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Corrosion products characterisation aimed at restoration of Bronze Age metal artefacts from Garda Lake

M Labate^{1,4}, C Sirello², C Longhi³, M Aceto⁴, L Operti¹, A Agostino¹

¹ Dipartimento di Chimica, Università degli Studi di Torino, via P. Giuria, 7 10125 Torino, Italy

² Carmela Sirello - Restauro Archeologico e Conservazione Opere d'Arte, Via Cigliano, 7/E 10153, Torino, Italy

³ Soprintendenza Archeologia, Belle Arti e Paesaggio per Bergamo e Brescia, piazzetta G. Labus, 3 25121, Brescia, Italy

³ Dipartimento di Scienze e Innovazione Tecnologica, Università degli Studi del Piemonte Orientale, viale T. Michel, Alessandria, 11 15121, Italy

⁴ Author to whom any correspondence should be addressed maria.labate@unito.it

Abstract. Conservation is a complex field that needs an exchange of views among different professionals including archaeologists, conservators, restorers and scientists. Diagnostic analyses can give useful information able to lay down the documentation about the artefacts conservation status before and after the restoration; to define the restoration plan and to lead to the most suitable conservation strategies, materials and methods; to evaluate and track the restoration work and to reproduce it in similar contexts. For all of these reasons, a scientific restoration treatments on cultural heritage need materials and alteration products characterisation as a propaedeutic phase. This awareness has guided the study approach of some Bronze Age metal findings from Garda Lake, analysed in order to know the nature of corrosion products in case of upcoming restoration.

1. Introduction

The study concerns an integrated analysis of 90 metal artefacts belonging to important larger collections of findings required to be restored. Their archaeological study is in progress and unfortunately there is not much information about the finding context because they were seized in the '80s from illegal excavation. They date back to the Bronze Age of pile-dwellings in the Garda Lake area and are currently exhibited in Museo Civico Archeologico G. Rambotti and Museo Civico Archeologico della Valtenesi (Brescia, Italy). The collection is from settlements listed into UNESCO World Heritage Sites. It follows that the consideration given to pass them on to future generations must be well ensured.

Since information is the fuel of conservation [1] some artefacts were analysed in order to know the nature of corrosion products on occasion of their restoration by Carmela Sirello company and according to direction of Soprintendenza Archeologia Belle Arti e Paesaggio per le province di Bergamo e Brescia. The well-established crucial importance of preservation metal artefacts requests appropriate conservation methodologies which take account of noble or protective *patina* preservation and facilitate the readability of the object, by removing sediment deposits and inhibiting any active corrosion processes. This is only possible through a careful study of materials and degradation



characteristic features. Results and discussions given here relate only to six copper alloy artefacts, chosen because they had representative degradation explanatory even of other artefacts to be restored (Figure 1).



Figure 1. The artefacts before the restoration: three dagger blades (a, b and c) and three harpoons (d, e and f) from Lugana Vecchia (Sirmione, Brescia).

Inventory numbers: a)ST.132167; b)ST.132175; c)ST.132177; d)ST.132321; e)ST.132310; f)ST.132285

2. Methods

Artefacts' alteration products characterisation was performed by different analytical techniques, adopting non-invasive methods or micro-invasive ones on some fallen fragments or little sampling of the corrosion layers. The adopted methodology has provided the acquiring of magnified images by optical stereo microscope (OM), colorimetric analysis by spectrophotometer, optical analysis by fiber optics reflectance spectroscopy (FORS), compositional analysis by X-ray fluorescence spectrometry (XRF)[2] and mineral phase identification by powder X-ray diffraction analysis (XRPD) and by Raman spectroscopy. The last two techniques were conducted on a limited number of samples; conversely the previous ones have allowed a significant collection of data.

3. Result and Discussion

In many cases the artefacts' visual inspection allows us to appreciate a thick crust which entirely or partially covers them. Incrustation was quite fragile and tending to fragmentation. Photographic documentation and magnified images acquired by optical microscope showed the surfaces and cross section features. Among the items surface it is observable uniformity on degradation aspect suggesting the common conservation history into the lake, but also a marked heterogeneity of corrosion products of each individual artefact in which colourful alteration products are visible. The sample crust cross

section (Figure 2) shows different layers or *strata* very typical of archaeological copper alloy artefacts [3][4].

Colorimetric characterisation allows a first superficial corrosion products discrimination: points of measurement can be divided in two typology into CIEL*a*b* space as white-yellow-brown (WYB) areas or black-green-azure (BGA) ones. Furthermore the scientific definition of the colour should be considered a fundamental phase, useful to track unavoidable variations due to restoration and also the artefact optic behaviour over time [5].

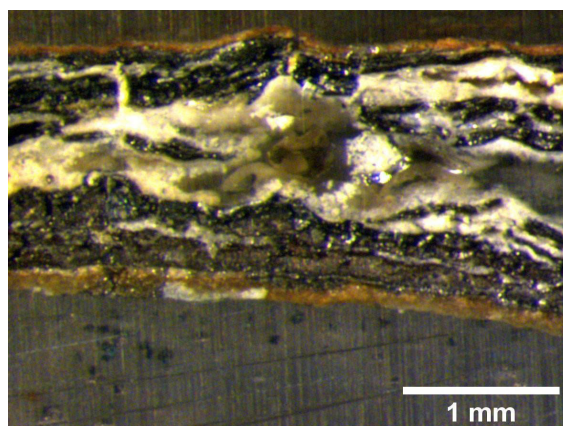


Figure 2. Cross section incrustation sample of artefact C showing a typical periodic corrosion products of archaeological bronzes.

XRF measurements were conducted in the same areas defined by colorimetry. Despite the presence of altered layers, XRF data revealed that the six artefacts are made of bronze since copper and tin were originally the main components. There are minor concentrations of iron, arsenic, nickel, antimony and lead. These elements could refer to impurities of the raw materials but the interaction with burial ground modify the composition and original alloy can not be investigated by non-destructive methods [6] on altered surfaces. Moreover any consideration about trace elements for provenance studies is strongly questioned by the frequent recourse to the re-melting and recycling of metal objects [7].

Measurements on BGA areas detected copper, sulphur and tin as major elements meanwhile in WYB areas measurements the tin amount definitely decreased, replaced by a significant increase in concentrations of iron and sulphur (Table 1). The sulphur availability could be related to the action of sulphate-reducing bacteria in the burial context. The presence of iron, silica and calcium is due to the interaction of artefacts surface with lakebed soil [8].

A large number of FORS measurements have easily consented to characterise the spectroscopic trends in range 370-1100 nm, with diagnostic value especially useful to identify green or azure copper sulphates and to exclude the presence of copper carbonates or chloride [9]. Green reflectance spectra have double absorption bands: the first at 730-750 nm and the second one at 920 nm. Azure reflectance spectra have only an absorption band with minimum in the range 700-800 nm. Green brown spectra are difficult to interpret and, naturally, black reflectance spectra are hardly recognisable spectral features.

XRPD analyses were performed on only three samples from different artefacts (a, c and d) and results revealed a complex mineral mixture well known in literature. Mineral phases are defined thanks to the database, taking into account that alteration products often have a very similar structure and are not always comparable with pure or synthetic minerals because of their impurity, vicariance and low

crystallisation degree [10]. BGA areas consist mainly of copper sulphide, tin oxide and hydrated copper sulphate (e.g. antlerite and calchantite); measurements in WYB areas primarily identified iron and copper sulphide (chalcopyrite), hydrated iron sulphate (siderotil) as well as hydrated copper sulphate.

These alteration products are detected also by Raman analysis with the exception of sulphide and this consented also to better define the measurement location, unlike the powder diffraction techniques in which it needs sample grinding. Despite the complexity of corrosion phenomena, it is possible to conclude that a first alteration was due to reaction of main elements of copper alloy and secondly these alteration products degrade into species in which iron has a prominent role [11].

Table 1. BGA represents black-green-azure areas and WYB white-yellow-brown ones. XRF analysis results referring to major elements. XRD and Raman results show the major alteration products.

Measurement points	XRF Results >1(wt%)	XRD and Raman Results
BGA	Cu, S, Sn, Fe, Ca	Copper sulphide, tin oxide, Hydrated copper sulphate
WYB	Cu, Fe, S, Ca, Si	Iron and copper sulphide, hydrated iron and copper sulphate

4. Conclusions

The study allowed us to define a protocol in which non-invasive techniques and micro invasive ones are perfectly complemented. Micro-invasive analysis results of few samples could have been generalised by means of widespread measuring point analysed by non-invasive methods. This was possible because of the similarity of artefacts degradation due their common conservative history into lakebed. Indeed, corrosion features here identified could be considered a sort of artefacts burial fingerprinting. Analyses highlight the presence of heterogeneous layering mainly consisting of sulphide and hydrated sulphate.

In order to define the restoration plan, it has been possible to ensure the absence of active corrosion by chlorides. Furthermore, it has produced useful documentation to check and evaluate the treatment overtime and eventually to repeat it in similar contexts. The knowledge obtained during the investigations went with the conservation documentation delivered to Soprintendenza Archeologia Belle Arti e Paesaggio per le province di Bergamo e Brescia. Hopefully, it should become a common practise increasingly adopted by relevant departments and museums [12].

Collecting data relating to degraded bronzes is part of a larger work aiming to set up a dataset containing multi-technique and multidisciplinary information about copper alloys alteration products. This provides a fundamental step to training machine learning models able to easily predict type of degradation just by the input of non-invasive analysis data such as colorimetry, XRF and FORS. Data obtained with this study are certainly a valuable contribution given the need for a rather large amount of items to better work [13]. Achieving the purpose of a fast characterization of degradation would be particularly relevant for pursuing restoration goals in order to improve the assessment and the planning phases as well as the intervention one.

References

- [1] Ward P 1986 *The Nature of Conservation. A race against Time*, GCI 63
- [2] Robotti S, Rizzi P, Soffritti C, Garagnani G L, Greco C, Facchetti F, Borla M, Operti L and Agostino A 2018 *Spectrochim Acta Part C At Spectrosc* **146** 41-49
- [3] Scott D A 1985 *Stud. Conserv.* **30** 2 49-57
- [4] Piccardo P, Mille B and Robbiola L 2007 *Corrosion of Metallic Heritage Artefacts* **48** 239-262
- [5] Giumlia-Mair A, Albertson C, Boschian G, Giachi G, Iacomussi P, Pallecchi P, Rossi G, Shugar A N and Stock S 2010 *Mater Technol* **25** 5 245-261
- [6] Nørgaard H W 2017 *Open Archaeol.* **3** 101-122
- [7] Radivojević M, Roberts B W, Pernicka E, Stos-Gale Z, Martínón-Torres M, Rehren T, Bray P, Brandherm D, Ling J, Mei J, Vandkilde H, Kristianen K, Shennan S J and Broodbank C 2019 *J.Archaeol.Res* **27** 131-185
- [8] Schweizer F 1994 *Proc. Symp. on Ancient and Historic Metals by the J. Paul Getty Museum and Getty Conservation Institute, November 1991* 33-50
- [9] Liu W, Li M, Wu N, Liu S and Chen J 2021 *J.Cult.Herit.* **49** 19-27
- [10] Fabrizi M and Scott D 1987 *Recent advances in the conservation and analysis of artifacts. Jubilee conservation conference July 1987 London* 131-134
- [11] Rémazeilles C, Langlet-Marzloff V, Creus J, Lotte G, Deshayes C, Baleux and F Robbiola L 2020 *Corros. Sci.* **175**
- [12] Dillman P, Watkinson D, Angelini E and Adriaens A 2013 *EFC Series, Corrosion and Conservation of Cultural Heritage Metallic Artefacts*, Woodhead Publishing, 1-5
- [13] Fiorucci M, Khoroshiltseva M, Pontil M, Traviglia A, Del Bue A and James S 2020 *Pattern Recognit.Lett* **133** 102-108