METHODOLOGICAL APPROACH TO THE STUDY OF ARCHAEOLOGICAL MORTARS AND PLASTERS FROM MEDITERRANEAN SITES

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The archaeometric study of ancient mortars and plasters has recently seen substantial development. This type of approach has been particularly interesting in order to obtain information on the raw materials used for the mixtures of these materials, their provenience and the technological processes involved in their manufacture, and therefore to shed some light into different aspects related to past life and technology.

At the same time, the archaeometric study of mortars and plasters provides information on the history of the buildings/monuments analyzed, identifying the constructive phases and/or the different manufactures (Bakolas *et al*., 1995; Vendrell-Saz *et al*., 1996; Franzini *et al*., 2000; Moropoulou *et al*., 2000, 2003; Crisci *et al*., 2001, 2004; Damiani *et al*., 2003; Meir *et al*., 2005; Silva *et al*., 2005; Riccardi *et al*., 2007; Pavía & Caro, 2008; Franquelo *et al.*, 2008; Barba *et al.*, 2009; Jackson *et al*., 2009; Miriello *et al*., 2010, 2011a, 2011b, 2013a, 2013b; Barca *et al*., 2013).

The present work proposes a methodological approach to be followed for the archaeometric study of ancient mortars and plasters. The methodology is based on the characterization of the samples through the application of a series of diagnostic methods. The analytical techniques used are: optical microscopy in transmitted polarized light (OM), X-ray powder diffraction (XRPD), X-ray fluorescence (XRF), scanning electron microscopy with energy dispersive spectroscopy microanalysis (SEM-EDS), image analysis by JMicroVision software, and methods of statistical multivariate analysis of the compositional data.

These analytical techniques have been applied to the study of mortars and plasters from three archaeological sites in the Mediterranean, to verify the real need to execute all of them and to define the guidelines to be followed for the archaeometric study of these materials.

The archaeological sites studied are: *i*) *Pollentia*, located on the north-east coast of Majorca (Spain; Fig. 1), which is considered the most important Roman archaeological site in the Balearic Islands (Orfila, 2000); *ii*) Hierapolis of Phrygia in Anatolia (Turkey; Fig. 2), located close to the modern village of Pamukkale; *iii*) the Roman city of Pompeii, in southern Italy (Fig. 3).

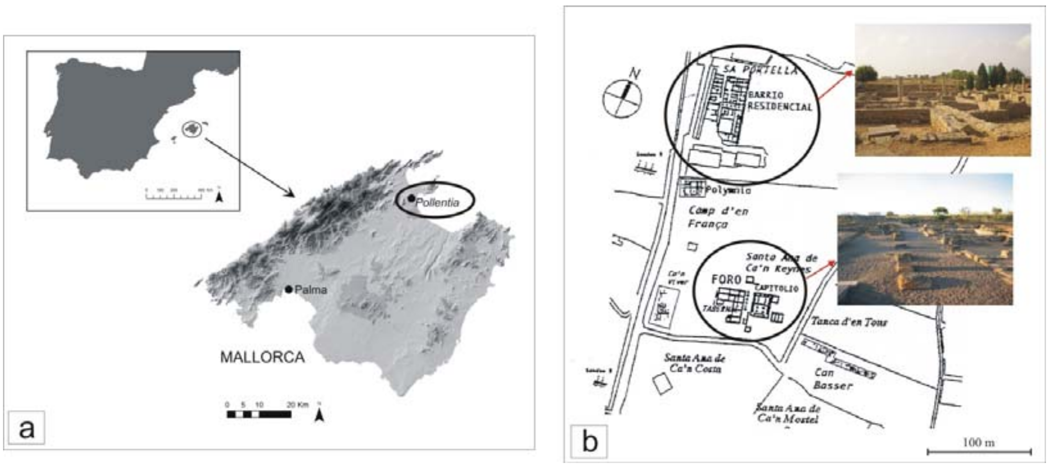

Fig. 1 - a) Location of the archaeological site of Pollentia (from De Luca *et al*., 2013); b) sampling areas of Pollentia (modified from Orfila, 2000).

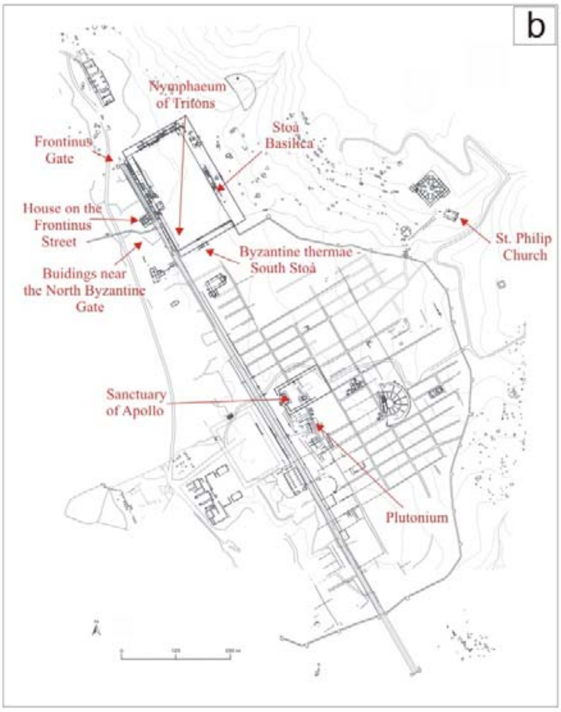

Fig. 2 - a) Location of the archaeological site of Hierapolis; b) plan of Hierapolis with sampling areas (modified from D'Andria *et al*., 2008).

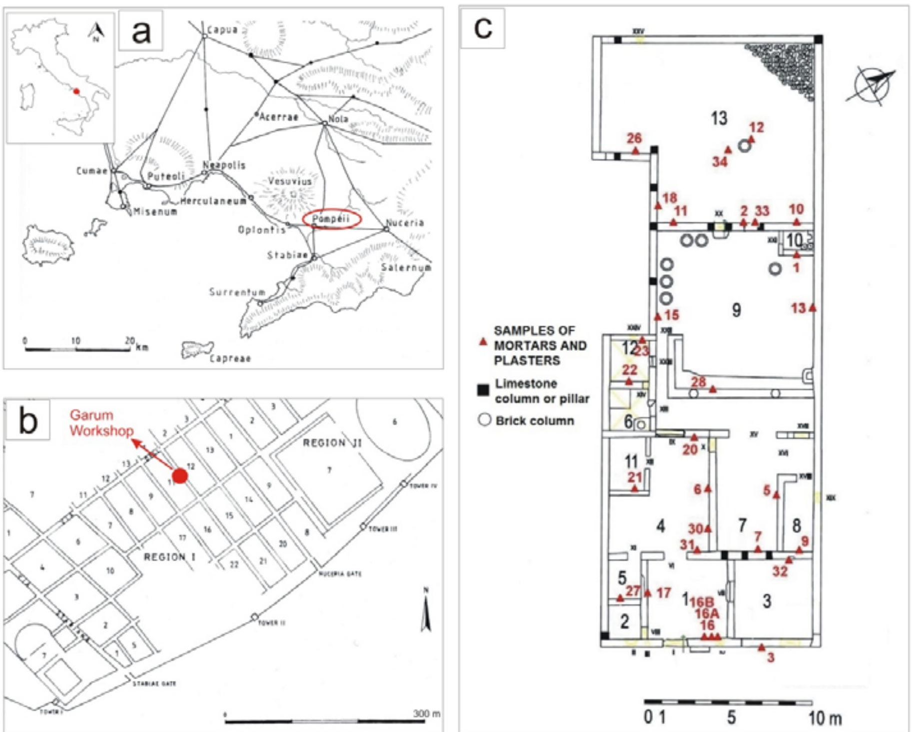

Fig. 3 - a) Location of Pompeii (from Ling, 2005); b) plan of Pompeii with the location of the Garum Workshop (modified from Ling, 2005); c) map of the Garum Workshop with sampling points (modified from Cottica *et al*., 2009).

In particular, 45 samples of mortars and plasters from *Pollentia* were analyzed. These samples came from the residential area of the city named "*Sa Portella*" where the remains of three important *domus* were uncovered, and from the *Forum*, the central part of the city, where the most important politic and religious buildings were situated (Fig. 1b; Arribas *et al.*, 1973; Arribas & Tarradell, 1987; Orfila & Cau, 2004).

The mortar and plaster samples from Hierapolis are 65 and come from different buildings of the city (Fig. 2b) dated between the 1st and the 11th centuries AD (D'Andria, 2003; Arthur, 2006; D'Andria *et al*., 2008). The buildings analyzed are: the Frontinus Gate, the houses on the Frontinus street, the buildings near the North Byzantine Gate, the Nymphaeum of the Tritons, the Stoà Basilica, the Byzantine Termae-South Stoà, the Sanctuary of Apollo, the Plutonium and the St. Philip Church, built around the tomb of the martyred apostle Philip (D'Andria, 2012).

A total of 35 samples of mortars and plasters were taken from the so-called "Garum Workshop" (Fig. 3c) at Pompeii. This building is located in the Regio I (I, XII, 8; Fig. 3b) and was probably a private residence built in the late-Samnite period (2nd century BC) and later transformed, probably after the earthquake of 62 AD, into a workshop devoted to the manufacture, storage and sale of *garum*, the famous Roman fish sauce (Bernal *et al.*, 2012; Cottica *et al.*, 2009).

For each archaeological site, the archaeometric study of the samples was carried out using a series of analytical techniques. The petrographic analysis was performed on thin-section, using polarized light microscopy with a Zeiss-Axioskop 40 microscope. The mineralogical composition of the samples was determined by X-ray Powder Diffraction using a Bruker D8 Advance X-ray powder diffractometer (XRPD) with Cu-*K*a radiation, operating at 40 kV and 40 mA. Using the EVA software program (DIFFRACplus EVA) it was possible to identify the mineral phases in each X-ray powder spectrum, by comparing experimental peaks with PDF2 reference patterns. The chemical analysis of the whole samples for major (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5) and trace (Nb, Zr, Y, Sr, Rb, Ni, Cr, V, La, Ce, Co, Ba) elements, was carried out by X-ray Fluorescence (XRF), on pressed powders, through a Philips PW 1480 spectrometer. XRF data were processed by the Aitchison's model regarding compositional data (Aitchison, 1982, 1983, 1986), using the Multivariate Cluster Analysis. The binder and the lime lumps present in the samples were analyzed by scanning electron microscopy with energy-dispersive X-ray spectroscopic microanalysis (SEM-EDS), using a FEI Quanta 200 instrument equipped with an EDAX Si/(Li) detector. The image analysis of the samples was carried out using the JMicroVision 1.2.7 software (Roduit, 2008a, 2008b) to calculate the percentage of aggregate, binder and macroporosity (IUPAC, 1972) on the images of the samples in thin section.

The application of these methodologies to the study of mortars and plasters permitted a complete petrographic, mineralogical and chemical characterization of the samples. For each archaeological site the raw materials used in the mixtures were identified, which are closely related to the geology of the sites.

In particular the samples from the archaeological site of *Pollentia* show two different typologies of aggregate, one principally constituted of bioclasts (Fig. 4a) and sedimentary rock fragments (Fig. 4b) and the other composed principally of quartz and multiciclic fragments of rocks of different nature. As demonstrated in De Luca *et al.* (2013), these typologies of aggregate are index of two different sources of raw materials used for the preparation of the mixture. In both cases the aggregate is compatible with the sedimentary nature of the island (De Luca *et al.*, 2013).

The samples coming from Hierapolis have an aggregate constituted principally of travertine (Fig. 4c) and metamorphic fragments (Fig. 4d), in agreement with the outcrops present near the site (Altunel & Hancock, 1993a; 1993b).

The aggregate of the samples from Pompeii is instead composed principally of pozzolana (Fig. 4e), that can be classified as volcanic tuff with a variable texture (Myron Best, 2003; Jackson *et al.*, 2005), and calcitic nodules (Fig. 4f), usually found in the Plinian eruptions of the Vesuvius (Barberi & Leoni, 1980). Both the raw materials are compatible with the pyroclastic deposits of the Vesuvius (Miriello *et al*., 2010).

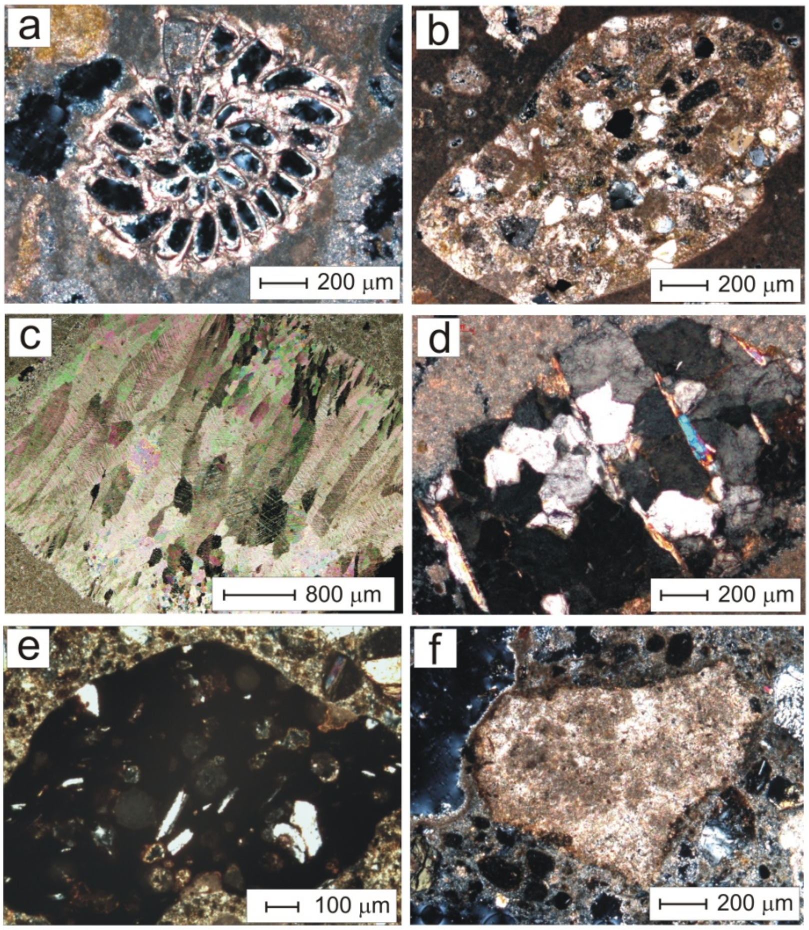

Fig. 4 - Microphotographs in thin section by optical microscopy (crossed nicols). a) Gastropod in sample SP_03b from *Pollentia* (from De Luca *et al*., 2013); b) arenite fragment with carbonate matrix in sample SP_03 from *Pollentia* (from De Luca *et al*., 2013); c) travertine fragment in sample HCCF_2 from Hierapolis; d) metamorphic fragment in sample HPF_1 from Hierapolis; e) pozzolanic fragment with plagioclase in sample BG28 from Pompeii; f) calcitic nodules in sample BG15 from Pompeii.

The archaeometric study also provided information on the production technology of the materials and the history of the buildings studied, allowing the identification of different constructive phases that corresponded with those proposed by the archaeologists.

For example, it was possible to identify among the samples from Pollentia a plaster made in the first constructive phase of the city (70-60 BC), that differs from all the others (De Luca *et al*., 2013).

On the other hand, at Pompeii, most of the samples of the "Garum Workshop" belong to a main group, probably related to the first constructive phase of the building. However there are also samples that have been attributed to different manufacturers or later restoration works.

The complete characterization of mortars and plasters of different constructive phases and buildings allows us also to identify mortars that can be considered ideal for restoration works with compatible materials. These mortars are chosen among the samples studied according to their high degree of conservation, the value of macroporosity and the degree of cohesion, which can be considered index of a good resistance and preservation of the materials.

At the end of the study of all the samples from the three archaeological sites, it was possible to propose an ideal analytical and methodological approach for the study of ancient mortars and plasters.

The methodology proposed (Fig. 5) is based on a multidisciplinary approach, which is necessary for a complete knowledge of the material studied.

Indeed, each of the analytical techniques used (optical microscopy, XRPD, XRF, SEM-EDS and image analysis) is able to provide specific information and, in most cases, tends to highlight only some specific aspects of the material studied. For example, while the chemical analysis shows similarities and differences among the samples based only on the chemical composition, the petrographic analysis provides information about the raw materials and the production technology of materials, mainly concerning their characteristics related to the texture. Therefore, to obtain complete information on the samples it is necessary to perform both analyses (chemical and petrographic), integrating all the data obtained.

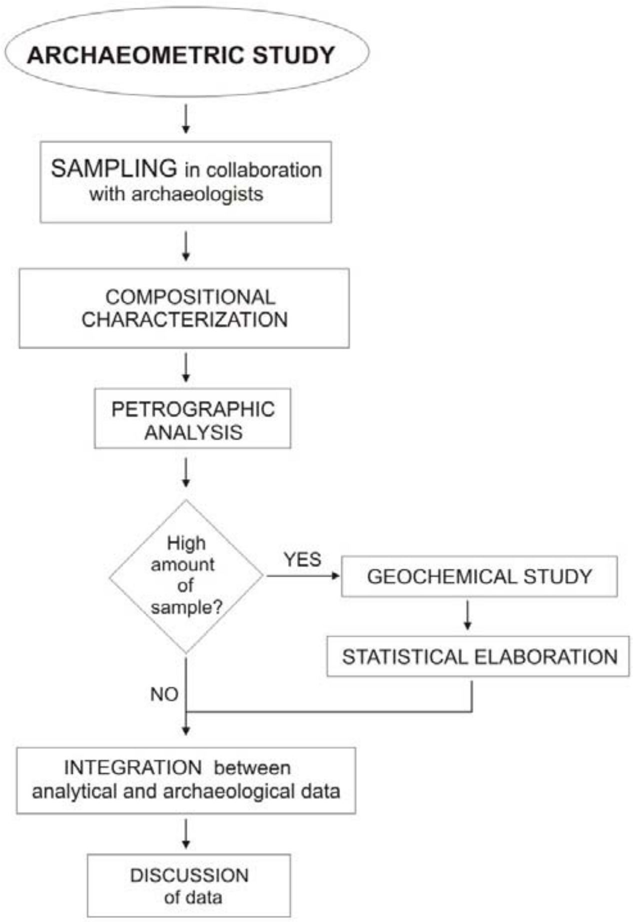

Fig. 5 - Schematization of the multidisciplinary methodological approach proposed.

After the archaeological and architectural investigation of the building/monument object of study, it is necessary its sampling, that must be carried out in collaboration with the archaeologists, to contextualize the samples at the site. During the sampling it is necessary to pay particular attention to all the pre-diagnostic elements (macroscopic recognition of different types of samples, their conservation status, etc.). After these preliminary observations it is possible to establish the diagnostic process to be carried out in the laboratory.

The first analysis that must be conducted on the samples is the petrographic analysis through optical microscopy, to obtain information about the raw materials and the production technology used. Then, if the sample is large enough, the other analytical techniques must be applied so as to obtain other information about the mineralogy (by XRPD), the chemical composition (by XRF), the porosity and the aggregate/binder ratio (by the image analysis) and the chemical composition of the binder and the lime lumps (by SEM-EDS). When there is an abundant amount of data it is also necessary to process them using multivariate statistical methods.

At the end, the data obtained through the various techniques must be integrated with the archaeological data, in order to suggest valid scientific and archeological interpretations.

As demonstrated in this work, the methodology proposed appears to be an optimal approach for a complete study of ancient mortars and plasters. It should be followed by every researcher specialized in the study of these materials, because only through a multidisciplinary approach it is possible to minimize the errors that can be made during the interpretation of the data.

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