2022 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
University of Calabria, Italy, October 19-21, 2022

Preliminary study for the characterization of Roman plasters from the cetariae in Porto Palo (Sicily).

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Abstract **– This investigation concerns the characterization of plasters samples taken from archaeological vats from production installations for fish by-products from the archaeological site of Portopalo in Sicily (Italy). The main purpose of this work is to characterize the plasters in order to understand if specific plasters production technologies were used in relation to the function of the vats and if there is a change in time/space among the vats studied that apparently belonged to different phases of occupation of the site.**
The compositional characterization of the distinct types of materials used, necessary for the plasters production, required a multi-analytical approach [1-2-3-4], which included techniques such as optical microscopy with transmitted polarized light (OM); X-ray diffractometry (XRD); scanning electron microscopy coupled with microanalysis (SEM-EDS); ion chromatography (CI). The first preliminary elaboration allows to suggest the presence of two distinct hydraulicizing materials used and a different content of salts in the different vats that could be related to a difference in the processing of fish or the duration of use.

I. INTRODUCTION

The study of mortars and plasters have helped to solve important archaeological questions such as the techniques used in their manufacture, the origin of the raw materials used in their production, the presence of different constructive phases in the buildings and/or raw material procurement [1-2-5-6-7-8]. Since its introduction in architecture, mortars and plasters become increasingly popular, and by the Roman era, this material was systematically used for the construction of all the architectural structures.

Plasters from production vats in the archaeological area of Portopalo (Sicily, IT) were studied to identify the raw materials used and comparing the samples to see if there was a change in time or space in the making process of the plasters; verify if a specific technology was adopted and understand if that technology may correspond to the function of the vats that had to come in contact with liquid and salty materials.

II. THE ARCHAEOLOGICAL CONTEXT

Fishing is a practice that has characterized the coastal territory since ancient times, becoming in some cases the main source of subsistence. Over time, specialized workers have established themselves in many areas of the Mediterranean basin and have created factories for the conditioning, processing and conservation of fish by-products [9]. The example of Portopalo in Sicily, among the most significant archaeological sites known for this type of production, is of particular importance [10-11-12-13]. The first excavations in the area took place in the 1980s, allowing researchers to uncover evidence of a Hellenistic-Roman route that established this location as a major fish sorting and processing center [14]. The first excavation campaigns of the ARCHAEOFISH project, directed by professors Daniele Malfitana (University of Catania) and Darío Bernal-Casasola (University of Cadiz), whose main objective is to analyse and reveal the socio-cultural phenomena connected to the practice of fishing and the consequent processing of fish in the context of the Western Mediterranean in Roman and Late Antique times, begun in 2019. The research at the archaeological site was mainly aimed to collect

information about the organization, structure, and sequence of occupation of the site, as well as the chronology. As a result of the excavation activities carried out, five areas of the settlement have been unearthed (from AR1 to AR5), with a specific attention towards areas AR1 and AR2, located near the Scalo Mandrie beach in Portopalo (Sicily). It is there that most of the production and processing vats could be observed (Fig. 1). Each vat can be located in a production unit called *cetaria* [9].

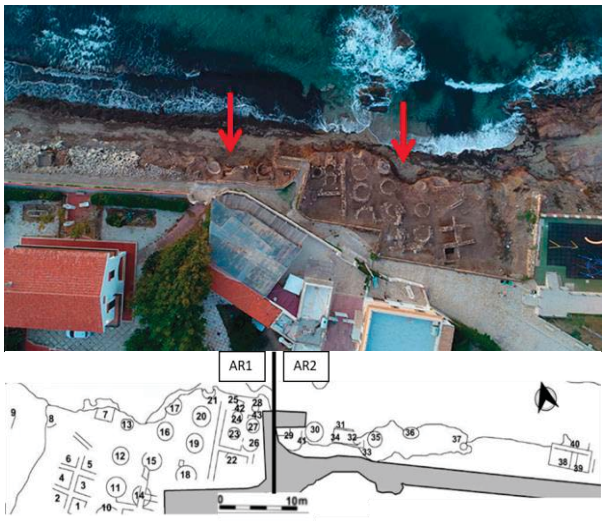

Figure 1 The figure shows the different vats visible on the archaeological area of Portopalo (Scalo Mandrie, Sicily).

Teams of experts analysed all the most relevant materials, from pottery and amphorae, to malacofauna [10-11-13-14-15-16]. What emerges is a high-production site that probably allowed the export of a variety of fish products, from garum to salsamenta [11], which had a protracted sequence of occupations that goes from the 5th century BC to the 5th century AD, with more activity during the Hellenistic-Roman period [10].

Over the years, with the succession of the various phases of occupation, various structures were built and today it is still possible to observe the presence of many vats with circular or quadrangular shapes. Since the excavation process began, more than sixty vats have been found [16]. In some cases, they were excavated directly into the rock and then coated with plasters, in others they were made directly in masonry.

III. MATERIALS AND METHODS

For this study, a total of twenty-two plaster samples were taken from vats located in the areas AR1 and AR2 of the archaeological site of Portopalo. Samples are indicated from C1 to C22 in Table 1 together with their localization.

Table 1. The table shows the samples and the relative localization in the production units (Cetaria) and in the different vats.

Sample	Cetaria	Vat
PP19_C-1	I	V-1
PP19_C-2	I	V-4
PP19_C-3	I?	V-7
PP19_C-4	II	V-12
PP19_C-5	II	V-13
PP19_C-6	II	V-17
PP19_C-7	III	V-27
PP19_C-8	II?	V-42
PP19_C-9	IV	V-29
PP19_C-10	II?	V-41
PP19_C-11	IV	V-30
PP19_C-12	IV	V-34
PP19_C-13	IV	V-34
PP19_C-14	IV	V-31
PP19_C-15	IV	V-32
PP19_C-16	IV	V-33
PP19_C-17	IV	V-35
PP19_C-18	IV	V-35
PP19_C-19	IV	V-36
PP19_C-20	V	V-39
PP19_C-21	I	V-1
PP19_C-22	?	V-64

The methodology used to study the plasters involved:
- The petrographic analysis on thin sections using an optical petrographic microscope Zeiss equipped with a Canon PowerShot A640 camera.
- X-ray powder diffraction (XRPD) for the study of the mineralogical composition of the samples using a Bruker D8 Advance X-ray powder diffractometer.
- Energy Dispersion Microanalysis by Scanning Electron Microscope (SEM-EDS) using an Ultra High-Resolution SEM (UHR-SEM) - ZEISS CrossBeam 350, equipped with an EDS - EDAX OCTANE Elite Plus, Silicon drift type spectrometer for the study of the chemical composition of the binder.
- Soluble salts analysis was made with a Thermo-Dionex ICS-1100 Ionic Chromatograph.

IV. RESULTS AND DISCUSSIONS

From the first observations made with OM, two main types of plasters can be identified (Fig 2). In particular, two samples (C12 and C17) are characterized by the abundance of *cocciopesto* (crushed pottery), which is supposed to be used to confer hydraulicity to the plasters. On the contrary, the other samples display the presence of pozzolan as hydraulicizing material.

The two samples with *cocciopesto* come from the outermost layer of vats V-34 and V-35. The samples taken from the underlying layer are completely different because of the presence of pozzolan instead of *cocciopesto*. These samples probably correspond to a pre-existing phase.

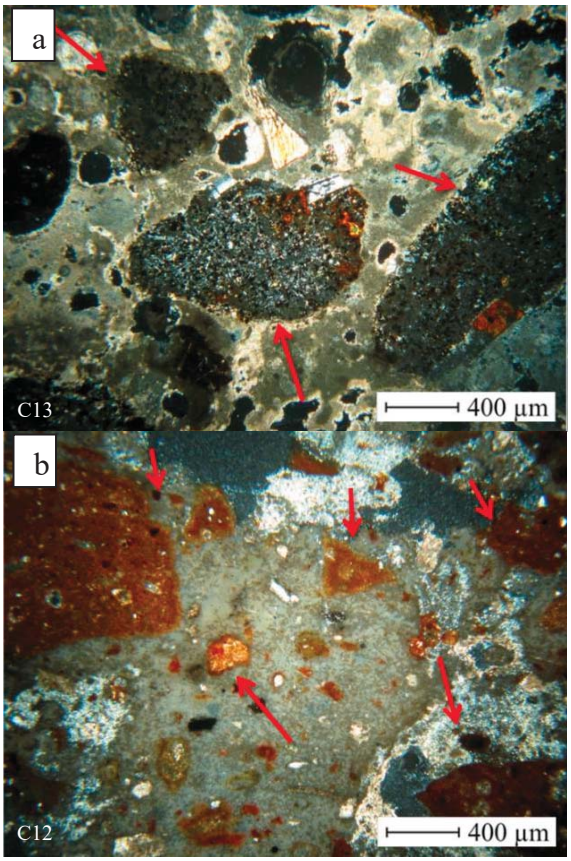

Figure 2 Thin section images taken with polarized light with (a) presence of pozzolan (sample C13); (b) presence of *cocciopesto* (sample C12).

In all the samples it is also possible to highlight the presence of bioclasts. An example is shown in Figure 3 where it is possible to observe details of samples characterized by bioclasts of many sizes and shapes.

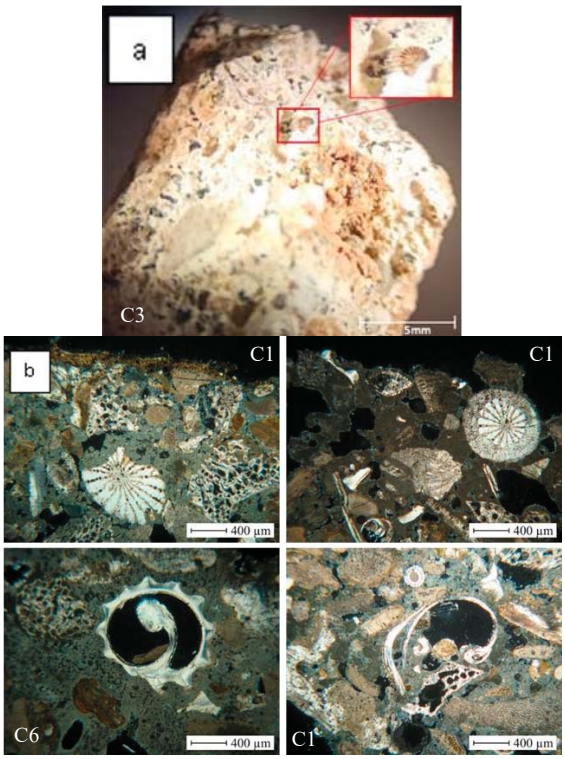

Figure 3 This figure highlights the presence of bioclasts of various shapes and sizes.

(a) Macroscopic evidence (sample C3) (b) Images of bioclasts in thin section with polarized light (samples C1 and C6).

The preliminary analysis also points out other differences among the samples with pozzolanic aggregate. It is possible to hypothesize that the differences in the percentages of aggregate and binder correspond to the presence of different construction phases, but this has to be confirmed with further studies. In particular, the determination of the percentages of aggregate and binder made by visual estimation with comparison tables allows to identify two types of plasters characterized by (Fig.4):

- The abundance of pozzolan in association with a low amount of bioclasts.
- A high amount of bioclasts together with a low percentage of pozzolan.

The samples C7, C16 (that have a low percentage of pozzolan) and C10 and C14 (that have pozzolan in trace) differ from the others because they are characterized by the presence of several superposed layers that have the same composition and petrographic features, which suggests a frequent re-plastering of the vats. These samples do not belong to the categories listed above.

Among the samples having *cocciopesto* aggregate, only the sample C12 has a thin external layer.

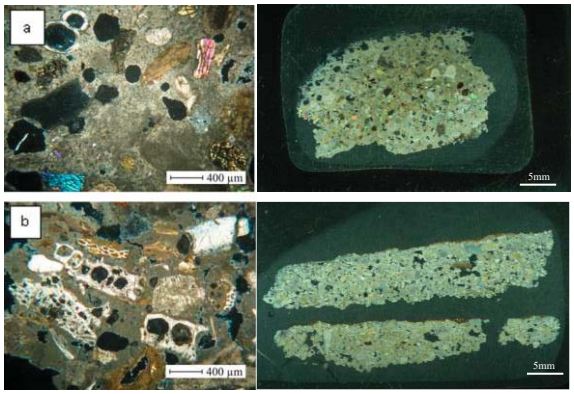

Figure 4 Example of thin section images taken with polarized light with (a) high amount of pozzolan and low amount of bioclast (sample C3); (b) low amount of pozzolan and high amount of bioclast (sample C1).

The X-Ray diffraction results of all the samples, support the thin section study and confirm the presence of the mineralogical phases observed in thin section such as calcite, pyroxene, plagioclase, quartz and opaque oxides. Magnesium calcite was identified in all the samples by XRD. The SEM-EDS analysis are in progress; but for samples from C1 to C15 data have already been collected and confirm the presence of magnesium in the binder (from a minimum of 0,8% by weight to a maximum of 6% by weight). For the samples analysed with this technique also the hydraulicity index (HI) of the binder has been calculated. Low HI values have been verified despite the presence of hydraulicizing aggregate, this may be related to dissolution and recrystallization phenomena of the binder. The samples have a lime-based binder, and the HI is between 0,01 and 0,3. This allows to identify samples that have a hydraulic index comparable to aerial lime, while others to weakly, medium and properly hydraulic lime (Tab.2).

Table 2. The table shows the samples and the relative hydraulicity index (HI) calculated for each layer of the samples.
A: aerial; W: weakly; M: medium; P: properly.

Sample	Layer	HI	
C1	I	0,03	A
C2	I	0,34	P
C3	I	0,02	A
C4	I	0,02	A
C5	I	0,02	A
C5	II	0,02	A
C6	I	0,05	A
C7	I	0,01	A
C7	II	0,39	P
C8	I	0,18	M
C8	II	0,18	M
C9	I	0,06	A
C10	I	0,04	A
C10	II	0,08	A
C11	I	0,04	A
C12	I	0,23	M
C12	II	0,12	W
C13	I	0,04	A
C14	I	0,10	A
C14	II	0,20	M
C15	I	0,12	W

It is interesting to observe that through the determination of soluble salts, the samples showed high content of Na and Cl, suggesting the contact with abundant salts. Analysing the data for each identified cetaria for which more than one sample was taken, the vats with a higher Na and Cl content are:

C2 (Cetaria I): 12.867 ppm (Na), 20.698 ppm (Cl)
C4 (Cetaria II): 4.457 ppm (Na), 6.719 ppm (Cl)
C12 (Cetaria IV): 44.721 ppm (Na), 32.267 ppm (Cl).
For cetariae III and V only one sample was taken.

As the location of the vats is similar (all of them are located near the sea), it is possible to suggest that the highest values of NaCl correspond to the addition of more abundant salts for the processing of the fish by-products.

All samples display SO_4^{2-} (maximum value of 4.244 ppm in the sample C14) while PO_4^{3-} was detected only in the samples C11 and C4. Future analyses are needed to better understand the origin of these compounds.

V. CONCLUSIONS

The preliminary data obtained on samples from the Portopalo archaeological site allow to make some general observations regarding the manufacture of the plasters.

First of all, the characterization of the plasters makes it possible to suggest the presence of two distinct hydraulicizing material (*cocciopesto* and pozzolan). The fact that *cocciopesto* is present only as a re-plastering layer suggests that it was applied in a later moment. Therefore, it is possible to say that the plasters with *cocciopesto* represent a change in the making of the plasters, suggesting a change in the technology over time. Moreover, among the samples that display pozzolan, some samples are distinguished by different quantities of aggregate of the same type (bioclasts and pozzolan), and this could be related to the presence of different construction phases that have to be further investigated.

The analysis of the binder using SEM-EDS, shows an anomaly, as there are samples with a low hydraulic index (HI) (comparable to aerial lime) despite the presence of hydraulicizing pozzolan. This could be due to the probable presence of dissolution and recrystallization phenomena of the carbonate binder; however, it requires further investigation.

Some of the vats are characterized by various layers that may indicate the need of re-plastering possibly due to the deterioration of the plasters caused by its use for the processing of fish by-products.

Another interesting point is the presence of a large quantity of soluble salts detected with ion chromatography (CI). The high values of NaCl, detected for samples located in the same area but in different vats, can be due in part to the fact that the vats are located close to the sea, but it could also correspond to their use during a longer period of time or to the use of more abundant salt for processing of fish. Only two samples contain phosphate (PO_4^{3-}), which may be related to a specific function of the vats that need to be verified.

The local provenance of the raw materials used for the realization of the plasters has to be confirmed by further studies.

VI. ACKNOWLEDGEMENTS

This paper is part of the activities of the PhD project of Genea Girimonte at the PhD program Sociedad y Cultura of the Universitat de Barcelona, of the projects ARQUEOFISH (P18-FR-1483, PAIDI 2020) (D. Bernal-Casasola and D. Malfitana), the I+D+i Project RACA-Med II (PID2020-113409GB-I00) (A. Pecci, P. Reynolds), financed by the MCIN/AEI/10.13039/501100011033, the Dipartimento di Biologia, Ecologia e Scienze della Terra of the Università della Calabria, the ERAAUB research group, and the Instituto de Arqueología of the Universitat de Barcelona.

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