

Non-invasive characterization of ancient Cu-based coins using Raman spectroscopy

Leila Es Sebar¹, Leonardo Iannucci¹, Yuval Goren², Peter Fabian², Emma Angelini¹, Sabrina Grassini¹

¹*Department of Applied Science and Technology, Politecnico di Torino, Torino, Italy,
leila.essebar@polito.it, leonardo.iannucci@polito.it, emma.angelini@polito.it,
sabrina.grassini@polito.it*

²*Department of Bible, Archaeology and Ancient Near East, Ben Gurion University of the Negev,
Israel, ygoren@bgu.ac.il, fabian@bgu.ac.il*

Abstract – Characterization of archaeological finds is a challenging case study for researchers, as the need of non-invasive measurements strongly affects the investigation strategies. Moreover, it is almost not possible to follow a fixed protocol, because the measurement conditions should be tailored to the samples under study. This paper presents a preliminary characterization of bronze coins coming from an archaeological site located in the south of Israel. The superficial corrosion layers have been analysed by means of Raman spectroscopy in order to investigate their composition and assess the conservation state of the finds. Reference samples of known composition have also been used to help peaks identification in the Raman spectra. Results coming from this study can help in defining the correct conservation strategies for the artefacts.

I. INTRODUCTION

Corrosion of archaeological artefacts buried in soil for long times depends on many variables related to the microclimate conditions and to the soil chemico-physical properties, such as the moisture content, the temperature, the acidification and the salt contents. Moreover, it has to be considered that the soil water acts as an electrolyte on the buried object surface, and in the case of Cu-based artefacts a minimum value of pH is required to induce the formation of stable corrosion products layers. Eventually, the position of the object in the soil has to be considered as well because the diffusion of oxygen, one of the main aggressive agents, could be different near the soil surface or toward an item deeply buried.

Many chemical and electrochemical processes are involved, but in the right conditions the object can reach an equilibrium with the surrounding environment and, therefore, it can be preserved for long periods.

Indeed, nowadays it is still possible to find ancient Cu-based artefacts still well-preserved after been buried for centuries in the archaeological sites [1]. However, long-term corrosion of Cu-based artefacts in soil is complex

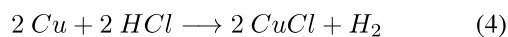
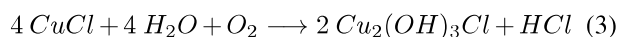
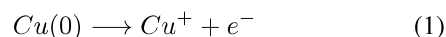
and the degradation could proceed very fast after the excavation and the re-exposure of the items to the atmosphere.

Basically, corrosion in soil leads to the formation of different patinas and corrosion products layers, whose chemical composition and microstructure depend on the environmental conditions and on the composition of the soil itself. Usually, an inner layer of cuprite, Cu_2O , is formed on metal surface and then, an outer layer composed of different corrosion products grows on it.

The composition of the outer layer mainly depends on three fundamental components of the soil: organic or inorganic particles, the presence of gas and moisture [1]. Usually the outer layers are composed of copper oxides and hydroxychlorides, sulphates and carbonates such as malachite, brochantite, atacamite and paracamite, etc.

Eventually, when dealing with Cu-based archaeological artefacts the presence of chlorides as corrosive agents is a relevant aspect. Indeed, chloride ions coming from the soil can react with water and oxygen leading to the formation of green corrosion products and to the fragmentation of the surface, with material loss.

In details, chloride ions react at the metal/corrosion layer interface leading to the formation of reactive cuprous chloride (nantokite, $CuCl$), responsible of the cyclic copper corrosion process well known as "bronze disease" [2]. Nantokite exposed to humidity reacts with oxygen and water, thus, green-blue basic cupric hydroxychlorides are formed (as atacamite and paratakamite), together with hydrochloric acid. Hydrochloric acid (HCl) reacts again with the metal (Cu) to form nantokite in a continuous cyclic process. The self-sustaining reaction continues until the copper is completely consumed and the artefact is destroyed. The catalytic reaction is reported below:



This kind of reaction proceeds when active phases as nantokite are in direct contact with the metal surface. Otherwise, when Cl^- ions are trapped in the outer layer and a protective cuprite patina is formed on the metallic surface, the reaction is slowed down.

Investigating the corrosion mechanisms together with the chemical and microstructural characterisation of the corrosion products is necessary in order to understand their stability toward the inner metal of an archaeological find. Indeed, only a deep knowledge of these issues can lead to the development of tailored projects for the conservation and restoration of the artefacts, such as the application of corrosion inhibitors of bronze disease [3], the application of cleaning treatments able to remove the reactive corrosion products, and the deposition of reversible protective coatings with high barrier effects against humidity and aggressive agents present in the environment [4, 5].

At the same time, investigations carried on within the field of cultural heritage have to satisfy several requirements, first of all the non-invasiveness of an analytical technique.

In this contest, a non-invasive study on bronze archaeological artefacts coming from the archaeological site of Rakafot 54 (Israel) is presented.

The main aim of the study is to characterize, from the chemical and microstructural point of view, the outer corrosion products layers by means of portable Raman spectroscopy. The proposed measuring approach was applied in many studies [6, 7, 8] and can be very appropriate as a preliminary investigation, which could be performed in the field in order to collect information about the stability and the conservation state of the artefacts immediately after the excavation, leading therefore to the development of tailored preservation strategies for the storage of the items.

II. MATERIALS AND METHODS

The archaeological finds subject of this study came from an excavation carried out at the site of Rakafot 54 near Beersheva (Israel) and involving a settlement dating back to the Roman period. The site dates from the first century AD (Second Temple) period to the Bar Kochba revolt against Rome, in 135 AD.

The excavations were conducted by Dr. Peter Fabian of the Department of Bible, Archaeology and Ancient Near East at Ben-Gurion University of the Negev (Beersheva, Israel) and Dr. Daniel Varga of the Israel Antiquities Authority.

Some of the remains showed signs of a fire, indicating a settlement crisis, probably during the Great Revolt against Rome that occurred around 70 AD. Dozens of bronze coins were also discovered on the site, most of which belonged to the Roman procurators' period (6-66 AD).

Some coins were minted in Ashkelon and some in other



Fig. 1. Photograph showing the 25 coins and the pendant excavated in the Rakafot 54 archaeological site. The figure shows both the front (on the top) and reverse (bottom) side of the items

cities from around the Roman Empire.

The artefacts selected for the study are 25 bronze and Cu-based coins, belonging to different periods, and a bronze pendant. A picture showing the front and the reverse side of the objects is presented in Fig. 1.

Raman spectroscopy, proved to be a powerful tool in corrosion studies [9, 10], was the selected analytical technique for the characterization of the outer corrosion products present on the items surface. Raman measurements were performed by means of the i-Raman Plus portable apparatus. Spectra were collected using a green excitation laser (wavelength: 532 nm) and a BWS465-532S spectrometer, working in the range between 150 and 4200 cm^{-1} with a 7.3 cm^{-1} resolution. The instrument is equipped with a CCD sensor with high quantum efficiency and wide dynamic range assisted by a cooling system.

In order to find the best analytical parameters for the coins investigation, different settings were used on some reference samples. Indeed, an hydroxyclochloride patina was formed on copper specimens following the procedure described in [5]. Three copper samples (Cu 99.96 wt%) were cut to the dimensions of 45 mm x 15 mm x 5 mm, polished on abrasive paper until 4000-grit, cleaned in ethanol in ultrasonic bath for 5 min and dried. Then, the copper refer-

ence samples have been immersed for two months at room temperature in 0.5 M sodium chloride (NaCl) aerated solution, without stirring, in order to form an homogeneous artificial patina on the metal surface.

Raman measurements were performed on these reference samples setting the integration time, the number of repetitions and the laser power in order to avoid any modification in the material and to have the best signal to noise ratio. Therefore, measurements were performed by increasing the integration time in the range of 2s to 20s and setting the laser power in the range between 1.5 to 6.0 mW and performing 1 to 10 repetitions for each analysed area.

The Raman spectra post-processing (such as baseline removal, smoothing, peak analysis and normalization) was performed by means of the BWSpec software. The identification of the collected spectra was performed using the RRUFF database. Moreover, a comparison with Raman spectra collected on a set of copper reference samples artificially-aged by the authors has also been performed.

The portable Raman spectrometer is set to work at a fixed distance from the specimen using a plastic spacer. However, due to coins shape and to their roughness, it was not possible to use the instrument in this configuration. Therefore, an initial measurement was performed with a continuous acquisition, that allowed to focus manually the laser beam until the best signal to noise ratio was reached. After that, the proper analytical conditions such as time, repetition and laser power were set, and the spectrum was acquired.

III. RESULTS AND DISCUSSION

In this section, the most relevant results related to the Cu reference samples and to the archaeological items characterization are presented and discussed.

A. Reference samples

In Fig. 2, as an example, spectra collected on the artificially-aged copper reference sample are reported. It is worth to notice that between 1000-2000 cm^{-1} no peaks have been detected, due to an overlapping fluorescence signal. To overcome this issue, many acquisitions have been made on the reference sample, in different conditions. Indeed, different laser power values were tested, keeping the integration time constant and vice versa. In Fig. 2a spectra acquired with increasing integration time are reported, while in Fig. 2b spectra acquired with increasing laser power can be observed.

In both the cases, it is worth noticing that no modification or degradation is induced in the material as a function of the laser power. Consequently, in order to optimize the signal to noise ratio the Raman measurements were performed using a laser power of 6 mW, performing 10 repetitions and the integration time was set to 20s. The Raman

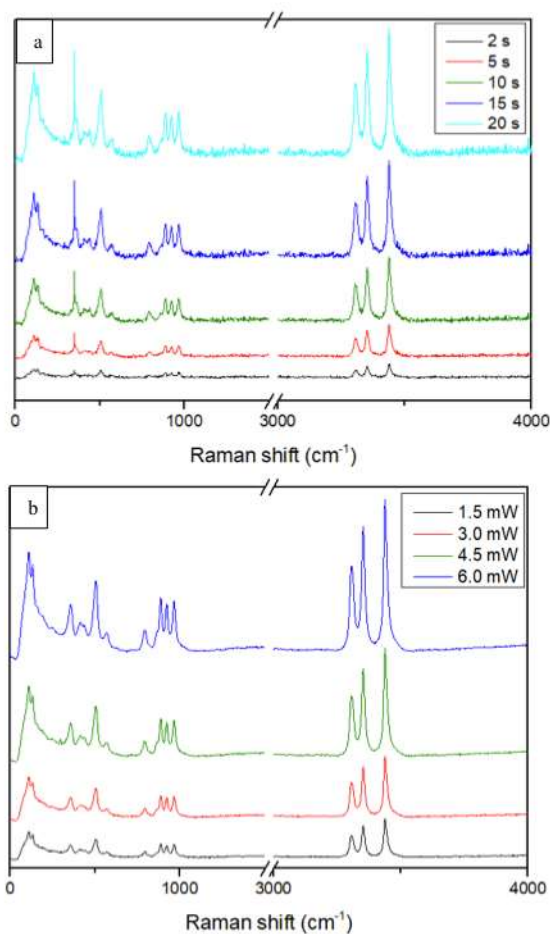


Fig. 2. Raman spectra acquired on the copper reference sample using increasing integration time (a) or increasing laser power (b)

spectra show the presence of a polymorph of atacamite, possibly clinoatacamite, as expected [11, 12, 13, 14].

As the measurement conditions were found to be non-destructive for the samples, it was decided to proceed with the characterization of the archaeological coins with the same parameters.

B. Archaeological artefacts

Before any analysis, the coins have been subjected to visual inspection. Multiple kinds of corrosion products were found, with different colour and morphology. Both thin and thick patina of green, bright green and red colour were present. As this study was performed before any cleaning or restoration process, also soil traces could be found on the artefacts.

Raman spectroscopy was performed on all samples, but it was possible to collect spectra with a good signal to noise ratio only on the bright green patinas. Indeed, in many cases the fluorescence signal was too relevant. It was not

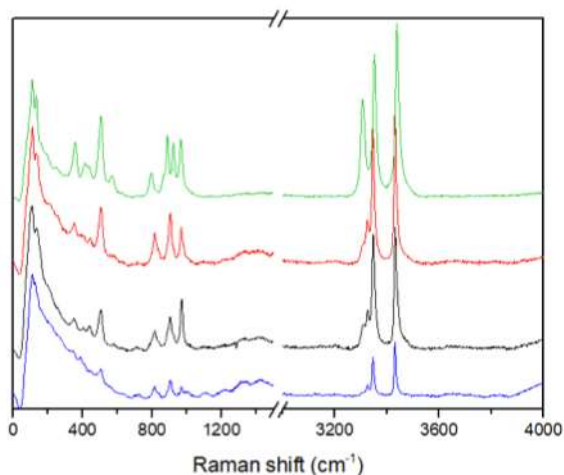


Fig. 3. Raman spectra acquired on coin "6058" (in red, black and blue) and on the clinoatacamite reference sample (in green)



Fig. 4. Reverse (left) and front (right) side of coin "6058"

possible to perform the analysis on red areas, that could possibly be related to the presence of cuprite, probably because of the low thickness of the layer.

Acquiring Raman spectra was not straightforward and, on each coin, multiple analyses were performed.

In many cases it was not possible to detect peaks due to the relevant presence of fluorescence signal. This problem can be explained considering the significant presence of soil on the coins surface. In order to overcome this issue, the coins surface was cleaned with a soft brush to remove the major part of the present soil.

In Fig. 3 some spectra collected on coin "6058" (Fig. 4) are reported as an example, together with a spectrum from reference sample of clinoatacamite. The analysis was performed on the front, on the reverse and on the side of the coin; all the investigated areas were characterized by a bright green patina. The spectra present a high fluorescence signal for Raman shift values below 400 cm^{-1} and in the range between 1400 and 3000 cm^{-1} . More-

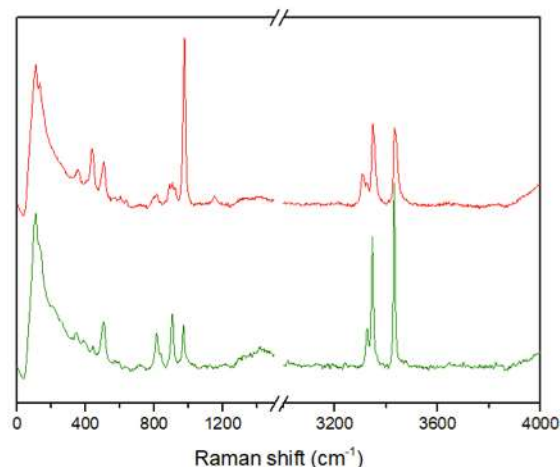


Fig. 5. Raman spectra collected on coin "B9803-b9816"



Fig. 6. Reverse (left) and front (right) side of coin "B9803-b9816"

over, broadening of the peaks around 900 cm^{-1} is present, probably due to the same reason. Besides these issues, it is possible to identify the characteristic peaks of clinoatacamite [12, 13, 14].

In Fig. 5 two spectra collected on coin "B9803-b9816" (Fig. 6) are reported. They were collected on the front and reverse side of the coin. In the spectrum reported in green it is again possible to identify the presence of clinoatacamite. On the other hand, the spectrum reported in red presents both the peaks of clinoatacamite and an intense peak at 974 cm^{-1} , relatable to the presence of a brochantite, posnjakite or langite [12, 8, 13, 14].

Finally, one spectrum for each coin is displayed in Fig. 7 together with a spectrum of the clinoatacamite reference sample. Comparing peaks position and intensity, it is possible to affirm that clinoatacamite is the predominant detected mineralogical phase.

This evidence can give important information about the stability of the corrosion products on the outer layers of the archaeological artefacts. Indeed, clinoatacamite is a polymorph of atacamite and botollaktite. Between these polymorphs, clinoatacamite formation is usually related to

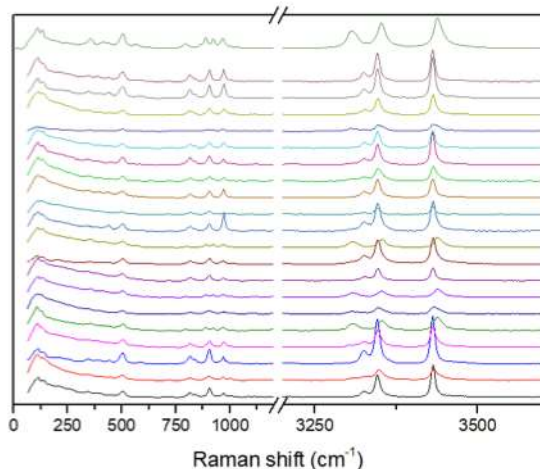


Fig. 7. Raman spectra of samples (from the top) Clinoatacamite reference; B9883-b9902; B9830-b9834; B8603-b8612; B8599-b9043; B8591-b9044; 9483; 9024; 8893; 8892; 8299; 8891; 8261; 8260; 8054; 8103; 6151; 6101; 6081; 6015; 6059.

the end of the degradation sequence of copper in presence of chloride ions [12, 13, 14].

IV. CONCLUSIONS

A preliminary characterization of a set of 25 archaeological bronze coins excavated in the Rakafot 54 site has been presented. Raman spectroscopy has been used to identify the different corrosion products forming the samples superficial patina. Thanks also to the use of reference samples of known composition, it was possible to identify the clinoatacamite as the major phase present. Moreover, this investigation can represent an interesting starting point from different points of view. First of all, it gave important information for the definition of the correct conservation strategy of the finds. Then, performing additional analysis on the soil collected near the artefacts, it could be possible to study the interaction between the metal and the soil, better clarifying the corrosion processes occurring over the centuries on the artefacts.

V. ACKNOWLEDGMENT

This research is performed in the frame of a Joint Project for the Internationalization of Research between Italy and Israel, financially performed by Politecnico di Torino and Compagnia di San Paolo (Torino, Italy) in 2019.

REFERENCES

[1] R. Francis, "The Corrosion of Copper and Its Alloys: A Practical Guide for Engineers", National Association of Corrosion Engineers, Houston, TX, USA, 2010
 [2] D. Scott, "Bronze Disease: A Review of Some Chem-

ical Problems and the Role of Relative Humidity", *Journal of the American Institute for Conservation*, 29, 193, 1990

[3] A. Mezzi, E. Angelini, T. De Caro, S. Grassini, F. Faraldi, C. Riccucci, G.M. Ingo, "Investigation of the benzotriazole inhibition mechanism of bronze disease", *Surface and Interface Analysis*, Vol. 44, No.8, August 2012, pp. 968–971
 [4] L. Iannucci, J.F. Ríos-Rojas, E. Angelini, M. Parvis, S. Grassini, "Electrochemical characterization of innovative hybrid coatings for metallic artefacts", *European Physical Journal Plus*, vol. 133:522, 2018
 [5] E. Di Francia, R. Lahoz, D. Neff, E. Angelini, S. Grassini, (2018). "Laser cleaning of Cu-based artefacts: Laser/corrosion products interaction", *ACTA IMEKO*. 7. 104, 2018
 [6] L. I. McCann, K. Trentelman, T. Possley, and B. Golding, "Corrosion of ancient Chinese bronze money trees studied by Raman microscopy", *Journal of Raman Spectroscopy*, vol. 30, no. 2, Feb. 1999, pp. 121–132.
 [7] W. Martens, R. L. Frost, J. T. Klopogge, and P. A. Williams, "Raman spectroscopic study of the basic copper sulphates-implications for copper corrosion and "bronze disease"", *Journal of Raman Spectroscopy*, vol. 34, no. 2, Feb. 2003, pp. 145–151.
 [8] V. Hayez, J. Guillaume, A. Hubin, and H. Terryn, "Micro-Raman spectroscopy for the study of corrosion products on copper alloys: setting up of a reference database and studying works of art", *Journal of Raman Spectroscopy*, vol. 35, no. 89, Aug. 2004., pp. 732–738.
 [9] P. Rostron, S. Gaber, and D. Gaber, "Raman spectroscopy, review", *International Journal of Engineering and Technical Research (IJETR)*, vol. 6, no. 1, Sep. 2016, pp. 50–64.
 [10] P. Colombari, "On-site Raman study of artwork: Procedure and illustrative examples", *Journal of Raman Spectroscopy*, vol. 49, no. 6, Jun. 2018, pp. 921–934.
 [11] G. Bertolotti, D. Bersani, P. P. Lottici, M. Alesiani, T. Malcherek, J. Schlüter, "Micro-Raman study of copper hydroxychlorides and other corrosion products of bronze samples mimicking archaeological coins", *Analytical and Bioanalytical Chemistry*, Volume 401, 2012, pp. 1451-1457
 [12] R.L. Frost, "Raman spectroscopy of selected copper minerals of significance in corrosion", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 59, Issue 6, 2003, pp. 1195–1204
 [13] M. Bouchard, D. C. Smith, "Database of 74 Raman spectra of standard minerals of relevance to metal corrosion, stained glass and prehistoric rock art", in *Raman Spectroscopy in Archaeology and Art History*, ch. 25, (Eds.: H. J. M. Edwards, J. M. Chalmers), Royal Society of Chemistry, Cambridge, 2005, pp. 429–460.

- [14] M. Bouchard and D. C. Smith, "Catalogue of 45 reference Raman spectra of minerals concerning research in art history or archaeology, especially on corroded metals and coloured glass", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 59, no. 10, Aug. 2003, pp. 2247–2266.