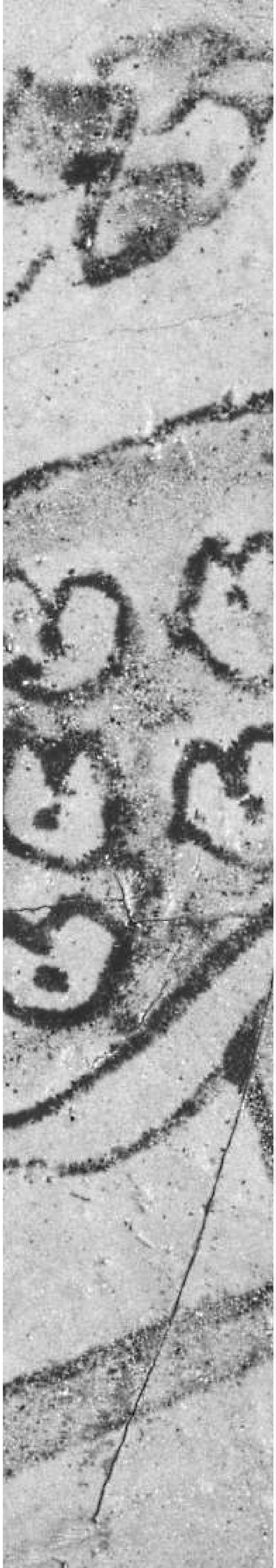
# TECNOLOGÍA DE LOS VIDRIADOS EN EL OESTE MEDITERRÁNEO:

## *Tradiciones islámicas y cristianas*

J. Coll Conesa · E. Salinas Pleguezuelo (Eds.)



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GOBIERNO DE ESPAÑA
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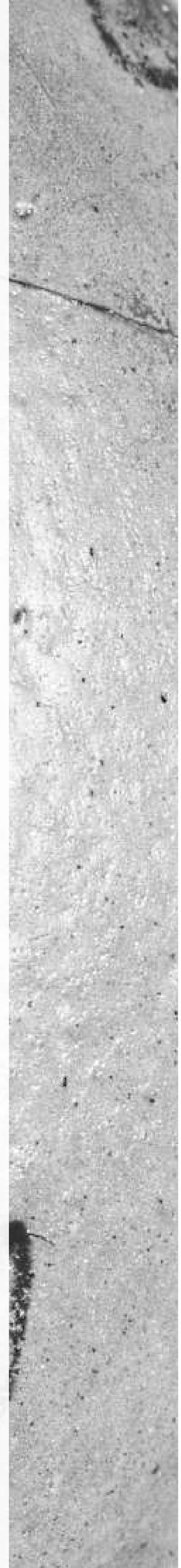

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# SUMARIO

# THE SOURCE OF CALCIUM AND PHOSPHORUS IN THE ISLAMIC GLAZED CERAMIC RECOVERED IN THE TOWN PORT OF MÉRTOLA (PORTUGAL)

# LA FUENTE DE CALCIO Y FÓSFORO EN LAS CERÁMICAS VIDRIADAS ISLÁMICAS RECUPERADAS EN LA CIUDAD PORTUARIA DE MÉRTOLA (PORTUGAL)

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ABSTRACT
This text presents the potential of a micro-analytical approach for the characterization of different inclusions identified in the ceramic paste and on the glazed decorations of some green and manganese Islamic ceramics recovered in the town port of Mértola (South-

SOMMARIO
Il testo presenta il potenziale di un approccio micro-analitico per la caratterizzazione di differenti inclusioni identificate nella pasta ceramica e nella decorazione invetriata di alcuni frammenti di ceramica Islamica decorata a verde e manganese recuperate presso la città

ern of Portugal). The samples were analysed using a stereoscopic microscope, by scanning electron microscope coupled to an energy dispersive X-Ray spectrometer (SEM-EDS) and by μRaman spectroscopy. The complementarity and potentials of these analytical techniques allowed the chemical, microstructural and molecular characterization of the inclusions identified in the ceramic paste and on the glazed decorations. Results established that they were enriched calcium and phosphorous. Moreover, μRaman spectroscopy established that apatite was added in the for of bone fragments, both to the glaze and to the ceramic paste.

KEY WORDS
Calcium, Phosphorous, Apatite, Ceramic paste, Glaze

di Mértola (Sud del Portogallo). I campioni sono stati analizzati utilizzando un microscopio stereoscopico, un microscopio elettronico a scansione accoppiato con un detector ai Raggi-X a dispersione di energia (SEM-EDS) ed un microscopio Raman (μRaman). La complementarietà e il potenziale di queste tecniche analitiche hanno permesso la caratterizzazione chimica, micro-strutturale e molecolare delle inclusioni identificate nella pasta ceramica e nella decorazione invetriata. I risultati hanno stabilito che le inclusioni erano arricchite in calcio e fosforo. Inoltre i risultati μRaman hanno stabilito che apatite, sottoforma di frammenti di ossa, è stata aggiunta sia all'impasto ceramico che alla decorazione vitrea.

PAROLE CHIAVE
Calcio, Fosforo, Apatite, Pasta ceramica, Invetriatura

## 1. INTRODUCTION

The characterization of archaeological ceramics can be accomplished using different analytical techniques such as ceramic petrography (OM), powder X-ray diffraction (XRD), X-ray fluorescence (XRF), inductively coupled plasm mass spectrometry (ICP-MS), fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy. In some cases, the restriction in the sample mass and the size of specific features identified on the ceramic paste and on the decorative layers, such as glazed and painted decorations, constrains the material analysis. Depending on the goals of the research, really satisfactory results can be accomplished also coupling micro-analytical techniques (Schiavon et al., 2016) (Rosado et al., 2018) (Mercurio et al., 2018) which require very small amounts of sample. In this current case, we decide to use a stereomicroscope, a scanning electron microscope (SEM-EDS) and a μRaman spectrometer for the study of specific inclusions observed in some green and brown glazed decorated ceramic from the 11$^{th}$ century recovered in the town of Mértola. The stereomicroscope is usually utilized during initial analysis of the artefact in order to observe and to collect images of specific features of the sample. **μ**Raman spectroscopy studies vibrational, rotational and other low-frequency modes in a system. It is commonly used in analytical chemistry to provide a structural fingerprint by which molecules can be identified. It relies on inelastic scattering, or Raman scattering, of monochromatic laser light in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, resulting in the energy of the laser photons being shifted. The shift in energy gives information about the vibrational modes in the system and allow the identification of specific compounds (Frezzotti, Tecce and Casagli, 2012). µRaman spectroscopy is extensively applied for the study of cultural heritage both using in-lab (Rosado et al., 2018) (Silvestri, Nestola and Peruzzo, 2016) or in-situ (Colomban, Milande and Lucas, 2004) equipments. Scanning electron microscopy coupled to an energy dispersive X-Ray spectrometer (SEM-EDS) is a micro analytical technique that uses a highly focused and accelerated beam of electron to analyse a specimen. When the beam hit the target it generates backscattered electrons, secondary electrons and characteristcis X-Ray. The secondary and backscattered electron allows the morphological analysis of very fine details in the samples while the characteristics X-Ray allow the micro-chemical analysis of specific point/area/region in the sample. This technique is widely adopted for the study of cultural heritage and especially in the analysis of ceramic materials both for the study of the ceramic paste as well as of the decoration (Tite, 1991) (Molera, Vendrell-Saz and Pérez-Arantegui, 2001) (Freestone and Middleton, 1987) (Froh, 2004). In the present study these analytical techniques were applied on the characterization of specific inclusions, observed during the preliminary analysis of the ceramic paste and of glazed decoration of some green and brown glazed decorated ceramics. Regarding glazed analysis we focused our attention on brown/black glazed decorations. The main goal was to utilize micro-destructive and micro-analytical techniques to determine the morphological characteristic of the inclusion, its chemical composition and to get the structural fingerprint, by vibrational spectroscopy.

## 2. METHODOLOGY

Before analysis small portion of the samples were impregnated using an epoxy resin. The resin blocks were afterward polished using and automatic polishing machine using first grinding papers and then diamond pastes until a particle size of 1 μm. Preliminary observations of the impregnated blocks were carried out using a Leica M205C stereomicroscope coupled to a camera model Leica DFC295. Microanalyses were performed using a variable pressure HITACHI S3700N SEM coupled with a Quanta EDS microanalysis system. The Quanta system was equipped with a Bruker AXS XFlash® Silicon Drift Detector (126 eV Spectral Resolution at FWHM/MnKα). PhiRhoz quantitative elemental analysis was performed using the Bruker ESPRIT software. The system was checked using 7 Standard Reference Materials (SRM), namely 5 glasses (CMOG B, CMOG C, SGT5, SGT7, SGT8) and 2 micro analytical reference materials (BIR-1G, BCR-2G). For oxides concentration below 0.3 wt% the error could be higher than 20% of the certified values; for oxides concentration between 0.3 and 1 wt% the error was maximum of 10% of the certified values; for oxides concentration higher than the 1 wt% the error was lower than of 10% of the certified values. The operating conditions for EDS analysis were as follows: backscattering mode (BSEM), 20 kV accelerating voltage, 10 mm working distance, 100 μA emission current and 40Pa pressure in the chamber. Scanning electron microscopy was utilized to characterize the ceramic body, the temper and the decorative layers (glazed or painted when present). Chemical concentrations were normalized to 100% and uncertainty is 1σ.

μRaman analyses were performed using a HORIBA XPlora spectrometer equipped with a diode laser of 28 mW operating at 785 nm, coupled to a BX41 Olympus microscope. Raman spectra were acquired in extended mode in the 100–1400 cm-1 region. The equipment was previously calibrated using a quartz reference sample. The laser was focused with an Olympus 100x lens, 10% of the laser power on the sample surface, 15 s of exposure, 20 cycles of accumulation. Results were acquired and interpreted using LabSPEC5 software.

## RESULTS

The study focuses on the analysis of green and brown decorated glazed ceramic samples. During the preliminary observation with the aid of the stereoscopic microscope we identified some inclusion in the ceramic

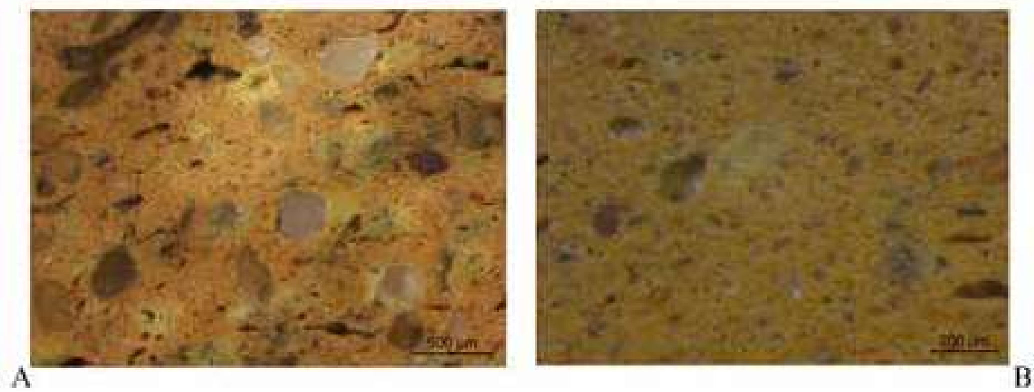

Fig. 1. Glassy inclusion observed on two different ceramic samples. In figure A the glassy inclusion is partly absorbed in the ceramic paste and bordered by a creamy coloured rim. In figure B the glassy inclusion in the centre of the picture it does not show a rim.

body. These inclusions were mostly circular or slightly elongated in shape (fig. 1 A-B). In some cases, the borders of these particles were not very clear. This was probably the result of the firing process, and inclusions were partially absorbed in the cermic paste forming a light brown rim. These inclusions were mostly sub-rounded and they were completely different from temper inclusions, mainly for their colour (white), for the presence of a rim or for their opacity.

The analysis of these inclusions by SEM-EDS revealed that they were mainly glassy fragments sometimes with inclusion of quartz. In other cases, they were composed by spongy like inclusion surrounded by a silica lead glass. The elemental mapping distribution of the inclusion in (fig. 2 A-B-C) clearly shows that the spongy core is extremely enriched in calcium and phosphorous and partly by potassium, while the border of the inclusion is mainly composed by silicon, tin and lead. The results of this preliminary study indicate that the inclusion observed is not the result of a contamination, but conversely it was probably added to the ceramic paste voluntary during the manufacturing process of the artefact.

Calcium and phosphorous rich inclusion were also identified during SEM-EDS analysis on the decorations, especially on green and black glazes. The inclusions were involved in the silica lead glaze and they showed different sizes (1-25 μm). In some cases, these particles appeared

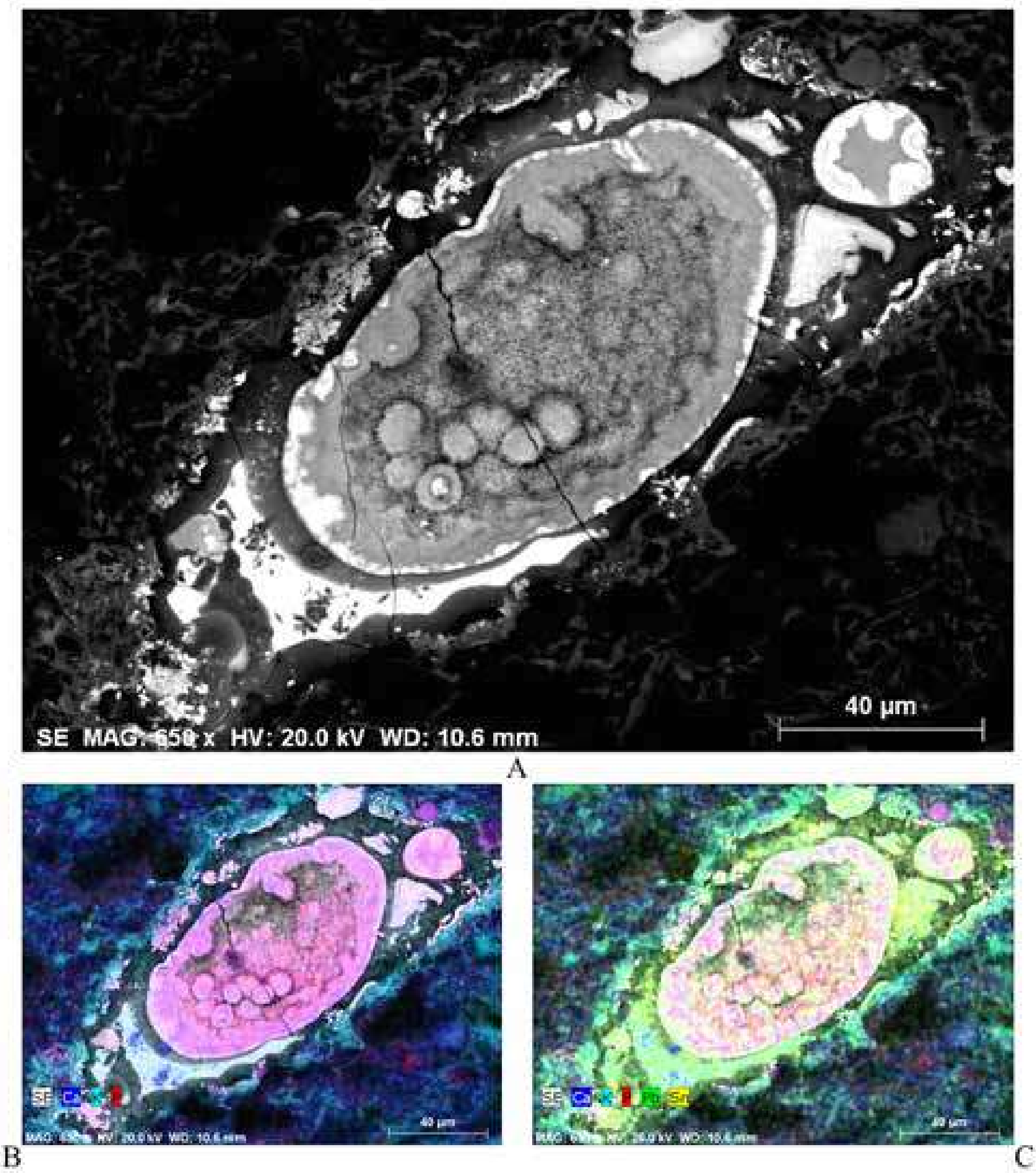


Fig.2. BSE image (A) and chemical elemental mapping distribution of a glassy inclusion detected inside the ceramic paste (see Fig. 1B). The maps show that the core is enriched in calcium and phosphorous while the borders are more enriched in potassium, lead and tin (B-C).

as isolated inclusion while in other cases were observed as micron sized particles dispersed over the whole surface of the glazed decoration. The inclusion did not present the typical features of a weathered glaze that

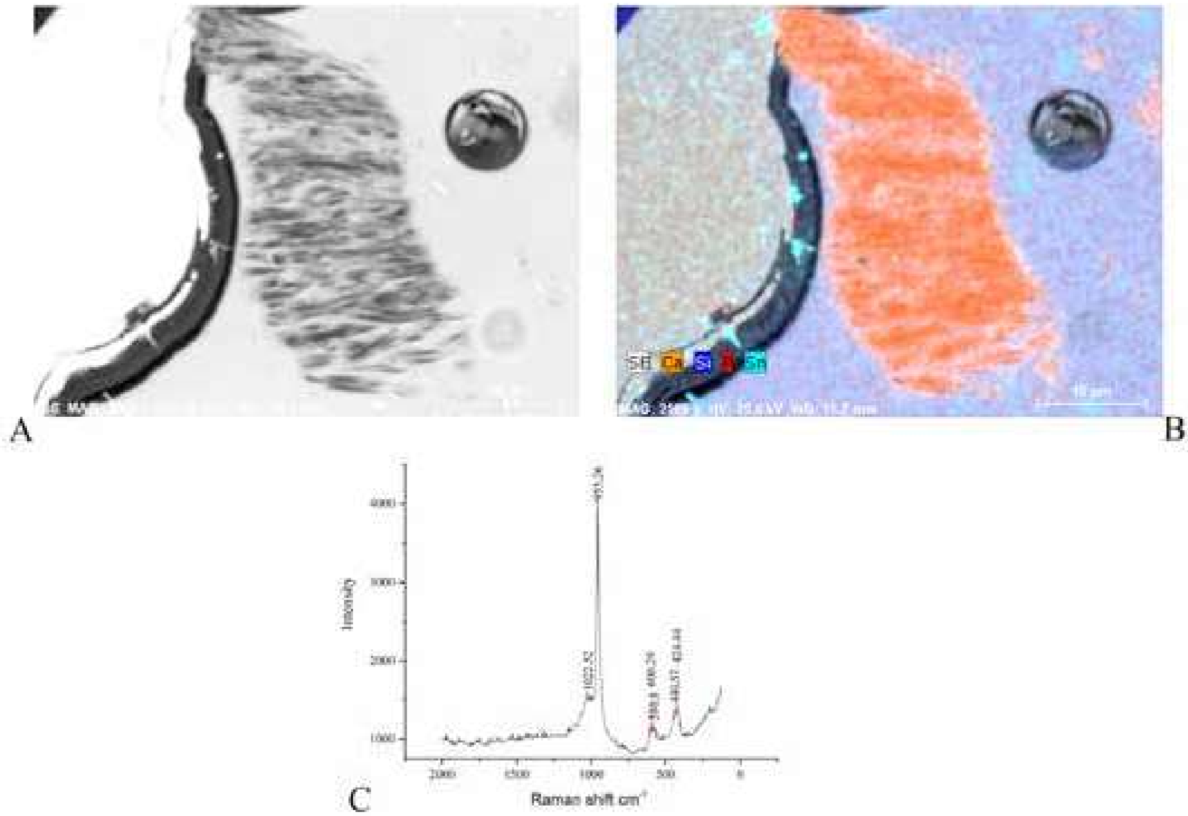


Fig. 3. BSE image and chemical elemental mapping distribution of a spongy inclusion detected on the black glaze (A-B). The maps show that the core is enriched in calcium and phosphorous while the borders are more enriched in silicon and tin (B). Image C show the µRaman spectra obtained from the analysis of the inclusion with the identification of the main bands.

usually appear first on the surface of the glazed decoration. In the case of black glazed decoration punctual analysis performed by SEM-EDS showed a significant amount of oxide of calcium (37.72 wt%), phosphorous (25.85%), silicon (12.84 wt%) and lead (20.57 wt%) along with oxides of aluminium (0.71 wt%), potassium (0.13 wt%), magnesium (0.17 wt%), manganese (0.55 wt%), iron (0.33 wt%) and sodium (1.12 wt%). In the same area tin was also detected (fig. 3 A-B). The analysis by µRaman spectroscopy, basing on the identification of the bands 1022, 955, 600, 580, 440 and 424 cm$^{-1}$, identified the inclusion as being composed mainly by carbonate-apatite (Penel et al., 1998) (fig. 3C), mainly encontered on bones.

## CONCLUSIONS

This contribution showed the potential of the application of a micro-analytical and micro destructive approach for the characterization of specific inclusions identified both in the ceramic paste and on the glazed decoration. Results of the inclusion identified on the ceramic paste indicate the presence of a glassy inclusion with a spongy like shape enriched in calcium and phosphorous. The analysis of the inclusion identified on the glazed decoration showed that is spongy in shape, it is enriched in oxides of calcium and phosphorous and that it was mainly composed by carbonate apatite, reltated to the addition of bone fragments to the frit. This frit was afterward utilized for the preparetion and application of green and brown glazes.

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