Micro-Raman investigation of dangerous corrosion products of archaeological bronzes from Tharros (Sardinia-Italy)

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Micro-Raman investigation of dangerous corrosion products of archaeological bronzes from Tharros (Sardinia-Italy)

Tilde de Caro[1], Leila Es Sebar[2], Emma Angelini[2]

[1] *ISMN–CNR Rome Italy, tilde.decaro@cnr.it*
[2] *Dipartimento di Scienza Applicata E Tecnologia, Politecnico di Torino, Italy*

Abstract –**A large number of bronze artefacts have been found during archaeological excavations carried out at Tharros (Sardinia, Italy). The composition of corrosion products have been determined by the combined use of optical microscopy (OM), micro-Raman spectroscopy (*μ*-Raman), scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS).**

In particular, we will use *μ*-Raman spectroscopy to identify the corrosion products of natural patinas. This technique is equivalent or sometimes more efficient than microscopic and diffraction techniques to identify archaeological corrosion products. It is able to discriminate between different polymorphs, has a high spatial resolution and assures a correlation between the colour and the mineralogical nature.

Furthermore has the advantage of being a non-destructive technique, quality highly valued in the cultural heritage.

I. INTRODUCTION

The ancient city of Tharros, located along the north-western coast of Sardinia (Italy), was inhabited since the Nuragic period, the Phoenicians during VIII century BC and then, the city was governed by Carthaginians up to the Roman conquest (III century BC).

During archaeological excavations carried out in Tharros, it was found a large amount of Punic, Roman and Carthaginian bronze artefacts, such as coins, nails, rings and everyday tools.

Because of the long-time burial in the soil, the surface of the archaeological artefact was covered with corrosion products.

Furthermore, most bronze artefacts were in very hazard conditions. To investigate the chemical and structural nature of the corrosion products (i.e. the patina) grown on the bronze artefacts, some bronze Punic coins have been chosen as representative and analysed by means of micro-Raman spectroscopy and optical microscopy.

These analytical techniques were useful to identify the corrosion agents and mechanisms, to ascertain the actual state of conservation and provide recommendations for the selection of tailored conservation approaches and materials able to stop degradation phenomena.

II. EXPERIMENTAL

The corrosion products analysis has been carried out by means micro-Raman spectroscopy (μ-Raman), Leica optical microscopy and field emission scanning electron microscopy (FE-SEM) coupled with energy dispersive spectrometry (EDS).

Non-destructive Raman measurements were performed with a Renishaw spectrometer equipped with a cooled CCD detector in conjunction with a Leica microscope.

The patinas were examined using a 50x or occasionally 100x objectives to focus the laser light on the samples and to collect the Raman signal. The excitation source was both the 514.5 nm line of an argon ion laser and the 785 nm line of a laser diode depending on the sample analysed.

To avoid damage of the patina the laser power was lowered and to prevent that the fluorescence covered the Raman signal. No baseline was subtracted from the recorded spectra. The spectra obtained were compared with databases available in the literature.

FE-SEM–EDS were carried a high brilliance LEO 1530 field emission scanning electron microscope (FE-SEM) apparatus, Oxford Instr. (UK), equipped with an energy dispersive X-ray spectrometer (EDS) and INCA 450, and a four-sector backscattered electron detector (BSD).

III. RESULTS AND DISCUSSION

The interaction between material and the soil leads to the formation of a heterogeneous patina on the surface of the metal.

Because of its particular geographic position, soil of Tharros is particularly rich in chlorine, which is the main responsible for the metal corrosion. In the case of copper-

based alloys, in particular, chlorine causes a cyclic and self-sustaining degradation process defined "bronze disease" that destroys the artefacts transforming it in a greenish powder.

The selected coins were found in a sewer of Tharros and are from the Punic period.

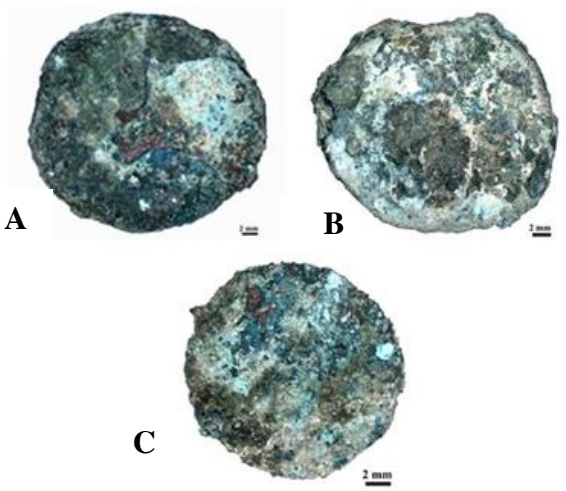

Fig. 1. Punic coins found at

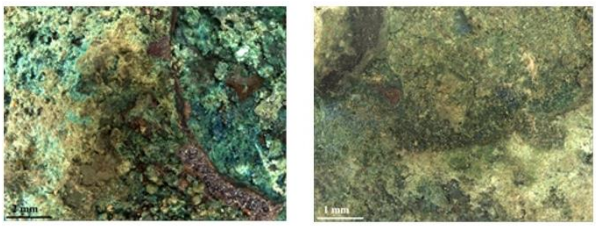

Fig. 2. Optical microscopy images of the patina of the Punic coins found at Tharros.

The coins were in a bad conservation state (Fig. 1) and have been analysed before any cleaning and conservation procedure.

Raman investigations, carried out on the selected samples, revealed that the main corroding agent is represented by chlorine-containing species which has induced the formation of dangerous copper chlorides and oxy-chlorides at the interface between the metal and the corrosions products layers.

The OM images (Fig. 2) display the surface of the Punic coin A. In particular, the selected area shows the presence of red-ruby crystals that can be attributed to cuprite (Cu_2O) crystals mixed with a small amount of components of the soil and other corrosion products.

As evidenced by OM characterization, the patinas did not show a homogeneous composition, so analytical investigation were repeated on different points of the surface.

The OM and SEM images (Fig. 3) display the red zone of the surface of the Punic coin A. In particular, the selected area shows the presence of well-formed red-ruby cuprite (Cu_2O) crystals, as confirmed by micro-Raman spectra as shown in Figure 4.

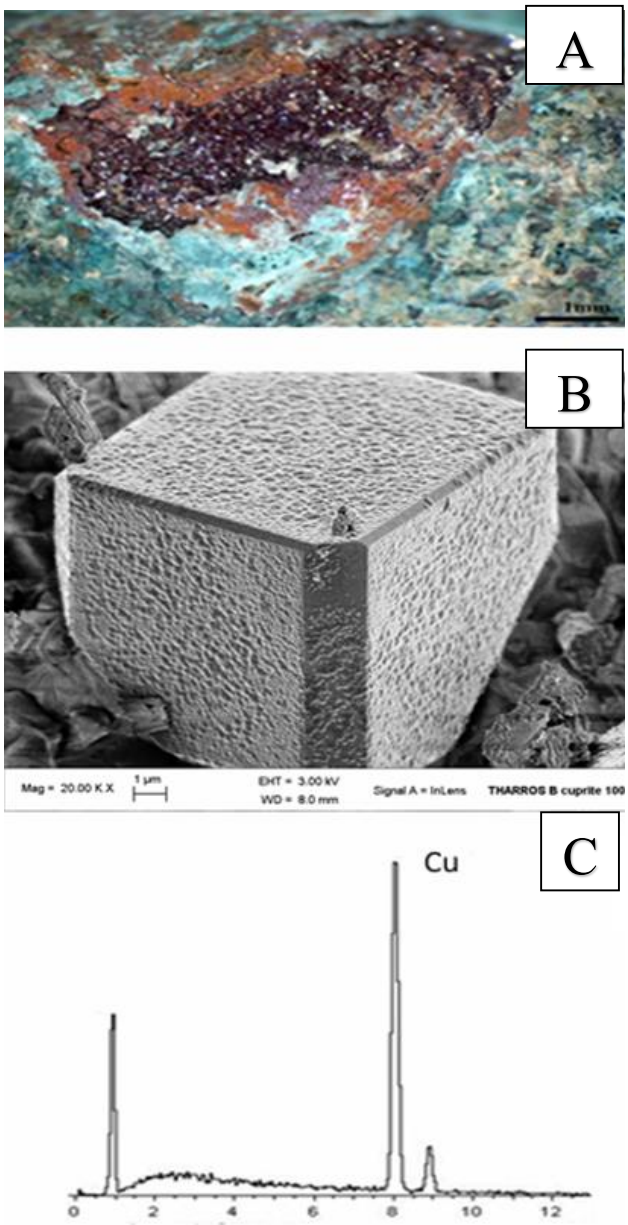

Fig. 3 Optical image (A), scanning electron microscopy images(B) and EDS spectrum (C) show cuprite (Cu_2O) crystals grown on the surface of the Punic coin A

Figures 5 and 7 show the presence of copper trihydroxychlorides [$Cu_2Cl(OH)_3$] polymorphs that reveal that the surface of this archaeological artefact is characterised by the occurrence of the self-sustaining process called 'bronze disease'.

The typical aspect of atacamite, that appear as a greenish powder on the surface of the archaeological bronzes, is shown in the FE-SEM image, and the energy dispersive (ED) spectrum reveals the presence of oxygen, copper and chlorine.

The Raman spectra, shown in Figures 4 and 6, identify the presence of the polymorphs clinoatacamite and of the dangerous atacamite [$Cu_2Cl(OH)_3$].

Bronze disease is a cyclic reaction that occurs when the archaeological object interacts with the chlorine of the soil that, with the presence of moisture, produces light green powdery copper chloride (nantokite-CuCl) and hydroxychlorides (atacamite and its polymorphs-$Cu_2(OH)_3Cl$).

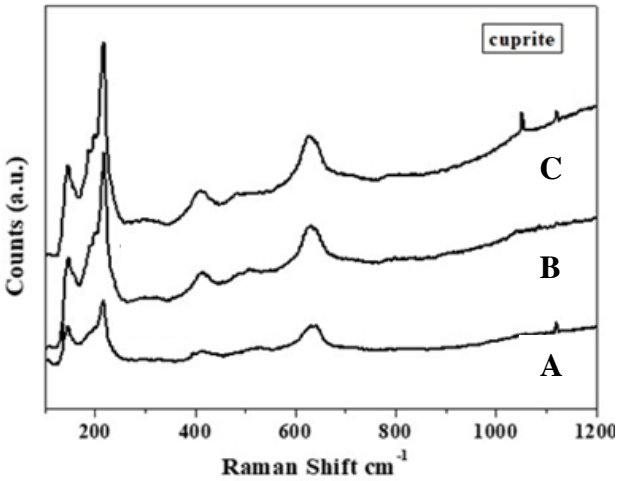

Fig. 4. Raman spectra of Punic coins confirm the presence of cuprite on the corrosion patinas of the Punic coins A,B,C

This reaction takes place at the interface between the metal surface and the internal corrosion layer and disrupts the metal surface corroding the alloy until the total crumbling [1].

The cuprite layer [2] should work as an electrolytic membrane allowing the transport of anions such as Cl^- and O_2^- inward and cuprous ions outward. The large amounts of chlorine and oxygen in the innermost layer can be interpreted as an autocatalytic reaction, which facilitates the oxidation of copper and the accumulation of chloride ions allowing the formation of cuprite and copper chloride [3].

The outermost green layer can be formed, as said above, from atacamite and its polymorphs that are botallackite and clinoatacamite. The thermodynamic data [4] show that the more stable phase between the three polymorphs is clinoatacamite and the less stable is botallackite that should be formed before, in this way when on an archaeological artefact is found atacamite it is only the intermediate step of the sequence while clinoatacamite is the completion. The nantokite phase is very unstable, it is the first phase that is formed and can be found as a corrosion product only under extremely desiccant conditions.

From this information, it can be deduced that some corrosion products, as clinoatacamite, highlighted in figure 7, are stable and therefore the artefact once is excavated will not encounter serious degradation processes. Other products, on the contrary, as atacamite change their crystalline structure over time, increasing, for example, their volume, and these processes lead to rapid destruction of the object. These products have to be neutralized and their harmful and irreversible action must be stopped if we want to preserve the artefact [2].

To neutralize and stop these degradation processes conservators have developed several recipes [6, 7].

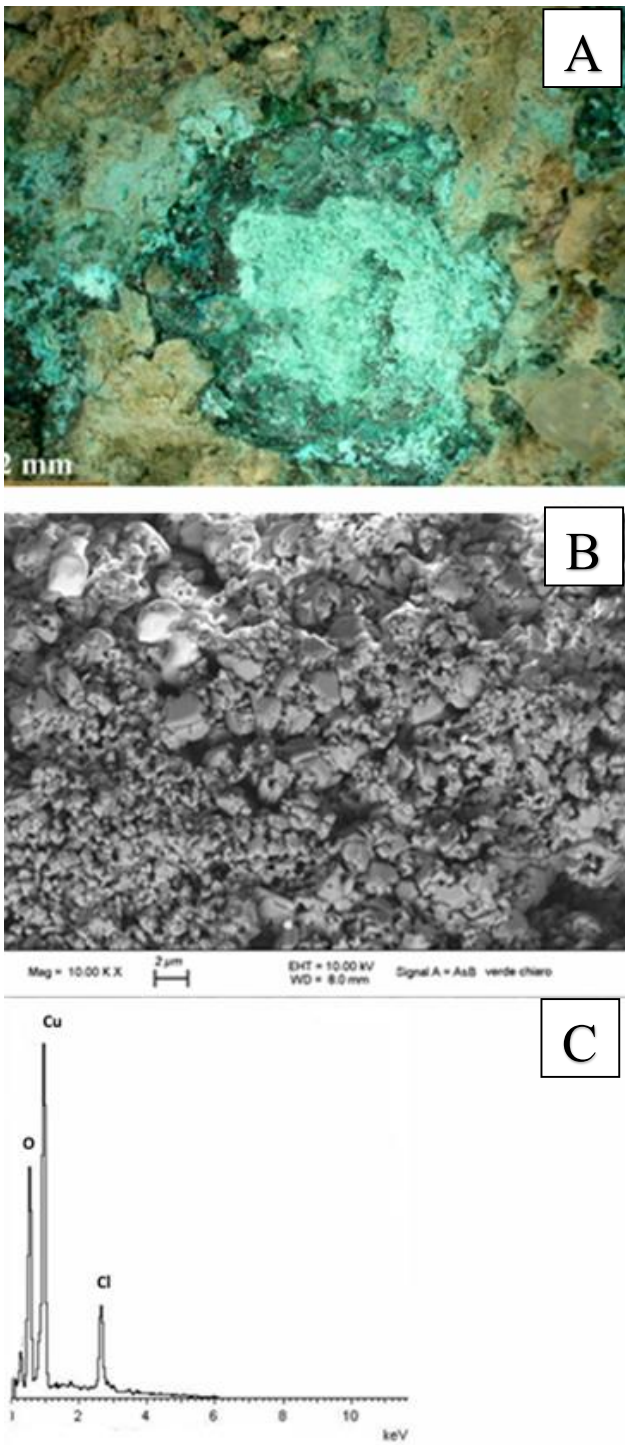

Fig. 5 Optical image (A), field emission scanning electron microscope image (B) and energy dispersive spectrum (C) for the surface of the area where 'bronze disease' is occurring in coin B

However, before using a new product is necessary to know in advance the behaviour of the patina once it is exposed to the new compounds [8, 9].

In fact, these corrosion inhibiting products must either stop the aggressive substances both preserves the colour and the composition of the patina in order not to alter the appearance of the archaeological artefact.

This information reveals the strict interaction between soil components and corrosion reactions and products and evidence the abundant presence of chlorine in the patina of the archaeological Cu-based artefacts found in Tharros [10, 11].

This latter occurrence is considered dangerous because it could induce the cyclic and self-sustaining corrosion reaction of copper that disfigures the artefact.

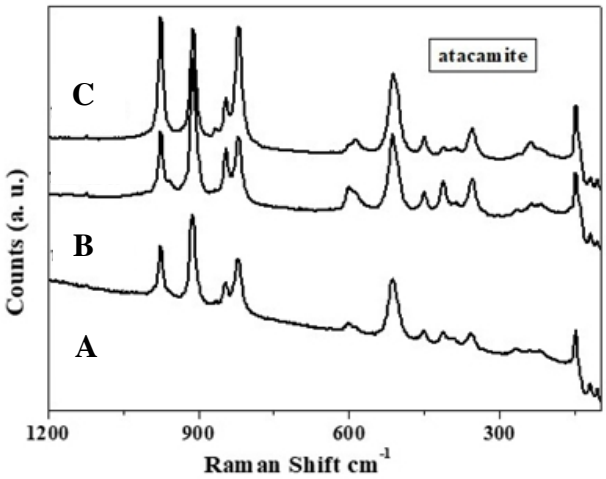

Fig. 6. Raman spectra of Punic coins (A,B,C) found at Tharros identify the presence of the dangerous hydroxychloride atacamite

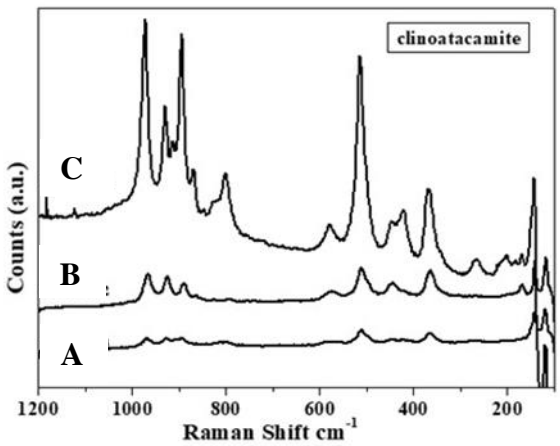

Fig. 8. Raman spectra identify the stable polymorph clinoatacamite on coins A,B,C

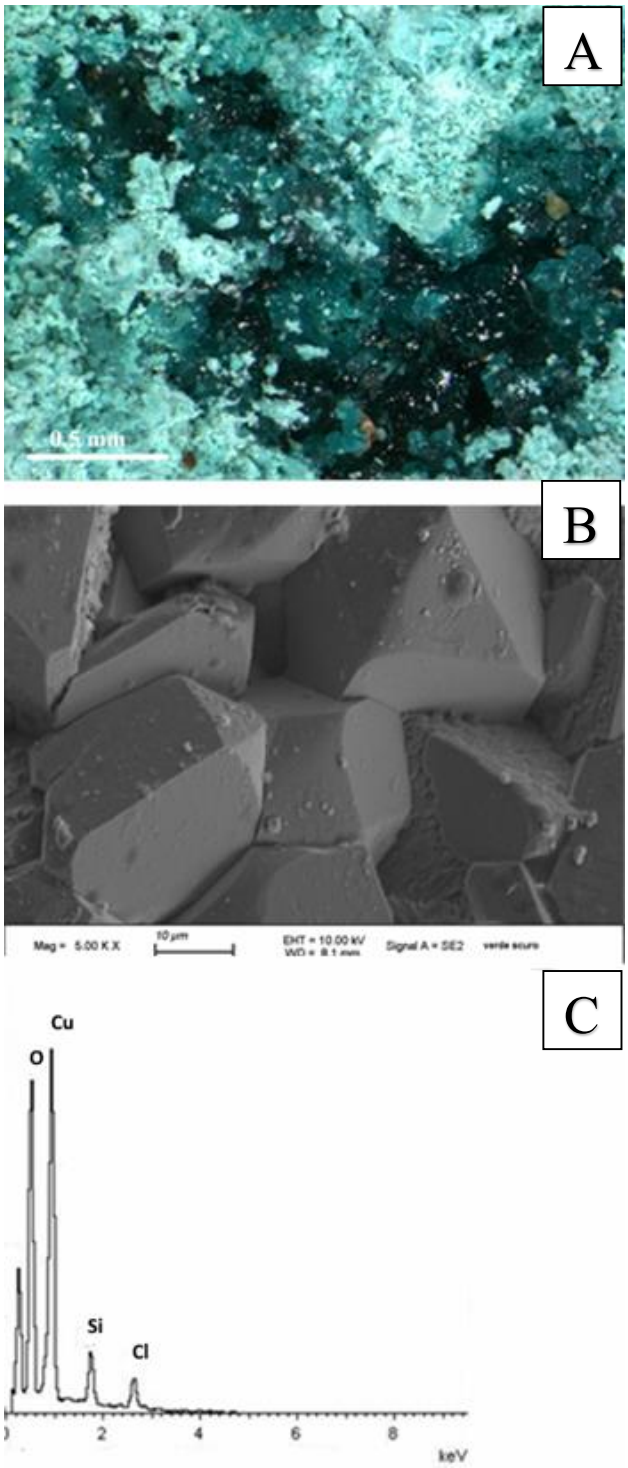

Fig.7 Optical image (A), field emission scanning electron microscope image (B) and energy dispersive spectrum (C) for the surface of the area identify the presence of hydroxy chloride minerals on coin C

IV. CONCLUSION

The micro-chemical structure of long-term corrosion products grow on bronze archaeological artefacts found at Tharros has been investigated .

The results propose a correlation of their nature with the chemical composition of the artefacts and the burial context characterised by a large amount of chlorine because of the location of the archaeological site along the western coast of Sardinia.

TheRaman results evidence the presence of Cu (I) species such as cuprite (Cu_2O) and of copper trihydroxychlorides $Cu_2Cl(OH)_3$, atacamite and clinoatacamite, in the outermost layers of the patina.

The obtained results confirmed the efficacy and versatility of the non-invasive Raman techniques, in particular, suggesting the need to select tailored conservation methods for these materials.

However, according to our opinion, the best tailored strategies for long-term reliable conservation should be taken into consideration the transformation of dangerous copper chloride or oxy-chlorides into some stable phase to ensure a long term chemical–physical stability of archaeological bronze artefacts.

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