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Original
Raman spectroscopic characterization of corrosion products of archaeological iron / Vietti, A; Angelini, E; Grassini, S; Donato, N. - In: JOURNAL OF PHYSICS. CONFERENCE SERIES. - ISSN 1742-6588. - 2204:(2022), p. 012066. (International Conference on Metrology for Archaeology and Cultural Heritage (MetroArchaeo) Milan, Italy 20-22 October 2021) [10.1088/1742-6596/2204/1/012066].

Publisher:
IOP publishing

Published
DOI:10.1088/1742-6596/2204/1/012066

Journal of Physics: Conference Series

PAPER • OPEN ACCESS

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To cite this article: A Vietti *et al* 2022 *J. Phys.: Conf. Ser.* **2204** 012066

Raman spectroscopic characterization of corrosion products of archaeological iron

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Abstract. Raman spectroscopy is a versatile analytical technique which allows the detection of different molecules analysing the vibrational modes. As a matter of facts, the vibrational frequencies are typical of a specific chemical bond or of a structural symmetry. In this study, the Raman technique is used for the determination of iron corrosion products, mainly oxides and hydroxides. Metallic artefacts buried in soil are affected, in dependence of their electrochemical nobility, by corrosion phenomena of various entities, which partially modify their chemical composition and their structure. The process may occur both during burial time and after the extraction from the archaeological site, implying the potential loss of information about the metallurgical technology and structure of the object. The study of the corrosion phenomena allows to propose tailored strategies for the restoration and conservation of the artefacts, especially in view of the storage of the artefacts in a museum. This study validates the use of the Raman technique for this purpose, showing its efficiency in the identification of the iron corrosion products in favourable conditions for the analysis of Cultural Heritage artefacts, as the possibility of performing *in situ* analysis without the need of a previous sample preparation.

1. Introduction

The archaeological site of Tharros, an ancient city located along the north-western coast of Sardinia (Italy), brought to light a wide variety of remains. The city was a crossroads between different dominations and cultures, starting from the Phoenicians, who brought along their knowledge about iron technology taking advantage of the mining resources of the city, up to the Romans, who totally modified the structure of the city. Since the 5th century AD, the city saw several Vandalic and Saracen raids forcing the inhabitants to leave the city around the 1070 AD [1].

Several metallic artefacts come from the Phoenician-Punic burial areas: jewelry, amulets, coins, iron nails [2]. They have been buried for a long time in an aggressive marine soil (rich in P, S, Cl) [3], which induced, in dependence of the electrochemical nobility of the metallic material, corrosion phenomena of different entity on the artefacts. As a matter of facts, metallic objects buried in soil spontaneously corrode, modifying partially their chemical composition and their structure. This dangerous long-lasting process may occur both during the burial time and after the excavation. Dealing with archaeological iron artefacts, the corrosion products are mainly iron oxides and hydroxides, which stratify in different layers with different chemical stability. Neff *et al.* [4] proposed a schematic description for the corrosion system: from the metal core (M) to the incrustation of soil

(S) (Figure 1). Generally, the Dense Product Layer (DPL) comprises well crystalized corrosion products whereas the Transformed Medium (TM) is characterized by the presence of less crystalized corrosion products mixed with external markers, for example quartz grains. In some cases, the initial iron structure slowly disappears during the burial time, giving back a very fragile artefact that needs to be safe-guarded.

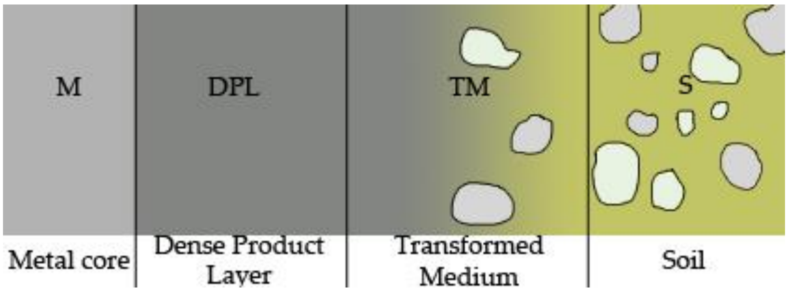

Figure 1. Description of the corrosion layers on an archaeological iron artefact.

The analytical investigation of the iron oxides and hydroxides provides information about the corrosion stratification and allows to establish restoration procedures based on scientific investigations and to propose tailored strategies to control the natural corrosion behavior of metallic artefacts [5].

The Raman effect provides a quick and relatively straightforward molecular identification of a material under examination. A Raman spectrum can be considered as a fingerprint that could be used for compound identification when a database of standard spectra is available for comparison purposes. The Raman spectroscopy turns out to be an efficient analytical technique that allows the identification of the corrosion products in a non-destructive, non-invasive manner [6-7].

2. Experimental

Three iron nails have been selected and cleaned using micro-sandblasting in order to eliminate the soil surrounding the sample. Thereafter, the nails have been embedded in epoxy resin; the samples were sectioned using a diamond blade to obtain longitudinal sections (Figure 2).

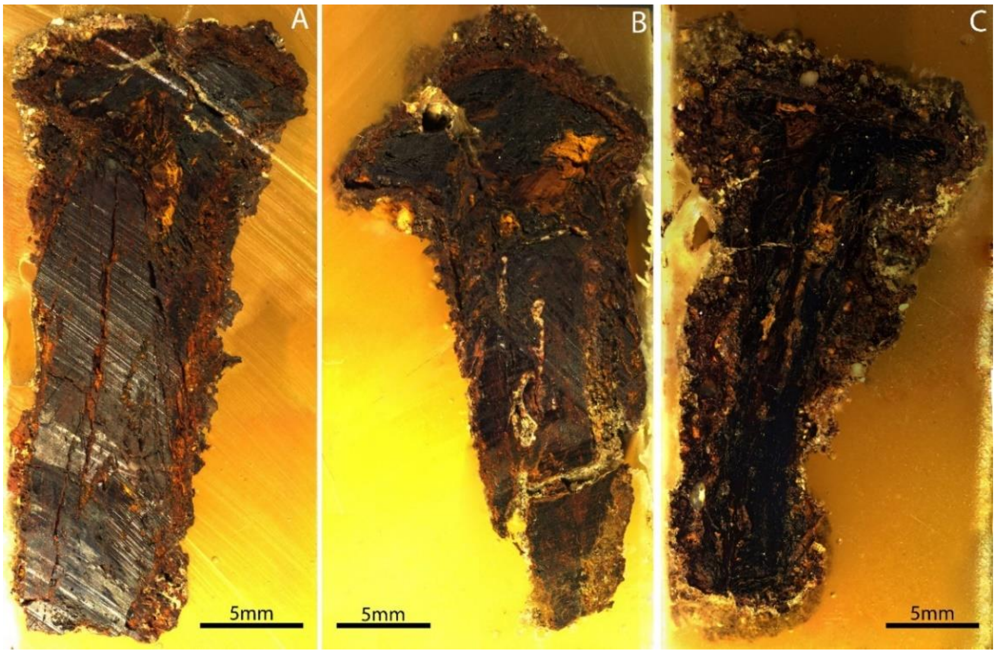

Figure 2. Cross-sections of the three iron nails analyzed by means of micro-Raman spectroscopy. A) sample CH_01, B) sample CH_02 and C) sample CH_03.

The preliminary observation was made using an IDS UI-1460SE micro-camera, obtaining high resolution images. In this way, it was possible to select the points of analysis.

The Raman spectroscopic analysis were carried out using a BWTEK i-Raman Plus spectrometer equipped with a cooled CCD detector coupled with an Opteka microscope. The excitation source is a 785 nm diode laser; it was focused on the sample using a 20x microscope objective, obtaining a laser spot of 90 µm. To avoid damage on the corrosion products, the laser power was lowered [8]. The acquisition of the spectra was performed in 150-4200 cm^{-1} range, with a 5 cm^{-1} spectral resolution; the settings used for the analysis are summarized in Table 1. The collected spectra were compared with databases available in literature [9].

Table 1. The setting used for Raman analysis.

Laser power (mW)	Laser exposure (s)	Repetitions (time)
15-30	10-20	5

3. Results and Discussion

The micro-Raman analysis allowed the detection of the main corrosion products of the archaeological iron findings. All the samples analysed are totally mineralized and the original iron core is disappeared, according to the long-lasting burial of the artefacts in a coastal soil rich in aggressive elements [10]. Magnetite and goethite are the main corrosion products, sometimes in a complex mixture, located especially in the Dense Product Layer (DPL), in the inner part of the nail. The Raman spectroscopy allowed the detection of these phases, thanks to the different characteristic peaks located around 670 cm^{-1} (magnetite) and 685 cm^{-1} (goethite) (Figure 3). This is more complex for the maghemite, which shows the same 670 cm^{-1} peak that could be overlapped.

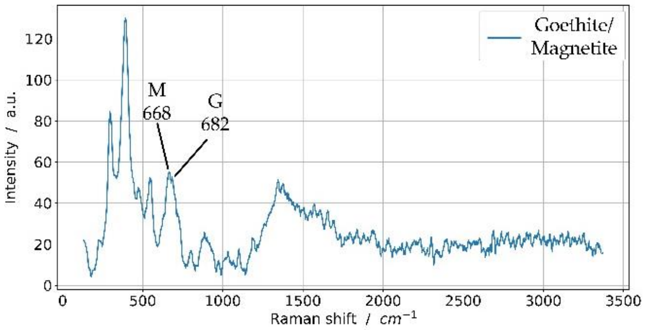

Figure 3. Raman spectrum of a goethite-magnetite complex mixture found on sample. CH_01, showing the characteristic peaks of the minerals.

Hematite is present in traces, mainly in the magnetite-goethite matrix. This mineral has a strong Raman signal, which allows an easy detection of this phase (Figure 4). Sometimes it is mixed with goethite in the Dense Product Layer.

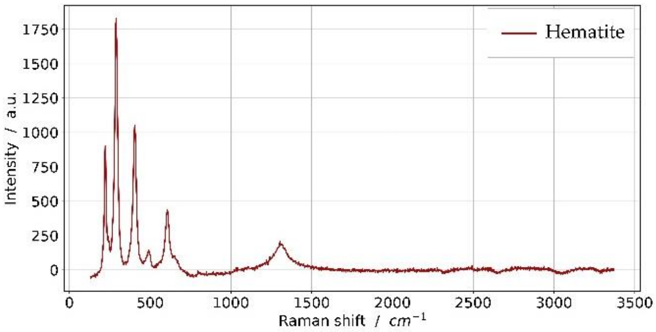

Figure 4. Raman spectrum of hematite, found on sample CH_03. In this spectrum are evident the characteristic peaks of the mineral around 410 cm^{-1} and 1310 cm^{-1}.

In Table 2 are briefly summarized the characteristic Raman peaks which permit the discrimination between the different corrosion products found in the archaeological samples.

Table 2. Characteristic Raman peaks (expressed in cm^{-1}) of the main corrosion products.

Hematite	**Goethite**	**Magnetite**	**Maghemite**	**Lepidocrocite**	**Akaganéite**
223, 289, 404, 496, 607, 817, 1310	244, 300, 390, 685, 980, 1100, 1300	538, 670	350, 512, 670, 720	250, 380, 528, 650, 1298	310, 390, 538, 720

The Transition Zone, where the corrosion products are less crystalized, is composed essentially of goethite, maghemite and lepidocrocite. Regarding the lepidocrocite, which is a very reactive phase most probably formed after the excavation, is located especially in the cracks of the nail or at the interface with the soil. An example of the general corrosion stratigraphy is briefly schematized in Figure 5.

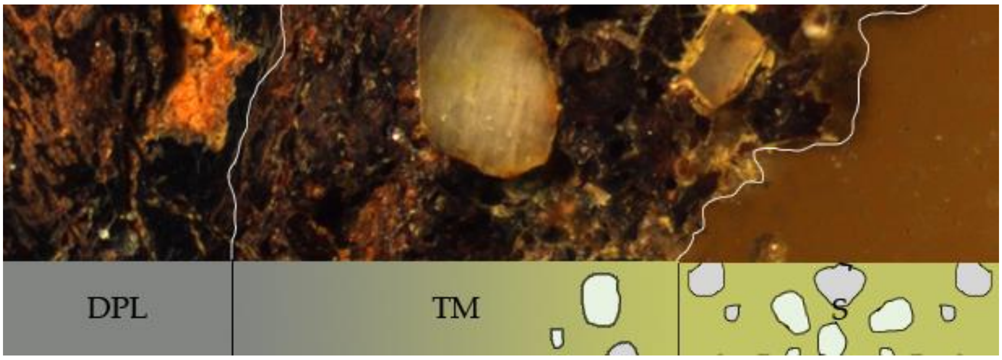

Figure 5. The schematic corrosion layers correlated with the section of sample CH_03. The soil layer (S) is not present anymore, because the sample was cleaned before the inclusion in resin.

According to the composition of the soil presented by Angelini *et al.* [8] and reported in Table 3, the presence of Akaganéite (β-FeOOH) can not be totally excluded. In fact, this chlorinated phase, is typical of a marine environment closely linked to the presence of rock salt (Halite) in the surrounding soil.

Table 3. Characterization of the soil of Tharros

pH (H_2O)	8,7
wt% $CaCO_3$	31,7
wt% C_{CaCO3}	3,8
wt% $C_{organic}$	4,5
Main metallic elements	Ca, Fe, Mg, Pb
wt% P_{total}	3,2
wt% Si_{total}	2.65
Texture	Sandy loam
XRD analysis	Calcite, Quartz, Halite, Görgeyite

A summary schedule of the preliminary Raman results is shown in Figure 6.

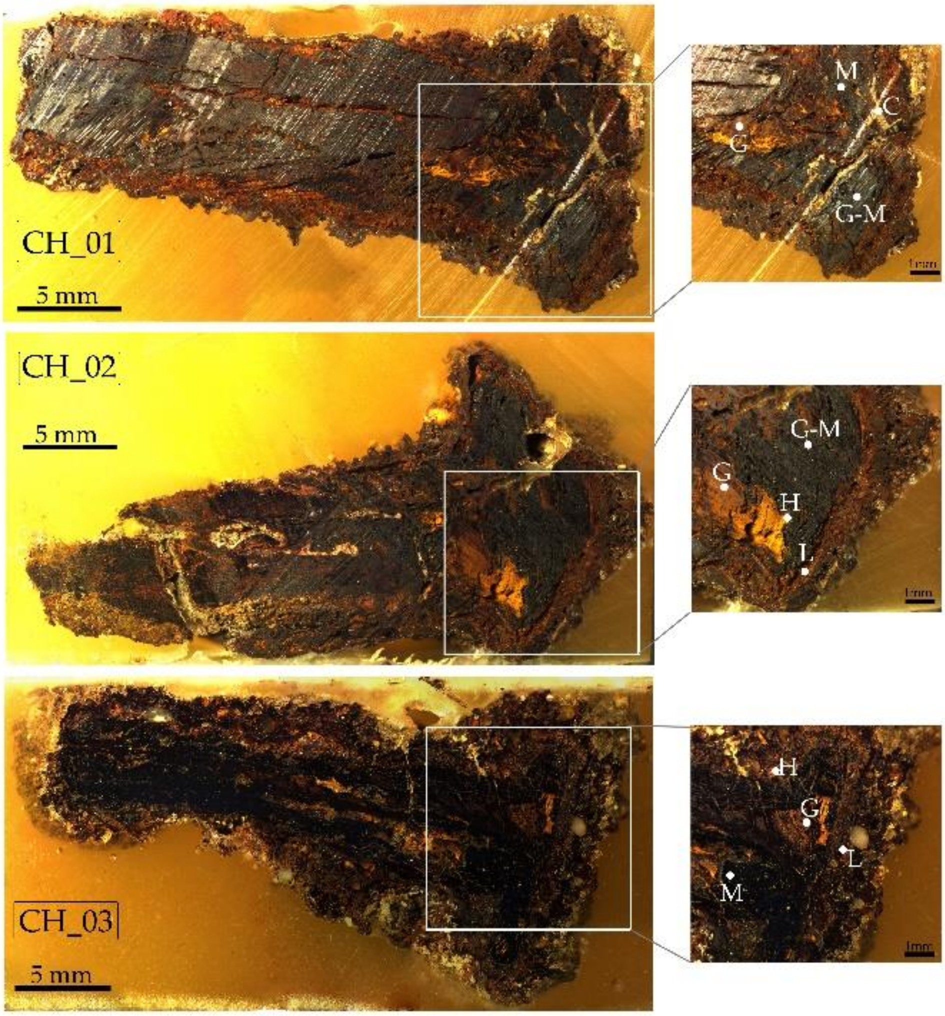

Figure 6. Cross-sections of the nails from Tharros with the identification of the different corrosion products by Raman spectroscopy. G = goethite, M = magnetite, H= hematite, L = lepidocrocite, G-M = mixture of goethite and magnetite.

4. Conclusions

The results obtained in this study confirm that the Raman spectroscopy is a versatile and efficient analytical technique suitable to the detection of iron corrosion products. This technique has the advantage of being non-destructive and portable, allowing the detection of iron corrosion products even directly on the archaeological site. As a matter of facts, it allows *in situ* structural and chemical analysis which permits to give information to archaeologists and curators about the state of conservation of the artefacts, in order to plan a proper tailored storage. Several techniques are available for this purpose (e.g., X-Ray Diffraction, X-Ray Fluorescence, Scanning Electron Microscope, Raman spectroscopy); concerning the Cultural Heritage field, it is preferred to choose a non-destructive analysis which does not necessitate the preparation of the sample and its destruction. Among these analytical methods, Raman micro-spectroscopy turns out to be an efficient technique to discriminate the iron oxides.

The iron nails under consideration are totally mineralized due to the long-time burial conditions. The initial iron core is no longer present, totally replaced by iron oxides. Goethite and magnetite are the main minerals found in the core of the samples, whereas hematite, akaganéite and maghemite are especially presents in traces mixed with other minerals. Lepidocrocite is mainly found at the interface with soil, sometimes mixed with carbonates.

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