INTEGRATED DIAGNOSTIC APPROACH FOR THE KNOWLEDGE OF THE ROMAN FRESCO IN HERCULANEUM

Maria Letizia Amadori, Sara Barcelli, Enrico Gurini
University of Urbino, Institute of Chemical Science; m.letizia@uniurb.it

Fabiano Ferrucci
University of Urbino, Laboratory of Restoration; fabiano.ferrucci@fastwebnet.it

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ABSTRACT

The Villa of Papyri is one of the most imposing architectural example of Herculaneum dated before the eruption occurred on 79 A.D. The traditional name derived from the discovery of a rich library of papyrus rolls. During the earliest years of the excavation of Herculaneum and Pompeii (1750-1765), under the direction of the engineer Karl Weber, the Villa has been explored through a thick network of tunnels dug into the hard bank of tuff rock. Between July 2007 and September 2008 part of the building discovered in the 90's has been restored and a diagnostic study mainly focused on mosaic floors, paintings and plasters has been carried out.
The scientific investigations carried out by optical microscope, X-ray diffractometer and ion chromatograph, firstly aimed to characterise natural and artificial stone materials, referring in particular to the wall painting, in order to acquire information on constitutive materials and executive techniques. Secondly the conservation status of materials has been analyzed in order to highlight degradation causes and their effects.
Investigations allowed to identify a typical vitruvian plaster with the following pigments: Egyptian blue, red and yellow ochre, limonite and hematite particles, green earth, carbon black particles and probably atramentum.
The high content of soluble salts in the walls and floors caused a worsening in the state of conservation, due to the position of the building, located few metres above a ground water rich in sulphates.

INTRODUCTION

The Villa of the Papyri (figs. 1 and 2) is one of the most impressive examples of architecture in Herculaneum [1, 2] existing before the volcanic eruption of 79 AD. It was discovered almost by accident in April 1750 while a well was being dug. After unearthing a semi-circular veranda with a magnificent inlaid polychrome marble floor, a peristyle with columns surrounding a rectangular pool was discovered. On the edge of the pool, a collection of works of art was found including objects and sculptures of bronze and marble, now kept at the National Archaeological Museum of Naples. The traditional name of Villa of the Papyri originates from the discovery of a rich library of papyrus rolls around 1826, consisting primarily of Greek texts.
During the earliest years of excavations at Herculaneum and Pompeii (1750-1765), the villa was explored by the engineer Karl Weber through a network of tunnels dug into the hard tuff bedrock [3]. The extremely accurate plan produced by Weber also contained the location of individual findings. This permitted the understanding of the meaning of the decorative scheme of the house, whose interior is one of the few known examples of a private art collection in Antiquity.
Because of the poisonous fumes, the so-called "mofète", excavations were suspended. Between 1996 and 1998 [4, 5], a portion of the building (about 500 square meters) located in a wide and deep excavation area was fully brought to light. Its lowest level is actually below sea level. In addition, a new excavation was carried out on the lower level through one of the villa's windows.
The excavations continued between November 2007 and March 2008, and an area (called the

Northern Area), entirely covered in *fresco* painting and polychrome stucco, was recovered.
A portion of the building that had been discovered in the 1950s, became the object of a conservation project [6]. The intervention focused mainly on the mosaic floors and the plaster coatings, both painted and not.
During the treatments, an analytical campaign was carried out to identify the natural and artificial stone materials from the Villa, especially those of the decorative layers. Information on constituent materials and techniques was also acquired [7]. This was followed by an investigation of the materials' state of conservation to assess the causes and effects of deterioration.

Figure 1: Excavation area of Villa of Papyri

Figure 2: Villa of Papyri planimetry

EXPERIMENTAL

Sampling

Twenty-four micro fragments of constitutive materials have been collected with the use of a scalpel and a brush [8] with the aim to study their original composition and the state of conservation. The description of their colour and location is given in table 1.
Before any analytical treatments all samples have been documented using a stereomicroscope (binocular stereomicroscope Leica MZ6, 60x) in order to have a first appraisal of the stratigraphic morphology.

Table 1: Samples description

Sample location	Alphanumeric code	Typology
Room A	C2	plaster
	P2	mosaic tesserae
Room D	P1	plaster
Room C	P4	mosaic tesserae
	S7	efflorescence
Room F	S5	efflorescence on painting
Room G	P5, P6, P7, P8, P9	mural painting
	P3	stucco
Room H	P10, P11, P12, P13, P14	mural painting
Room I	C1	plaster
	S6	efflorescence
Basis Villae	C3, C4	plaster
	S1, S2, S3	efflorescence

The C set samples constitute the inner plaster sampled on wall coverings. The P set samples are fragments of wall paintings representative of the chromatic range present in the rooms. The S set samples are efflorescences sampled close to inner plaster, mural paintings and mosaics [9].

Methodologies

The above-mentioned samples have been submitted on the following techniques:

1) Optical microscopic observations have been performed using a Nikon (Nikon, Japan), Mod. TK-1270E equipped with fixed oculars of 10× and objectives with different magnifications (2.5, 5, 10, 20, 50×).

Thin-section and cross-section photomicrographs have been recorded with a Nikon digital scanner camera directly connected to the microscope.

The transmitted light observations give information on natural and artificial stone materials and on their state of conservation; whereas, the reflected light observations contributed to characterize the wall paintings stratigraphy [10, 11];

2) Measurement of soluble salts by ion chromatography (IC) with qualitative and quantitative analysis of anions (NormaL Recommendation 13/83) have been carried out.

The instrument used is a Dionex model DX 120 chromatograph equipped with conductivity detector. The anions and cations have been determined using, respectively, a chromatographic column Dionex IonPac AS9-HC, with a guard column IonPac AG9-HC, and a Dionex IonPac CS12A column with a guard column IonPac CG12A, linked to a suppressor electro-osmotic with auto - regenerating ASRS-ULTRA, in the first case, and CSRS-ULTRA, in the second case. The eluent used for anions is a solution of sodium carbonate (9 mM) and for cations is a solution of acid methanesulfonate (20 mM).

The samples were first dried at a temperature of 60 °C for about 48 hours, then a share of samples have been weighed and dispersed in ultra-distilled water up to known volume. The suspensions were scrambled by magnetic stirrer for one hour and then filtered with Acrodisc filters chromatography cellulose acetate with micropores of 0.2 μm;

3) X-ray diffraction analyses (XRD) on powder have been performed to identify the main mineralogical composition of natural and artificial stone materials.

The instrument used is a Philips model PW 1830 (Philips, UK) connected to a PW 2273/20 generator and PW 1771/90 goniometer and equipped with copper anticathode tube.

RESULTS AND DISCUSSION

Plaster

The mineralogical analyses carried out by X-ray diffractometer show that all the samples of inner plaster are composed mostly by calcite and secondly by pyroxenes, plagioclase, K-feldspars, analcime, quartz and illite. In the sample C4 traces of gypsum have been detected as well.

Table 2: Mineralogical semi-quantitative composition (XRD) of inner plasters

Samples	Qtz	Cal	Pl	Px	Kfs	Gp	Ill	Ox-Fe	Anl
C1	X	xxxx	xx	xx	xx		tr		xx
C2	X	xxx	x	x	x		tr		x
C3	X	xxx	xx	xx	xx		x		x
C4	Tr	xx	tr	xx	tr	tr	tr	tr	

Cal=calcite; Qtz=quarzt; Kfs=K-feldspar, Pl=plagioclase, Px= pyroxenes; Ill= illite; Gp= gypsum (Kretz 1983; Chace 1956) Anl= analcime; Ox-Fe= iron oxides.

xxxx = very abundant; xxx = abundant; xx = quite abundant; x = low; ± = very low; tr = traces.

Wall paintings and stucco

The investigations have been carried out by optical microscope in transmitted and reflected light; the stratigraphic descriptions [12] of the samples (P set) start from the inner plaster layers to the outer pictorial layers.

The sample P1 (tab. 3, fig. 3) is characterized just by one preparation layer made of carbonate binder and silicatic aggregate. The aggregate is composed by sanidine, pyroxene, biotite, opaque minerals and fragments of lava rocks, in particular basaltic-andesitic and tefritic rocks with analcimized leucite.

Table 3: Sample P1 - Cross section stratigraphy

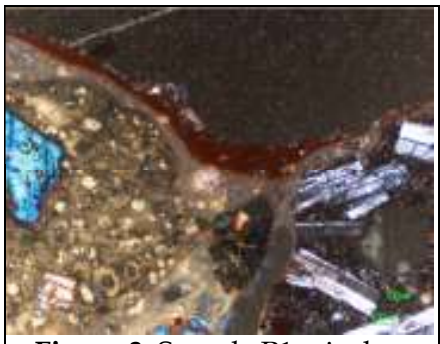


Figure 3: Sample P1, nicols +

thickness (µm)	typology	description
20-30		Concretion
20-80	pictorial layer	Red ochre, Egyptian blue
1600	plaster	Carbonate binder with silicatic aggregate (basaltic- andesitic and tefritic rock fragments, analcimized leucite, sanidine, pyroxenes, biotite, opaque minerals)

The samples P5, P6 (tab. 4, fig. 4), P7, P8, P9, P11, P13 and P14 are constituted by two plaster layers. The first one is made of a carbonate binder with a silicate aggregate. The aggregate is composed by phenocristals of plagioclase, sanidine, pyroxene, biotite, effusive rock fragments, lava fragments with phenocristals of plagioclase and leucite, sometimes analcimized. The second one is composed by a carbonate binder with an aggregate made of sparitic calcite fragments (sometimes dark). The fragments size is variable and the roundness is low.

Table 4: Sample P6 - Thin section stratigraphy

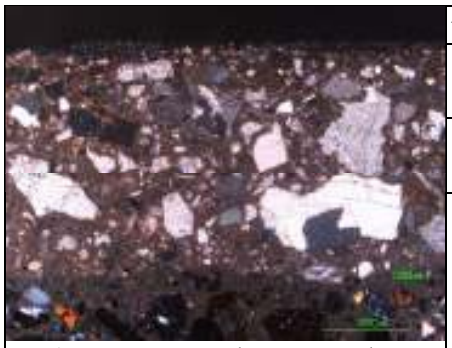


Figure 4: Sample P6, nicols +

thickness (µm)	typology	description
60-80	pictorial layer	Egyptian blue, hematite, green hearth, micritic and sparitic calcite
2200-2400	plaster	Carbonate binder with carbonatic aggregate (sparitic calcite fragments)
2700	plaster	Carbonate binder with silicatic aggregate (tefritic rock fragments, analcimized leucite, sanidine, pyroxenes, biotite, plagioclases, opaque minerals)

The sample P10 (tab. 5, fig. 5) is different from the other ones due to the presence of four plaster layers. A first plaster layer constituted of carbonate binder with coarse and scarce carbonate aggregate is overlaying to a second carbonate plaster layer with a fine to medium sparitic calcite fragments. The third and fourth plasters layer look like the second one in the composition.

Concerning the pictorial layer in the samples P5, P7, P8, P9, P10, P11 and P12 [13] the use of *a fresco* technique is evident. In samples P5 (fig. 6) and P11 the pigments identified in the pictorial layer are fine particles of red ochre, rare hematite and carbon black particles. Yellow and red ochre, with few limonite and hematite particles, are present in the pictorial layers of samples P7 and P10 (figs. 8 and 11). Red ochre with few calcite grains are dispersed in the carbonate matrix in the sample P8

(fig. 9). The sample P9 (fig. 10) is characterized by the presence of haematite, Egyptian blue, calcite and celadonite in a carbonate matrix with hematite and limonite fine particles.

Table 5: Sample P12 - Thin section stratigraphy

Figure 5: Sample P10, nicols +

thickness (μm)	typology	description
40	pictorial layer	Red and yellow ochre, haematite, limonite
1400	plaster	Carbonate binder with scarce carbonate aggregate (fine sparitic calcite fragments and haematitic particles)
1200	plaster	Carbonate binder with carbonate aggregate (coarse and rare sparitic calcite fragments)
1500	plaster	Carbonate binder with carbonate aggregate (fine/medium sparitic calcite fragments)
2400	plaster	Carbonate binder with scarce carbonate aggregate (coarse and scarce sparitic calcite fragments)

In the sample P12 (fig. 12) *atramentum* is incorporated in the microcrystalline matrix with a few particles of hematite. The overlaying pictorial layer is composed by a carbonatic matrix with Egyptian blue and few hematite particles. The interface presents between the inner part and the outer layer, suggesting that it was set after the inner layer was not very wet. A carbonatic matrix with Egyptian blue and rare hematite particles is visible in the samples P6 (fig. 7) and P13 as well. Probably in these three samples a lime wash paint was applied.

Cross sections micrographs

Figure 6: Sample P5

Figure 7: Sample P6

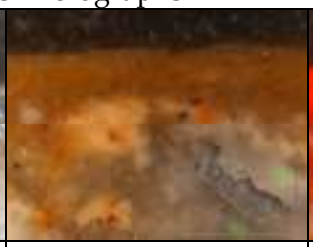


Figure 8: Sample P7

Figure 9: Sample P8

Figure 10: SampleP9

Figure 11: Sample P10

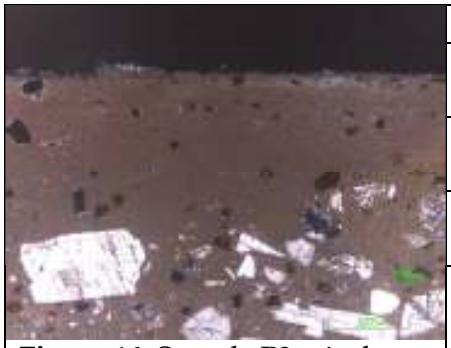
Figure 12: Sample P12

Figure 13: Sample P14

In the samples P1 (tab. 3, fig. 3) and P14 (fig. 13) the *a secco* technique was identified because of the clear interface between the plaster and the overlaying pictorial layer. The pigments used are fine red ochre, calcite, hematite and carbon black particles.

In the stucco sample P3 (tab. 6, fig. 14) the first plaster layer is made of a carbonate binder and sparitic calcite fragments. The two overlaying plaster layers are constituted by a carbonate binder with a microcrystalline aggregate. The last plaster layer consists of rare red ochre particles in a micritic binder.

Table 6: Sample P3 - Cross section stratigraphy

	thickness (μm)	typology	description
 **Figure 14:** Sample P3, nicols +	10-60	3	Micritic binder with rare red ochre particles
	40-25	2	Carbonate binder with rare and fine microcrystalline carbonate aggregate
	1300	1	Carbonate binder with rare and fine carbonate aggregate
	1600	0	Carbonate binder with carbonate aggregate (sparitic calcite fragments)

Mosaic tesserae

The sample P2 (fig. 16) is characterized by a porfic structure and a micro-crystalline matrix. The mineralogical composition is represented by phenocrystals of clinopyroxene, leucite, plagioclase and biotite. The lithotype can be related to an effusive rock and can be classified as a tefritic rock.
In a portion of the sample a mortar layer with carbonate matrix and silicate aggregate has been identified. The aggregate is composed of pyroxene, biotite and sanidine.
The sample P4 (figs. 15 and 17) is characterized by a porphyritic structure and microcrystalline matrix. The mineralogical composition is represented by phenocrystals of clinopyroxene, leucite, plagioclase and biotite. The lithotype can be related to an effusive rock and can be classified as a tefritic rock.

Figure 15: Mosaic in room C

Figure 16: Sample P2

Figure 17: Sample P4

Efflorescences

Ion chromatography analyses have been carried out on the efflorescence samples, in order to determine soluble salt's nature and their content.
The analytical results, expressed as the ion percentage content compared with the dry weight sample, are shown in table 7. In the plaster samples (S1, S2 and S3) the highest amount of sulphates have been detected together with a moderate amount of calcium. Nitrate content ranges from 0.11 to 0.77%, chloride varies from 0.06 to 0,30% and fluoride is very low. Ammonium is present just in one sample (S3). Potassium and sodium content are always low except sample S3; magnesium ranges from 0.19 to 4.34%.
In order to define the origin of the soluble salts, the groundwater, which come out from the rock

bank about five meters below the floor level of the villa, has been analyzed by ion chromatography. The results show the following ions concentrations: fluoride 4.2 ppm, chloride 9.8 ppm, bromide 0.9 ppm, nitrate 81.4 ppm, sulphate 92.6 ppm.

Table 7: Ions content in the efflorescence samples (% in weight).

Samples	F^-	Cl^-	NO^{3-}	PO_4^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	Na^+	NH^{4+}	K^+	Mg^{2+}	Ca^{2+}
S1	0.07	0.30	0.77		41.46		0.12		0.22	4.34	2.74
S2	0.08	0.13	0.31		32.32		1.20		0.20	0.19	9.13
S3	0.06	0.22	0.33		32.59		0.12	0.06	0.06	1.06	3.82
S5	0.31	0.27	0.33	0.25	8.79	0.37	27.05		2.25		
S6	0.07	0.06	0.11		62.26		5.94		23.11		0.25
S7	0.31	0.23	0.12		3.69		14.32		1.77		0.10

CONCLUSIONS

The executive technique used to realize the Villa of Papyri wall paintings is mostly characterized by two plaster layers (*tectorium*): the inner was realized by lime and effusive rocks fragments, the second one by lime and sparitic calcite, which come from concretionary rocks.

The aggregate presents in the inner plaster is composed by quartz, K-feldspar, pyroxenes, plagioclases and analcime. As a result the mineralogical composition and the peculiar presence of analcime, a typical mineral of the volcanic complex of Monte Somma and Vesuvius, are compatible with the local geology.

Concerning the pictorial technique the wall paintings have been realized on a rather compact plaster, with a well crystallized carbonate material. In most of the samples (P5, P7, P8, P9, P10, P11 and P12) the pigments are well embedded in the final plaster that do not forms a continuous layer. Probably the pigments were applied while the plaster was still wet, with a consequent partial homogenization of the components. As a matter of fact we can consider such painting as *a fresco* process.

In few samples the surfaces of the plasters are smooth and a clear interface is present under the red pictorial layer. That also suggests that the outer layers were set after the inner layer was already dried, therefore *a secco* technique was used.

Most of the samples show a highly polished finish layer due to superficial mechanical action (polishing with "liacula"). This hypothesis is confirmed by the orientation of sparitic calcite crystals, parallel to the external surface. As known from ancient treatises, plaster smoothing and crushing operations give to the wall paintings a brightness and lustre resembling marble.

The pigments utilized in the red pictorial layers are red heart, sometimes fine hematite, few grains of Egyptian blue and carbon black. The blue pictorial layer has been realized by Egyptian blue and fine hematite particles. In the yellow paint layers the pigments used are yellow and red ochre, limonite and hematite particles.

At the beginning the P1 sample has been considered as a preparatory layer but later it was identified as *a secco* paint layer overlaying a silicate aggregate plaster. During the restoration interventions similar plasters (one layer, no polished and so rugged) have been found also in other rooms (eg. A, G). Probably they represent an evidence of a previous wall paintings phase covered in a second time.

The mosaic tesserae are made of a black local tefritic rock. This rock is very deteriorated, much more than white limestone tesserae. The phenomenon is probably due to salt crystallization phenomena that are certainly facilitated by the porous structure of the pyroclastic rocks.
Concerning the decay products, the ion chromatography analysis of efflorescences sampled in the plasters of Basis Villae (S1, S2, S3) and from the floor of the room I (S6) shows firstly the high levels of sulphate and secondarily nitrate and low levels of ammonium ion. The efflorescences sampled from the *fresco* paints (S5, S7) are characterized by lower levels of sulphates; phosphates and oxalates are also present.
The sulphates presence can be related to rising groundwater which emerges from the rock bank about five meters below the floor level of the villa (about the same level of the floor of the North room. As a matter of fact the waters analysis shows a very high concentration of sulphates.
The damage caused by the saline crumbling effects mainly the lower parts of wall paintings, while the situation is less critical for the mosaics, at least the white ones. Probably the mosaic preparatory layers made of *cocciopesto* reduce the upward flow and the water passes mainly through the tuff walls and not through the floor.
As a matter of fact most of the mural paintings excavated about ten years ago are lost or seriously compromised by phenomena of crumbling and disintegration due to salt crystallization cycles.

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