected from the backside of the two plaques.

Plaque	Sb	As	Al	Cd	Mn	Fe	Ni	Pb	Sn	Cu	Zn
Axe	0.004	-	0.54	0.004	0.45	0.35	0.44	2.34	0.17	69.99	25.72
Horse	0.05	0.006	0.25	0.002	0.18	0.19	0.25	3.46	1.54	65.00	29.01

Table 2: Semi-quantitative elemental composition of the alloys (measured by EDS, weight%) of a wide area (1.0 x 0.5 mm^2) of one fragment collected from the backside of the two plaques.

Plaque	O	Al	Mn	Fe	Ni	Pb	Sn	Cu	Zn
Axe	1.15	0.51	0.36	0.57	0.56	1.77	2.19	66.19	26.71
Horse	1.29	0.49	0.24	0.27	0.46	1.16	1.76	64.34	29.97

The concentrations of trace elements were also important in the attempt to dating Benin brass objects because of the variation of their amounts in the alloy during historical time. For example, the elder objects are characterised by high amounts of trace elements [9].

As can be seen in Table 2, the amount of antimony is below 0.05 wt.%, whereas arsenic and cadmium are barely detectable (less than 0.005 wt.%). In particular, if the antimony content is below 0.1 wt.%, or even less 0.05 wt.%, this is a reliable argument for a manufacture of a later object [9]. Moreover, with regard to cadmium, it was a typical trace element, which came into brasses because of modern technologies of zinc production. In according to [9], Benin brasses from the XIX century were characterised by the cadmium concentration above 0.002 wt.%.

Therefore, the identification of high concentration of zinc, cadmium and antimony suggested that the alloys are coherent with modern material compositions. In general, it is noteworthy that a broad variety of alloys was used for casting Benin plaques during historical time, reflecting the habit of the smiths to cast whatever metal was easily to hand [14].

III.3.2 Alloy microstructures

Different microstructures of the two artefacts are reported in Fig. 2. In particular, both plaques are constituted of a cored alpha solid solution, typical of as-cast brasses as a result of zinc content lower than the solubility limit (about 35 wt.% Zn) in copper [26]. Tin-rich phase together with lead globules precipitates in the interdendritic spaces are visible in Fig. 2a and in Fig 2b, after chemical etching. In Fig. 2c the surface microstructure of both plaques is characterised by the presence of recrystallized non-homogeneous twinned grains in the areas corresponding to surface decoration. This microstructure is probably due to repeated cycles of hammering and annealing in order to outline the details of adornments and to restore workability and toughness of the metal [27].

(a) (b) (c)

Fig. 2: Optical images of plaques' microstructure: (a) Cu-Zn-Sn interdentritic phase together with some metallic lead (insoluble in copper) on polished surfaces; (b) dendritic structure on etching surfaces; (c) non-homogenous grains structure with thermal twin bands on etching surfaces.

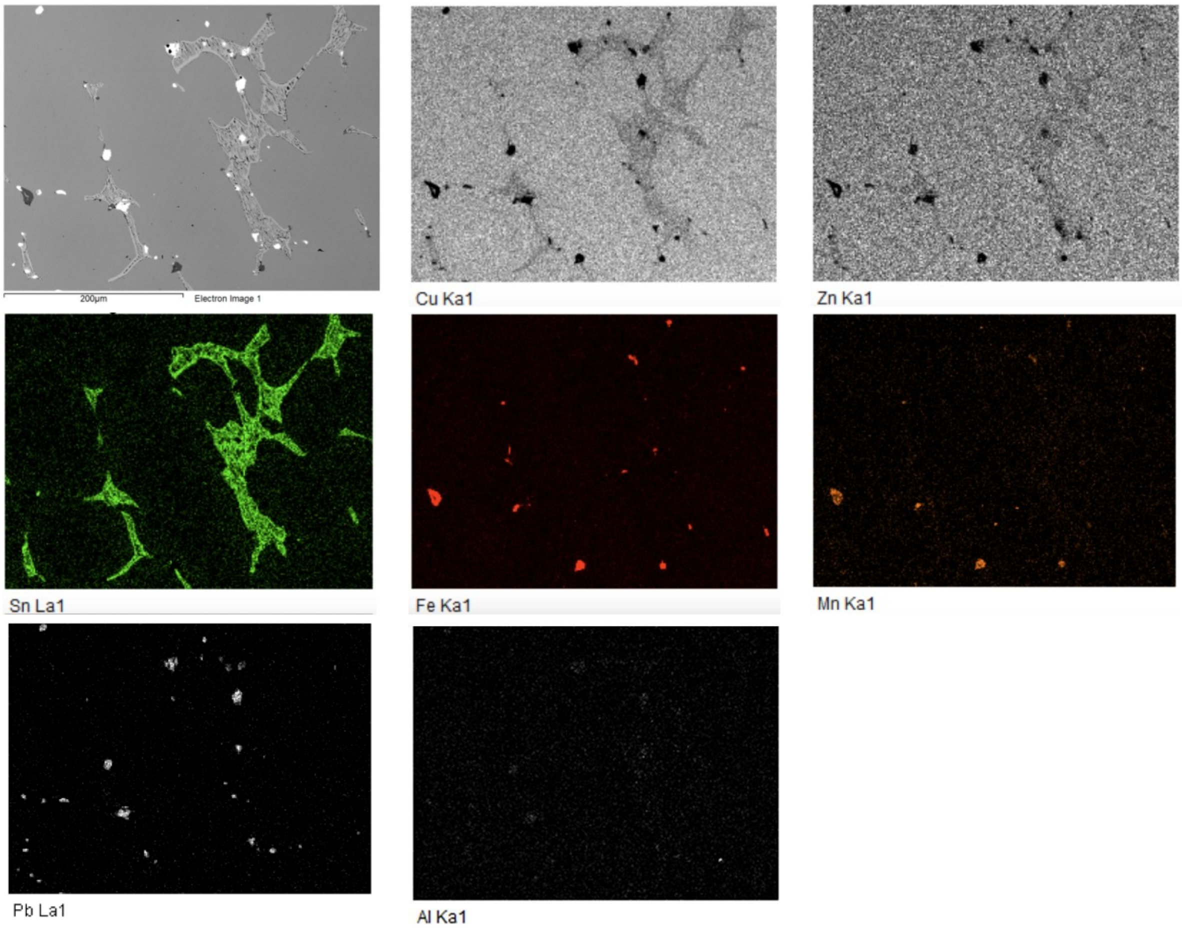

Fig. 3: SEM image and X-ray maps of elemental distribution in "axe" plaque (longitudinal section).

As an example, X-ray EDS maps in Fig. 3 show the elemental distribution in the "*axe*" plaque. In particular, it can be noted that the non-metallic inclusions, mainly consisted of lead and iron-manganese, are preferentially located in the interdendritic spaces. The intermetallic phases are characterised by hardness significantly higher than the alloy matrix and this feature could decrease the technological properties of the objects, such as machinability and corrosion resistance [28].

The EDS maps also show that aluminium is almost completely dissolved in the matrix, as already observed when discussing alloy composition (*Section 3.1*). Moreover, tin is also detected in interdendritic areas as a result of micro-segregation phenomena [29].

III.3.3 Characterisation of the corrosion phenomena

It is noteworthy that the stratification of corrosion products detected on both plaques is the same.

As an example, Fig. 4 shows SEM/EDS mapping of the cross section of the axe plaque. The thin layer of corrosion products is highlighted. In particular, a layer of copper compounds, probably cuprous oxide, very close to the metal surface was identified.

The thin copper-rich layer at the metal/corrosion products interface could highlight that the dezincification process did not occur to a significant extent and the cross section also do not show any sign of corrosion attack below the surface, towards the core metal. In general, the dezincification process was caused by a selective dissolution of zinc and followed by a specific deposition of copper on the metal surface.

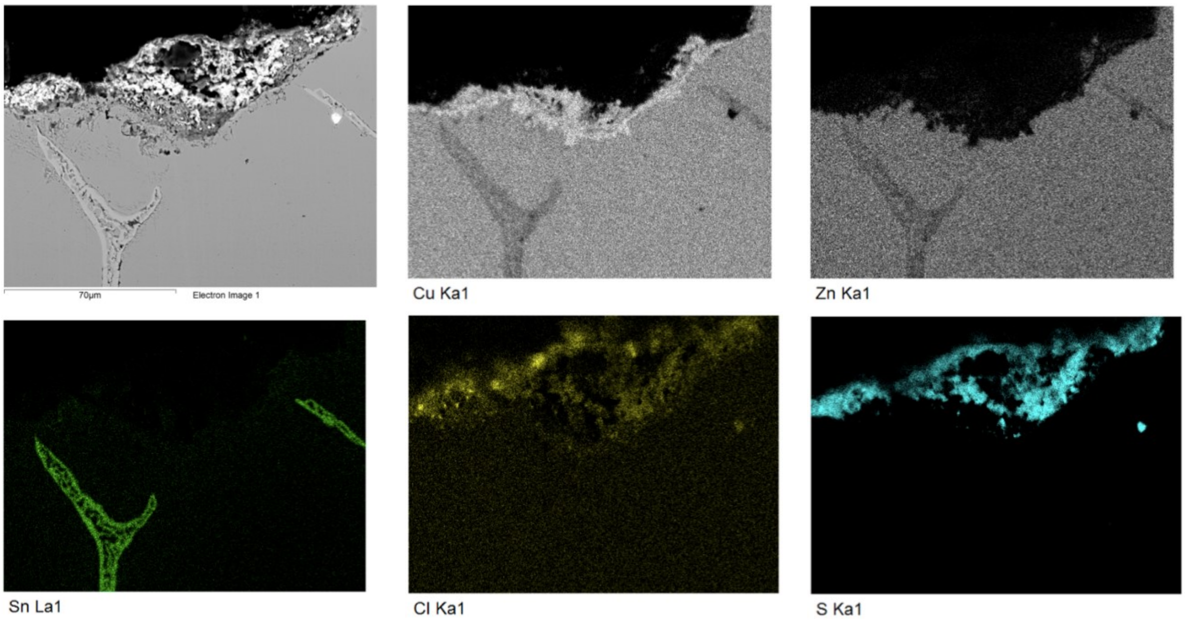

Fig. 4: SEM image and X-ray maps of elemental distribution on the patina cross section of axe plaque.

Furthermore, in this case, dezincification was probably prevented by the presence in the alloy of elements such as Sn, which are known to inhibit this kind of corrosion attack [33].

Sulphur, which could have both an endogenous (from inclusions) and exogenous (from soil) source, is also detected in a few points above the copper compounds layer. Moreover, small chlorine amounts non-uniformly distributed on the artwork surface are also identified.

Several studies reported that original Benin objects were generally placed outdoor [13], so the surface corrosion was caused by the interaction with the environment. In particular, the metal surface was characterised by compounds typically consisted of sulphur-containing contaminants or chlorine-containing species which were strictly dependent on the local atmospheric compositions [30-32].

The corrosion layer on both corrosion powders collected from inlaid regions of the decorations, was identified by XRD (Fig. 5) as mainly consisted of copper and zinc oxide, in particular tenorite (CuO), cuprite (Cu_2O) and zincite (ZnO).

In general, corrosion layer of a brass surface could be constituted of copper oxides together with copper chlorides and sulphates, which occurs in natural archaeological patinas in outdoor environments [13, 34]. In particular, cuprite (Cu_2O) and tenorite (CuO) can simultaneously exist at Eh values of 0.2 mV and at pH equal to 9 [36, 37].

On the other hand, tenorite is a rare component of natural patinas. However, the authors founded this alteration product in a previous work, dealing with an Achaemenid bronze bowl [38]. In particular, this artefact was characterised by a complex corrosion layers, produced during burial, with the surprising substitution of cuprite by tenorite layer. For kinetic reasons this oxide is quite rarely present in comparison to cuprite, even if the Pourbaix diagram predicts tenorite stability in a wide potential/pH region. In [38], authors suggested its presence could be due to a heating treatment or to an intentional patination process, applied for aesthetical reasons.

Zincite is completely unknown before the work of E. Pernika *et al.* [13, 30, 35]. Such compound could be preserved on the surface plaques since it was collected from inlaid regions in which the leaching process was inhibited.

Nevertheless, the presence of a low corrosion rate and the absence of artificial patination, which raised suspicion in their self, are not enough to state if the original patina was removed or if the artefacts were preserved.

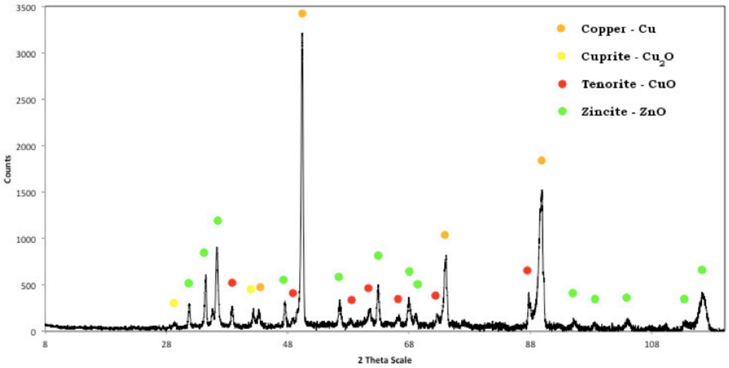

Fig. 5: Representative XRD spectrum of the corrosion products on horse plaque.

III.3.4. An attempt to compare ^{210}Pb and ICP-MS analyses

In archaeology, different analytical methods can be used in order to carry out the acquisition of lead isotopic data; in particular, thermal ionisation mass spectrometry (TIMS) was the first and only method used in this kind of measurements until the introduction of inductively coupled plasma mass spectrometry (ICP-MS) which afforded to investigate smaller samples [39].

In the present work, thermal ionisation mass spectrometry (TIMS) was used to assess the lead isotopic abundance contained in the two plaques. The results were shown in Table 3.

It is important to note that the results are reported in form of ratios between the three different lead isotopes ^{206}Pb, ^{207}Pb, ^{208}Pb and ^{204}Pb, the only one that is a non-radiogenic isotope. In fact, ^{206}Pb, ^{207}Pb, ^{208}Pb lead isotopes are formed by the well-known natural decay of uranium and thorium; conversely, the ^{204}Pb may be attributed entirely to common lead and it can be used like an index of lead impurity in the sample [40, 41].

The first application of this dating technique is the measurements of mineral age, such as meteorites and terrestrial rocks [42]. However, the intermediate members of the decay (e.g. ^{210}Pb and ^{214}Pb) are usually ignored for these studies because of their relatively short-lived [43].

The first discussion and analyses of dating metal artefacts emerged during 1960s with B. Keisch [11,12]. In particular, the author noted that it is possible to estimate the age of metal objects by determining the concentrations of ^{210}Pb and ^{226}Ra. In a nutshell, B. Keisch highlighted that the radioactive equilibrium between these isotopes can be disrupted during the extraction of lead from its ore and a stable situation can be restored by the decay of ^{210}Pb (around 22 years). For this reason, if an amount of ^{210}Pb is detected in studied samples, it is likely that the object is produced in the last 100 years; conversely, the absence of ^{210}Pb could indicate that the artefacts are older than a century [9].

Whilst some research was carried out in the past on using this technique, no recent studies established probably because of the difficult and expensive data acquisition method. In this work, the measurement of $^{210}Pb/^{204}Pb$ ratio is proposed to dating artefacts; in particular, the obtained results are first compared to those collected by ICP-MS quantitative alloy analyses and then compared to extensive database in literature [9]. It should be specified that the data are achieved by the same procedure used for determining the other ratios.

As shown in Table 3, a small amount of ^{210}Pb was ascertained in the axe plaque, whereas no detectable value was obtained for horse plaque. Even if it is not the main aim of this work, it is important to note that the values of ratios between the three different lead isotopes ^{206}Pb, ^{207}Pb, ^{208}Pb and ^{204}Pb are almost the same for both artefacts; moreover, the values are comparable to those obtained by W. Snoek *et al.* [44], which studied some copper-alloy archaeological artefacts from Tell Ahmar (Syria).

Notwithstanding the different isotopes acquisition method used to dating the plaques, the results are endorsed to those obtained by ICP-MS quantitative alloys analyses and they are comparable to those proposed by J. Riederer in his extensive Benin artefacts database [9]. Therefore, all the results suggest that both objects are not coherent with the features of ancient Benin plaques. The collected data could be indicative of brasses produced maybe shortly before or after 1900 A.D.

Table 3: Isotopic abundances (ratio in percent) obtained by TIMS.

Plaque	$^{208}Pb/^{204}Pb$	±	$^{207}Pb/^{204}Pb$	±	$^{206}Pb/^{204}Pb$	±	$^{210}Pb/^{204}Pb$	±
Axe	38.306	0.038	15.694	0.012	18.181	0.009	**0.000207**	**0.000043**
Horse	38.305	0.038	15.684	0.012	18.259	0.009	**n.d.**	**n.d.**

III.4 Conclusions

In this study, the combination of conventional metallography with chemical analyses of the alloys and corrosion products were used to assess the authenticity of the artefacts.

First of all, the microstructures are not fully homogeneous because of the manufacturing process but they are compatible with typical as-cast brasses which were subjected to repeated cycles of hammering and annealing. Moreover, the results highlight a few points which raise suspicion about the authenticity of the plaques:

∴ Both artefacts are consisted of slightly leaded brass alloys with low concentrations of tin, nickel, iron and manganese. The high concentration of zinc (above 20 wt.%), an amount of antimony exceeding 0.1 wt.% and a cadmium content higher than 0.002 wt.% suggest that the alloys are coherent with modern brass compositions.

∴ On both plaques the same corrosion product stratifications are detected. In particular, the patinas are characterised by a layer of tenorite (CuO), cuprite (Cu_2O) and zincite (ZnO). Moreover, a non-continuous layer of sulphur-containing contaminants and chloride-containing compounds are also detected. The corrosion layer of a brass surface could be constituted of copper oxides together with copper chlorides and sulphates, which occurs in natural archaeological patinas in outdoor environments. Nevertheless, zincite is completely unknown as corrosion compound and it could be preserved on the surface plaques since it was collected from inlaid regions in which the leaching process was inhibited. On the other hand, tenorite is a rare component of natural patinas and its presence could be linked to a heating treatment or to an intentional patination process, applied for aesthetical reasons. Finally, the presence of a low corrosion rate and the absence of artificial patination, which raised suspicion in their self, are not enough to state if the original patina was removed or if the artefacts were preserved.

∴ In this paper, the measurement of $^{210}Pb/^{204}Pb$ ratio is proposed to dating artefacts. The obtained results are consistent with those collected by ICP-MS quantitative alloys analyses and comparable to existing literature. In particular, the collected data are indicative of brasses produced shortly before or after 1900 A.D.

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Article IV

Characterization of gilded bronze corrosion behaviour during exposures to simulated outdoor environment

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Abstract

This paper presents some of the results obtained during a research project dealing with the conservation of bronzes and gilded bronzes by both preventive methods (e.g. microclimate control) and active methods (e.g. application of protective treatments/inhibitors). In particular, the wet & dry (stagnant rain) and dropping (runoff) techniques were used to simulate outdoor corrosion exposures.

The stratification of the corrosion products after accelerated ageing was evaluated by using spectroscopic and micro-spectroscopic techniques (FIB-FEG/SEM and SEM/micro-Raman) and it was possible to observe that this stratification was comparable to that detected on real artefacts.

Before and after silane coating application, measurements were performed on the surfaces by a "contact probe" coupled to EIS technique, so as to monitor corrosion rates during wet & dry (W&D) exposure.

The results were compared to the measurements obtained by the traditional three electrode cell. It was found that the corrosion rate assessed by the contact probe was underestimated, especially in the absence of silane-pre-filming treatment.

IV.1 Introduction

Bronzes and gilded bronzes represent an important part of our cultural heritage and their conservation has several economic and cultural implications.

The corrosion process is the most common form of bronze degradation [1]. Bronze artefacts exposed outdoors tend to react with the environment and corrosion products layers cover spontaneously their surfaces. Under some circumstances, the patina protects the alloy and changes pleasantly its colour, but usually the patina is very unstable (e.g. in many urban environments) and cannot avoid the formation of bulky corrosion products [2-6].

These phenomena are particularly critical in the case of gilded bronzes because in correspondence of the gold discontinuities (pores and defects) the corrosion of the bronze substrate starts and goes on, galvanically stimulated by the contact with the large noble gold area. The consequent growth of an interlayer of corrosion products between bronze and gold can cause the detachment of the gilded layer [6-8].

Since ancient times different techniques were used to produce gilded decorations, such as mechanical application of a thin layer of gold [9], use of adhesive materials [10] or the fire-gilding technique [10-11].

The gilded layer defects are due to the discontinuities on gilded sheets or, in other cases, to the deterioration of organic adhesives used to bond the layer to the metal or to inefficient burnishing [9-11]. Several works have reported that the presence of unstable corrosion products at the metal/gold interface are indicative of active corrosion processes [6, 12, 13] which require continuous delicate restoration works.

The study of degradation processes and their mechanisms favours the development of appropriate strategies that can be used to protect the artefacts and stimulate their valorisation.

In order to determine these strategies, it is important to get a deeper knowledge of the corrosion phenomena on the metal surfaces and to test new protective treatments and new methodologies on representative substrates developed in laboratory.

A continuous monitoring of surface corrosion products by non-invasive and *in situ* techniques is certainly recommended.

Electrochemical Impedance Spectroscopy (EIS) is seldom used in cultural heritage conservation studies, although it is widely adopted in industrial fields to study corrosion processes and protective treatments for metallic alloys. Recently, many studies evidenced that EIS can be also effective in monitoring corrosion phenomena on metallic cultural heritage assets and in the patina characterisation on artistic objects.

The cell geometry and the choice of the electrolyte in contact with the metal surface are very important aspects of in situ EIS measurements. For this reason, some studies explored the possibility to use gel-solution electrolytes [20] or electrolytes flowing in contact with the metal surface due to capillary forces [15-17] or investigated the possibility to adopt commercial electrocardiogram electrodes [18-19]. However, all these new solutions still require deeper fundamental investigations in order to improve the data modelling and their interpretation.

In this paper, the gilded bronze corrosion behaviour was investigated during both wet & dry and dropping exposure to concentrated acid rain (simulating conditions of stagnant rain or direct runoff, respectively). Under W&D conditions, the corrosion behaviour was monitored by a contact probe and the results were compared to those obtained by a traditional three electrode cell.

IV.2 Experimental

IV.2.1 Materials

The studied materials were a typical historical sculpture alloy (Cu, Sn, Zn, Pb) covered or not by a gilding layer. The bronze microstructure and composition are reported in Fig. 1a and in Tab. 1, respectively.

The gilded bronze was produced by the procedure used during the Italian Renaissance and clearly described by Benvenuto Cellini (1568) [21]. In particular, after mechanical polishing and acid pickling, the substrate was covered by an amalgam of gold and mercury (the Au/Hg ratio was 1:8). The amalgam of gold was uniformly applied on the metal surface and then it was heated by a flame to induce the mercury sublimation. The gold layer was then burnished by an agate tool, in order to obtain a smooth dense surface layer. The microstructure and composition of this layer are reported in Fig. 1b and in Tab 2, respectively.

Before testing, the surface of the bronze specimens was prepared by emery papers, polished down to 1 µm diamond spray, washed with deionized water and degreased with acetone; whereas the gilded bronze was only washed and degreased.

A silane-based compound, 3-mercapto-propyl-trimethoxy-silane (PropS-SH), was used as a protective treatment on some bronze and gilded bronze samples. Coupons were completely immersed for 1 h into a hydrolyzed silane solution (90/5/5 ethanol/water/PropS-SH %vol) at pH 4 (pH adjusted by sulphuric acid addition) and then a room temperature curing period of 10 days was adopted before exposing the pre-filmed specimens to the testing.

Tab. 1: Bronze composition (%wt.).

Cu	Sn	Zn	Sb	Pb	Ni	Other
88.5	5.5	3.6	0.4	0.8	0.9	traces

Tab. 2: Gold layer composition (%wt.) on gilded bronze.

C	Sn	N	Cu	Au	Hg	Other
7.1	4.4	1.8	1.0	78.3	7.2	traces

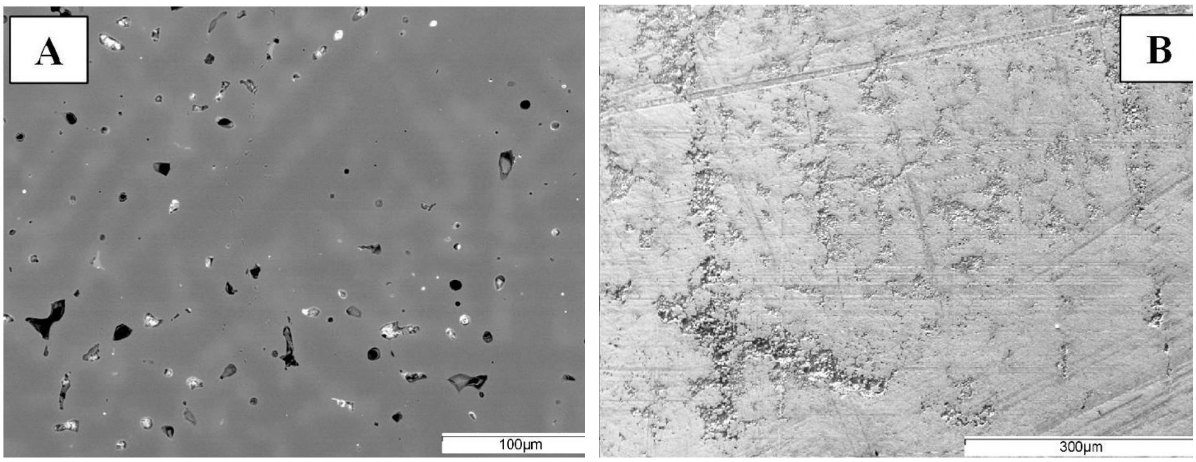

Fig.1 - Microstructure of the studied materials (BSE images obtained by SEM): A) Bronze; B) Gilded bronze.

IV.2.2 Accelerated ageing and characterisation of bronze corrosion

Bronze and gilded bronze were subjected to accelerated ageing under both wet & dry (stagnant rain) and dropping (runoff) conditions in order to assess the rate and morphology of the corrosion attack under conditions simulating real outdoor exposures.

The aggressive solution was a tenfold concentrated artificial acid rain that reproduced the average composition of natural winter rains collected in Bologna (Italy) [24].

The duration of one wet & dry corrosion cycle was 1 h (20 min of immersion and 40 min of emersion). Considering a time of about 20 min for the samples to get dry, a reasonable time of wetness (TOW) of 40 min per hour was assumed. The W&D tests took 15 days, for a total of 10 days of TOW.

The atmospheric exposure in unsheltered conditions was simulated through the dropping test: the artificial rain was periodically dropped onto the surface of the samples, alternating wetting and drying conditions. In particular, one-week cycle consisted in 2-days dropping/1-day drying/3-days dropping/1-day drying.

The morphology and the composition of surface samples were characterised before and after corrosion tests by Scanning Electron Microscopy equipped with Energy Dispersive Spectroscopy (SEM ZEISS MA 15 with Oxford INCA X-Act). In particular, surface sections of the samples were produced by FIB-FEG/SEM (TFEG-SEM FEI Dual Beam Strata 235M System, with ion beam Ga^+) to gather information about the corrosion products at the metal/gold interface.

IV.2.3 Electrochemical tests

The electrochemical tests were carried out on both bronze and gilded bronze samples in order to investigate their corrosion behaviour.

Both in the absence and in the presence of a PropS-SH pre-filming treatment, the samples were exposed for 60 days to W&D conditions in tenfold concentrated artificial acid rain.

The corrosion process was monitored by a “contact probe” coupled with EIS technique and the measurements were carried out using a Potentiostat/FRA/Galvanostat (PAR 2273) under the following conditions: ±10 mV (rms) alternating potential signal, 1 MHz – 10^{-3} Hz frequency range and 10 frequencies/decade.

A layer of filter paper soaked in concentrated artificial acid rain was placed at the sample/probe interface in order to perform the measurements (Fig. 2a and 2b). The tests were started after reaching a stable potential of the working electrode (evaluated with respect to a reference AISI 316 electrode, centrally positioned in the contact probe, Fig. 2a). Stable conditions were achieved after about a 20 min delay. At the end of each EIS measurement, the potential of each sample was also measured versus a saturated calomel electrode (SCE) applied on the filter paper, after contact probe removal.

The EIS results were compared to those obtained in a traditional three electrode cell, during the wet period of the W&D exposure.

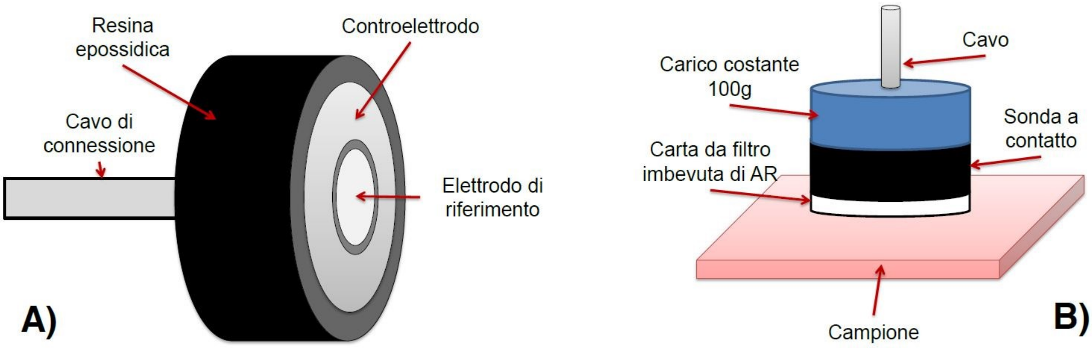

Fig. 2: EIS measurements: A) scheme of contact probe; B) cell with contact probe.

IV.3 Results and discussion

IV.3.1 Materials characterisation

The bronze specimens (Fig. 1a) showed a dendritic microstructure of cored alpha solid solution, typical of as-cast bronzes, with Pb globules and Sn- and Sb-rich precipitates in the interdendritic spaces. A residual shrinkage porosity was uniformly distributed in the samples.

The gilded bronze showed a complex surface morphology. As highlighted in Fig. 1b, uniform compact zones in the gold layer were close to other regions with a globular morphology connected to mercury evaporation, where inefficient mechanical burnishing occurred (Fig. 3a).

There, the aggressive solution can penetrate and come into contact with the metal substrate, causing localised corrosion attack.

A silane-based compound was used as a protective treatment on bronze and gilded bronze samples. SEM/EDS analyses have evidenced that on bronze the protective film was uniformly spread, whereas on gilded bronze it mainly collected in the porous zones, making more homogeneous the corrosion behaviour of gilded bronze. However, SEM-EDS analysis of the protective coatings showed that on average they are thicker on bronze than on gilded bronze, under fixed prefilming conditions (Tab. 3).

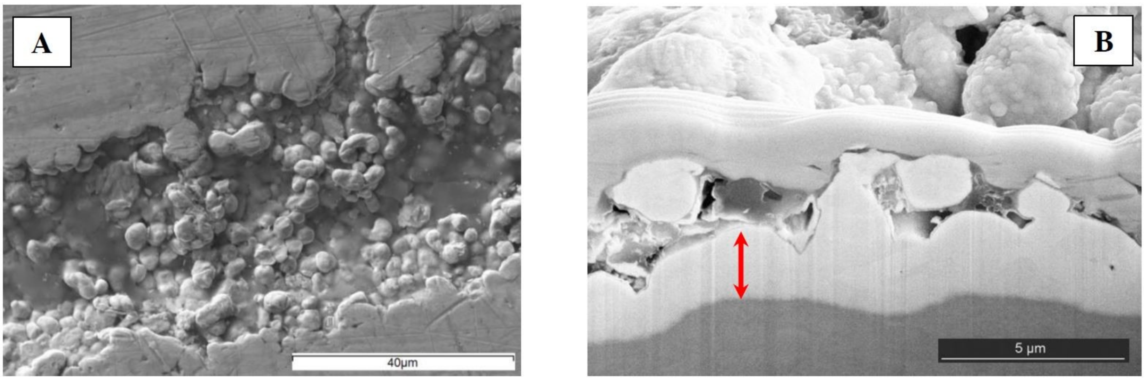

Fig. 3: Defects on the gilding layer: A) porous area; B) cross section of the porous area obtained by FIB-SEM.

Tab. 3: SEM-EDS analyses of PropS-SH films applied (%wt.) on bronze and gilded bronze.

	C	N	O	Si	S	Ni	Cu	Zn	Sn	Sb	Au	Hg	Pb
Bronze	15.3	/	10.2	3.9	2.9	0.6	60.1	2.5	3.5	0.2	/	/	0.9
Gilded bronze	9.3	2.1	8.7	1.4	2.2	/	4.3	/	0.4	/	65.5	6.1	/

IV.3.2 Gilded bronze characterisation after exposure to W&D and dropping test

The corrosion attack of gilded bronze after exposure to aggressive conditions was characterized by SEM/FIB. The cross section analyses highlighted that after already short exposure times localised corrosion forms appeared on bronze substrate in correspondence of the gilded layer defects (Fig. 4).

The damage extent was correlated to the exposure conditions: a limited number of craters were produced by W&D exposure, instead the dropping condition resulted more aggressive, as it caused several large pits filled by corrosion products.

The harmful effects of dropping were due to both the mechanical runoff action and the leaching of corrosion products induced by the dropping rain that exposed continuously new metal surface to the aggressive solution. A longer exposure produced an increase in the number and size of craters, together with the growth of a corrosion product layer at the bronze/gold interface.

SEM/EDS and micro-Raman analyses evidenced the formation of alternating layer of Cu and Sn corrosion products (Cu_2O/Sn_2O). According to the literature, this corrosion product morphology was already detected on outdoor gilded bronzes, so that it can be affirmed that the dropping exposure was representative of real exposure conditions.

Dropping tests (30 days of TOW) were also carried out on gilded bronzes protected by PropS-SH. Fig. 5 compares the corrosion attacks produced in the absence and in the presence of a PropS-SH pre-filming treatment. Corrosion products at the bronze/gold interface were visible on unprotected gilded bronze (Fig 5a), whereas the corrosion products were totally absent on gilded bronze covered by the silane film, as shown in Fig. 5b. In fact, the accumulation of PropS-SH in the porous gilded layer induced a significant increase in the corrosion resistance of gilded bronze.

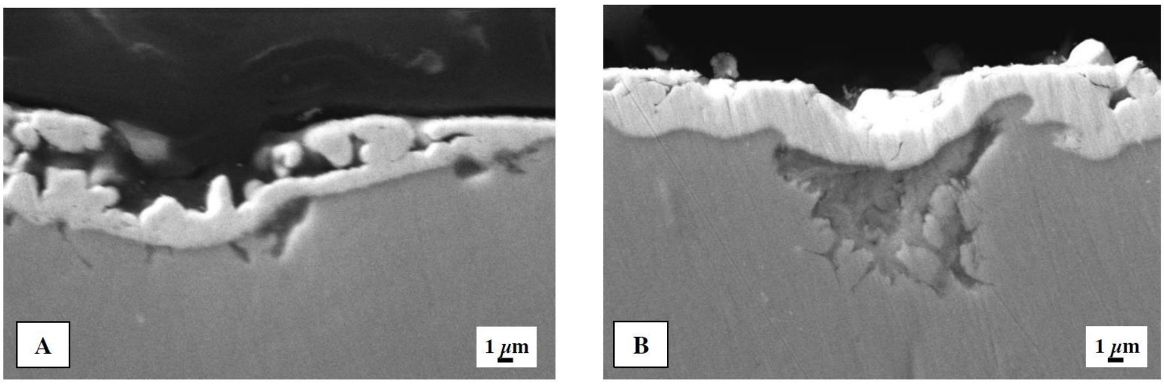

Fig. 4: Cross sections of gilded bronze after (10 days of TOW): A) W&D and B) dropping exposure.

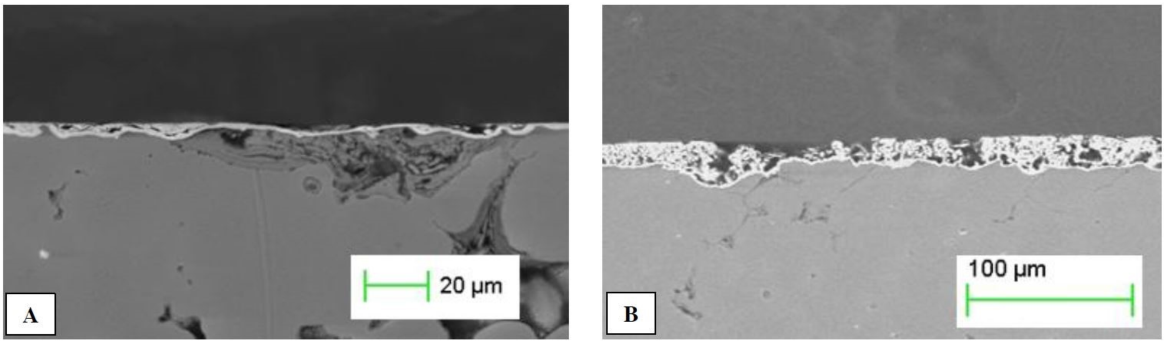

Fig. 5: Cross sections of the gilded bronze after dropping exposure (30 days of TOW): A) in absence and B) in presence of a PropS-SH film.

IV.3.3 Electrochemical measurements

EIS measurements are usually carried out in electrochemical cells of specific geometries, in the presence of aggressive solutions with well-known chemical-physical characteristics. In this paper, a special contact probe for non-destructive *in situ* measurements was applied, in order to monitor the corrosion processes.

Fig 6a shows the time trends of R_p values during W&D exposure, measured by the contact probe on bronze and gilded bronze. They show that, at the beginning of the exposure, R_p values tended to decrease for bronze samples and then increased, until settling at about 5.8 kohm.cm^2. Conversely, R_p values tended to increase for gilded bronze samples and reached values of about two orders of magnitude higher than those measured on bronze at the end of the exposure period. This latter trend, connected to the localization of the corrosion attack at the gilded layer defects, was caused by the slow stifling of the corrosion process, due to the precipitation of corrosion products at the gilded layer pores.

The presence of the silane film slowed down the corrosion process on both bronze samples [22] and gilded bronze. In the latter case, the effectiveness of the protective film was due to the capability of silane to adhere on gold and to accumulate in the porous gilded layer zones, as shown by dropping tests (Fig. 5).

In order to validate the EIS data obtained with the contact probe, bare and PropS-SH-coated bronze samples subjected to W&D exposure were also monitored by collecting EIS spectra in the traditional three electrode cell (Fig. 7a). The time trends of R_p values measured by the three electrode cell were similar to those detected by the contact probe (Fig. 7b). However, the R_p values collected on bronze by the latter method were much higher than those measured by the three electrode cell, while the two measurement techniques gave comparable results for PropS-SH pre-filmed bronze samples.

This means that the contact probe tended to underestimate the corrosion rate in the case of samples covered by a layer of unstable corrosion products (bare bronze specimens). In this case, during EIS spectra collection, lasting about 2h, occluded cell conditions could develop in the electrolyte-impregnated filter paper, due to diffusion obstruction. As a consequence, difficult oxygen access and local pH variation could have occurred, so making such conditions scarcely representative of real outdoor exposures.

On the other hand, in the case of samples affected by low corrosion rates (e.g. covered by protective films), the contact probe afforded a correct corrosion rate estimation. This was probably due to negligible solution pH variation and a minor impact of oxygen diffusion on surfaces characterized by very low rates of oxygen consumption and cation formation.

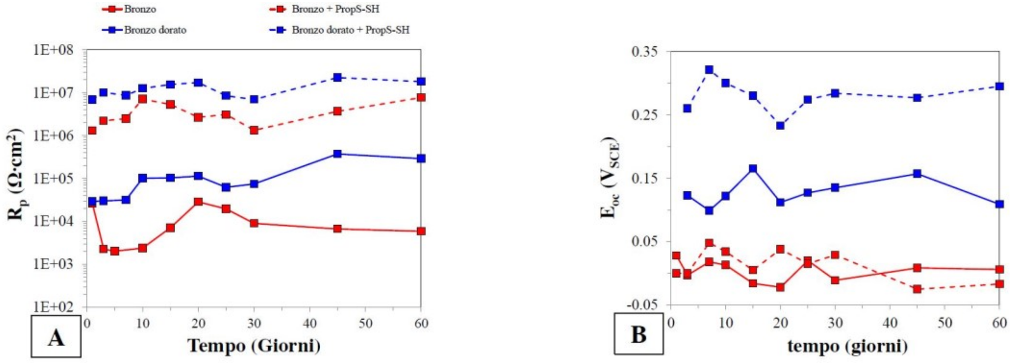

Fig. 6: R_p (A) and E_{oc} (B) values measured by contact probe during 60 days of dropping exposure. The measurements are referred to bronze and gilded bronze, both in the absence and in the presence of a PropS-SH-pre-filming treatment.

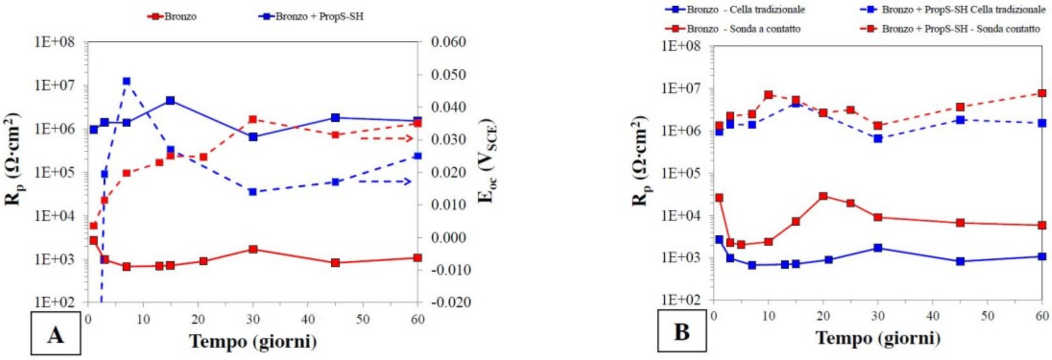

Fig. 7: A) R_p and E_{oc} values measured by usual three electrode cell during 60 days of W&D exposure both in the absence and in the presence of a PropS-SH-pre-filming treatment; B) Comparison between the different techniques used to measure the effectiveness of PropS-SH film on bronze and gilded bronze.

IV.4. Conclusions

∴ The wet & dry and dropping techniques (simulating stagnant rain and runoff conditions, respectively) applied on gilded bronze lead to the formation of surface corrosion products at the bronze/gold interface;

∴ The corrosion product stratification after dropping exposure is comparable to that actually detected on real artefacts;

∴ PropS-SH can protect both bronze and gilded bronze from corrosion;

∴ The contact probe tended to underestimate the corrosion rate of samples covered by a layer of unstable corrosion products;

∴ Correct estimation of the corrosion rate by the contact probe was achieved on PropS-SH coated bronze samples, likely because they are characterised by low corrosion rates.

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