ARCHAEOMETRICAL INVESTIGATIONS ON MORTARS AND PAINTINGS AT POMPEII AND EXPERIMENTS FOR THE DETERMINATION OF THE PAINTING TECHNIQUE

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INTRODUCTION

The characterisation of building materials, such as mortars and plasters, can give useful and unique indications when several technological, artistic and historical questions require answers (such as the definition of various construction periods, knowledge of technology and identification and provenance of raw materials). This may also be applied to the study of wall paintings, which aims to identify the nature of pigments, recipes, and techniques adopted.

A series of samples of mortar-based building materials (127 fragments) and paintings (73 fragments) from varying functional and chronological contexts were collected from the southern and northern areas of the Temple of Venus (Pompeii). Venus is the main polyad divinity of Pompeii, and her temple is one of the most important buildings in the town, located in the south-west area. This site has a long and complex history of construction and reconstruction (Curti, 2008). The present building itself underwent numerous restorations until the eruption of Vesuvius in 79 AD. Most of the samples were archaeologically dated from the end of the 4th Century BC to the 1st Century AD.

The aim of this study was to characterise these building materials and to determine their production techniques, to relate them with the function of the various buildings or rooms, and to follow their evolution over time. Experiments were also performed in order to determine objective criteria for the identification of the wall-painting technique adopted. Optical Microscopy (OM), Scanning Electron Microscopy (SEM, ESEM), X-ray diffraction (XRD), infrared spectroscopy (micro-ATR, FT-IR), Mössbauer spectroscopy, microprobe (EMPA) and colorimetric analyses were carried out to characterise materials, and then integrated with image analysis to define ratios among textural elements of the mortars (*i.e.*, aggregate, binder, porosity) with greater accuracy.

MORTARS

The mortars were preliminarily grouped into three macro-groups according to the architectural features of their provenance: walls, floors, and hydraulic structures (conduits, wells, cisterns), and then analysed petrographically and microstratigraphically. Identified aggregate particles were also compared with samples of sand collected from seven localities along the Neapolitan coastline, from Torre Annunziata to Castellammare di Stabia, and with four alluvial sand samples from borehole cores drilled in the area in front of the Temple of Venus, in attempt to identify the quarrying areas of the raw materials.

The three classes of mortar-based building materials analysed here had differing petrographic and microstructural features, and are briefly described below. Results showed that the aggregate in mortars is mainly composed of a volcanic sand composed of leucite-bearing volcanic rock fragments and volcanic scoria, leucititic or trachytic in composition, associated with abundant crystals of green and colourless clinopyroxene, black and yellow fragments of altered volcanic glass, rare crystals of feldspar and flakes of mica, and very rare crystals of melanitic garnet. These components are typical of the Somma-Vesuvio volcanoclastic deposits (Santacroce, 1987) and indicate an aggregate made with raw materials of local provenance. This was also confirmed by petrographic comparisons with the sand samples collected from the Neapolitan coastline and from borehole cores.

The differing amounts of components in wall samples distinguished two main groups; one characterised by the prevalence of fragments of volcanic rocks (Fig. 1a), and one by the abundance of clinopyroxene crystals (Fig. 1b). The mortars were often covered by a set of fine-grained layers of plaster, differentiated into several subtypes on the basis of the petrographic nature of the aggregate: i) silicates and silicate rocks (*intonachino*); ii) crushed pottery (*cocciopesto*); iii) limestone or crystals of calcite (*marmorino*).

Both floors and hydraulic structures were composed of two types of mortar, *cocciopesto* (Fig. 1c), or an aggregate of volcanic fragments (Fig. 1d). Pottery inclusions were helpful in further subdividing the *cocciopesto* fragments into two subgroups: *cocciopesto* made either of vulcanite or of quartz and feldspar crystals. The former was related to local production, and the latter indicated re-use of imported materials.

Observations by optical microscopy and measurement of the hydraulicity index (HI = Al_2O_3+Fe_2O_3+SiO_2 / CaO+MgO) of binder and lime lumps, identified two main types of binder - both composed of pure lime, but displaying different HI values, which turned out to be correlated to the extent of hydraulic reaction between binder and aggregate. Pozzolanic aggregates (*i.e.*, in mortars including

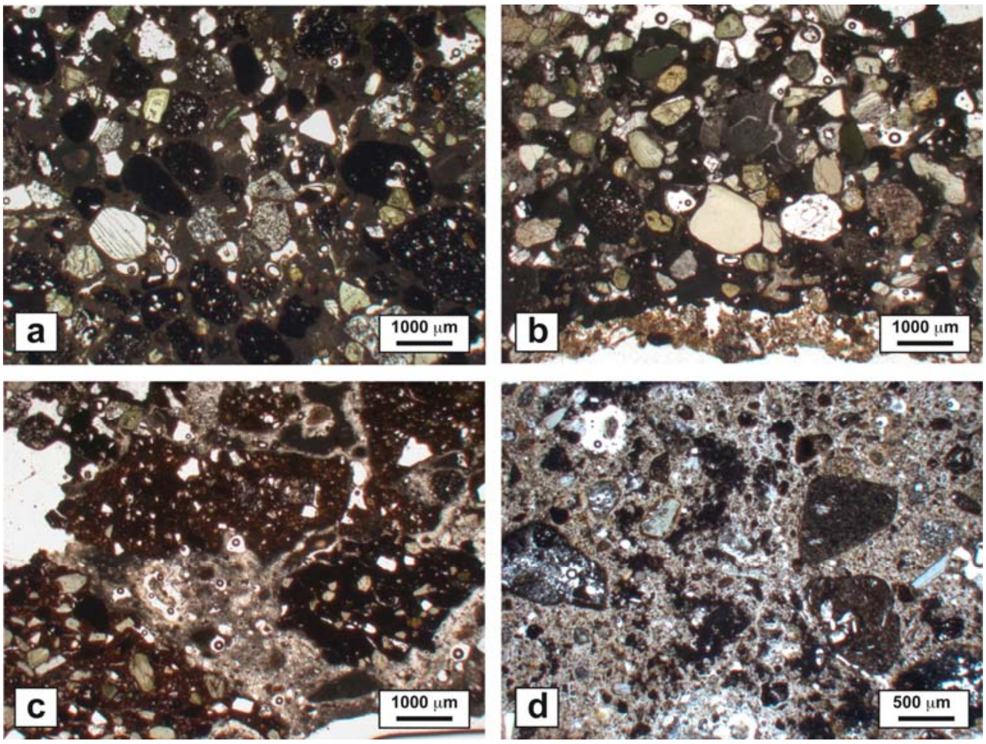

Fig. 1 - Polarising light micrographs of mortar samples. Walls: a) volcanic scoria-rich; b) clinopyroxene-rich. Floors: c) ceramic-rich; d) volcanic scoria-rich. All images taken in PPL.

cocciopesto and volcanic sand) reacted with the lime, producing a hydraulic binder with useful hydraulic properties. Only lime lumps in hydraulic structures had higher HI, with values between 0.08 and 0.27, indicating that true hydraulic lime was probably used to create these architectural features. The data showed that craftsmen could accurately select the materials on the basis of these characteristics, in order to ensure specific physical and/or aesthetic performance.

The occurrence of lime lumps in a large number of samples also indicates that some of the lime did not react completely with water during slaking or with atmospheric CO_2 (Hughes *et al.*, 2001) after application. This provides strong evidence that lime, water and aggregate were mixed without due attention, perhaps because of workers' lack of technological skills or acceptance by buyers of such wares.

As regards time evolution, recipes and raw materials were homogeneous from the 4th Century BC to the 1st Century AD, indicating that technological knowledge was already well established in the 4th Century BC and suggesting the persistence of technological tradition. The various types of mortars were correlated with architectonic structures and therefore with their specific function, such as the case of hydraulic structures, where pozzolanic aggregate was always used.

As regards image analysis, the approach adopted here allowed computation of the textural parameters of silicate aggregate. This approach turned out to be a powerful tool in determining the specific characteristics of the mortars - *i.e.*, aggregate:binder ratio and porosity - although the total porosity was underestimated. Nevertheless, further study is required to improve and test this approach before making it routine in studying mortars.

IDENTIFICATION OF PAINTING TECHNIQUE

Identification of the painting technique adopted by an artist is often a matter of debate in studies on the characterisation, restoration and conservation of mural paintings. During this research, an experimental study was undertaken in order to define objective criteria and analytical procedures to identify the *fresco* (*buon fresco*, *i.e.*, true *fresco*) and *mezzofresco* (lime-painting) techniques. In the case of the *fresco* technique, a very fine-grained pigment is diluted in water and laid on a damp, fine-grained plaster. Plasters only conserve their optimal characteristics for use as a background in *fresco* painting for a very short time (about eight hours), called the "golden period", during which they have a high degree of humidity. In the case of *mezzofresco*, pigments are mixed with slaked lime and spread on dry plaster (Botticelli, 1992).

In this study, two groups of 15 coloured strips were painted using various traditional pigments, including lime white, following both *fresco* and *mezzofresco* techniques. Samples were prepared as polished sections and analysed by optical and scanning electron microscopy for determination of microstratigraphy and microtextural features. Comparison of microstratigraphic sequences and distribution of chemical elements in each of the two sets of samples displayed systematic differences between *fresco* and *mezzofresco* techniques, independently of the pigment used, suggesting distinctive objective criteria and standardised operating procedures.

In the case of *fresco*, the pigment-bearing layer was relatively thin (generally below 50 μm) and its surface was rough and irregular. Coarser grains of pigment did not penetrate the plaster, but remained on the surface, bound by a thin film of calcite. In the case of *mezzofresco*, the pigment-bearing layer was systematically thicker (up to 650 μm), with a smooth surface. Grains were always regularly and completely distributed within a uniform layer of calcite. The distinction between the two painting techniques was even more evident with SEM. The elemental distribution maps of *mezzofresco* show a high-density, Ca-rich layer, a few dozen microns thick, typically found on the more superficial portion of the plaster, as shown in Fig. 2a. This evidence was more pronounced when SEM-BSE images of *fresco* and *mezzofresco* paints were compared (Fig. 2). Pores also progressively decreased towards the surface of the plaster and increased dramatically within the painted layer, highlighting the thin dense layer between the two. Similar dense, Ca-rich layer was also found on the surface of the paint in both *fresco* and

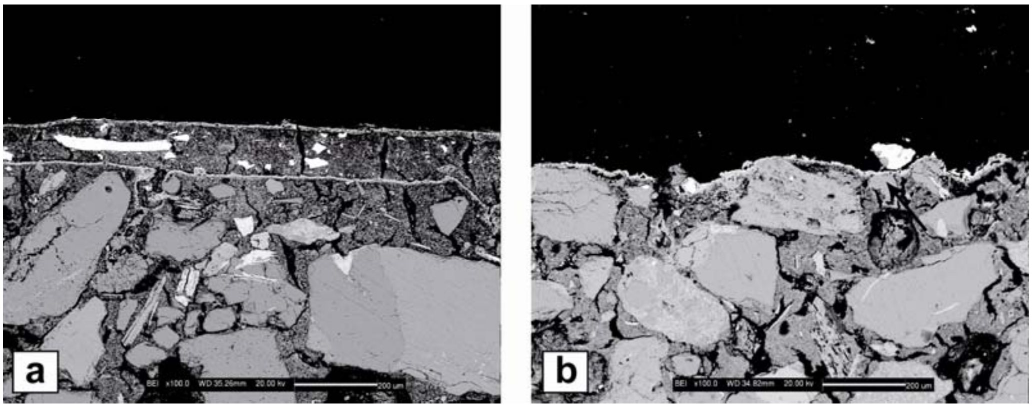

Fig. 2 - SEM-BSE images of azurite paint spread according to a) mezzofresco, and b) fresco techniques, respectively.

mezzofresco techniques.

Five samples from the Chiaravalle Abbey (Milan) for which the use of *fresco* and *mezzofresco* is well documented, were also analysed, and results were compared with experimental data to validate the proposed diagnostic criteria. Comparisons showed that the features of painted layers, their microstratigraphy, and the location of Ca-rich levels identified in these historical *fresco* and *mezzofresco* samples were very similar to those identified the experimental samples.

Microstratigraphic evidence in *fresco* and *mezzofresco* wall painting is closely related to the carbonation process, which takes place as the plaster and painted layers gradually dry. Good adherence depends on the reaction of the $Ca(OH)_2$, which is the binder, with atmospheric CO_2, producing $CaCO_3$ and releasing water. This process is more efficient on the surface, where the CO_2 concentration is higher and water evaporation more effective. It causes superficial hardening and porosity reduction, which both inhibit and retard carbonation in the inner portion of the underlying plaster. In the *mezzofresco* technique, drying and carbonation may take place before the pigment is applied, since the painted layer is applied to the plaster many hours later. This produces a dense carbonated crust on the plaster surface exposed to the air. When $Ca(OH)_2$ mixed with pigment is then applied to this layer, a new process of drying and carbonation starts on the surface of the paint, so that a second dense, carbonated level is created. In the case of *fresco* painting, a mix of water and pigment is applied on damp plaster, which has not yet undergone drying or carbonation. In this situation, the water guarantees good initial adhesion of the pigment to the plaster surface. Subsequently, evaporation and carbonation cause calcite to precipitate in the painted layer and the more superficial portion of the plaster, so that the painted layer is one with the upper portion of the plaster underneath. For this reason, with the *fresco* technique, the superficial carbonated layer includes all the grains of pigment, which are completely encased in a thin film of calcite. Moreover, no second, deeper carbonation level can form, since layers are continuously applied without interruption. On the basis of these pieces of evidence, microstratigraphic analysis of a wall painting can provide useful information defining whether the *fresco* or *mezzofresco* technique was used.

PAINTINGS

In the last section of this study, 73 fragments of wall paintings from the Temple of Venus were characterised and the painting technique was identified applying the criteria described above.

Results showed that the palette of colours used to decorate the Temple of Venus was varied, although not so extensive as that found in other buildings in Pompeii. The pigments are similar to those used elsewhere in Pompeii and in the Roman Empire, and also with the palette described both by Pliny and Vitruvius, with the exception of a volcanic natural yellow glass. The palette is composed of several natural earths, such as red, yellow and brown ochres and green earth (mostly celadonite), and other artificial pigments, such as whitewash, carbon black and Egyptian blue. The precious pigment cinnabar was also detected (Table 1). All pigments are of good quality. In particular, red ochre turned out to be haematite with a high degree of crystallinity, and cinnabar and the two types of Egyptian blue were made of very pure, well-selected cinnabar crystals and cuprorivaite, respectively, with negligible contents of

Table 1 - Preparation recipes. Number of samples and constituent pigments.

Recipes	**N° of samples**	**Pigments**	
		Major components	Minor components
Black 1	4	Coal black	-
Black 2	1	Burnt ochre	-
Black 3	1	Red ochre, coal black	-
Red 1	13	Red ochre	Yellow ochre
Red 2	4	Red ochre, yellow ochre	Clays, green earth, yellow glass
Red 3	4	Cinnabar	Red ochre
Yellow 1	3	Yellow ochre	Red ochre
Yellow 2	9	Yellow ochre and red ochre	Yellow glass, clays
Yellow 3	1	Red ochre, yellow glass	-
Yellow 4	1	Yellow and brown glass	Yellow ochre
Light blue	2	Egyptian blue	Yellow ochre, yellow glass
Green 1	4	Celadonite	Red and yellow ochre, Egyptian blue
Green 2	1	Red and yellow ochre, Egyptian blue, celadonite	Brown glass
Green 3	1	Celadonite, Egyptian blue	Red and yellow ochre
Grey	3	Yellow, red and brown ochre, Egyptian blue	Brown glass, cinnabar, glauconite
White 1	16	Lime, calcite	-
White 2	5	Lime	-

other mineral impurities. As regard Egyptian blue, the identification of malayaite ($CaSnSiO_5$) in one group of samples, and an unspecified K-Ca-Fe-bearing phase as tiny inclusions in pigment grains in another, clearly indicates that two different processes were used to prepare this specific pigment. In particular, the occurrence of malayaite indicates that the copper was derived from bronze, whereas the absence of malayaite suggests a different origin for copper, *e.g.*, a deposit of copper ore. Mössbauer spectroscopy on both red and yellow ochres confirmed that these pigments are basically composed of a single phase (*i.e.*, haematite and goethite, respectively) and that other Fe-bearing mineral phases are absent. In two cases, nano-sized oxide/oxyhydroxide particles were also identified. It is also worth noting that the Mössbauer spectra were acquired by a newly designed Mössbauer portable spectrometer, tested on wall paintings for the first time. The statistics of the spectra were sufficiently good, and the acquisition time was reasonably short, confirming the applicability of this new application of Mössbauer spectroscopy.

Paints were either composed of pure pigments or prepared as mixtures of pigments following a series of 17 recipes (Table 1), to obtain different hues and shades. Most of the recipes are quite simple and involve one or two main pigments, sometimes with the addition of minor impurities. In order to make colours darker or lighter, especially yellow and red, carbon (lampblack) and calcite (whitewash), respectively, were mixed with the appropriate pigment. In other cases, the paints contain the same pigments, but were mixed in different relative proportions according to different recipes (*i.e.*, recipes *yellow 1* and *red 1*), yielding a variety of hues. *Grey* and *green 2* were the most complex recipes, involving four different pigments and several minor components. In particular, grey colour was made by deliberately mixing yellow, red and brown ochre, Egyptian blue, brown glass, cinnabar and glauconite in precise proportions to obtain the desired hue. There are no analogies in the literature of such a complex admixture of pigments, which may reflect the painter's skill.

An additional important observation is that some of the colours, such as black, red, green and yellow, were prepared using various pigments. The adoption of differing recipes for the same colour suggests the presence of several groups of painters working in the Temple of Venus who had preferences for different methods to produce their colours. Chronological data show that the most common and inexpensive recipes are also widespread over time, such as pure haematite in *red 1*, haematite and goethite in *yellow 2* and *marmorino* in *white 1*. *Black 1* seems to be the most frequently used recipe for black paint, at least from the 1st Century BC to the 1st Century AD (Julio-Claudian Age). Egyptian blue in light blue paints seems to have been exclusively used in the Imperial Age, although this pigment had certainly been used since the end of the 4th Century BC, as demonstrated by its identification as a component in green admixtures. It is also important to note that the various methods adopted to produce Egyptian blue in the Imperial Age suggest that it was purchased from several different producers.

In addition, a new yellow-brown pigment, never before identified, was found and characterised. It is composed of fragments of a yellow or brown natural volcanic glass, chemically compatible with vulcanites from Somma-Vesuvius. This suggests that this pigment, which is undocumented even by Pliny and Vitruvius, was produced locally. It is relatively common in many paints, either as one of the main components (*yellow 3*, *yellow 4*) or as a minor one (*red 2*, *yellow 2*, *light blue*, *green 2*).

All the data, particularly the absence of a carbonation layer between paint and *intonaco* and of any trace of organic binders, confirmed that the most frequently used painting technique was *fresco*. All samples have very thin painted layers, with well-dispersed fine-grained pigment particles and sometimes medium to coarse grains coated by calcite (Fig. 3a,c). In the coloured samples, with strips or figures painted on a coloured background, the thickness of the painted layers and the presence of a carbonation layer between the two coloured layers (Fig. 3b,d) suggests that the more superficial paint was applied with the *mezzofresco* technique.

In conclusion, the importance and prestige of the Temple of Venus is also reflected in the quality and value of the pigments, and in the careful preparation of the mortars.

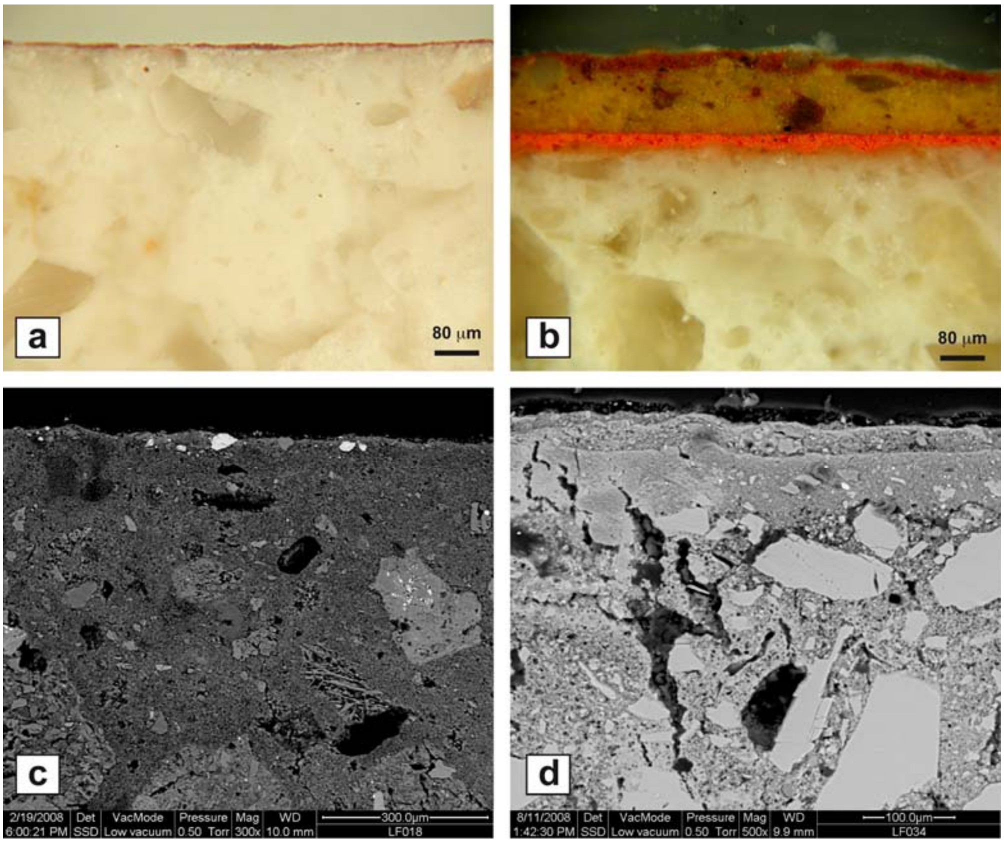

Fig. 3 - Reflected light micrographs of samples of wall paintings: a) single-layer painting; b) multi-layer painting. BSE images of wall paintings: c) *fresco* technique; d) *mezzofresco* technique.

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