

TECHNICAL ANALYSIS REPORT

Investigation of the phases of construction of the church. Laboratory analyses of samples taken from the facade, prothesis and north corridor.

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Conservation and Documentation of the Wall Paintings at the Red Monastery, Sohag.

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Index

1. Materials and methods..... P 3

2. Sample analysis sheets

Sample ICO 3 P 5

Origin of sample and its characteristics:

Sample PRO 9 P 11

Origin of sample and its characteristics:

Sample PRO 11A P 21

Origin of sample and its characteristics:

Sample PRO 11B P 28

Origin of sample and its characteristics:

Sample PRO 11C P 32

Origin of sample and its characteristics:

Sample PRO 14 P 35

Origin of sample and its characteristics:

Our ref. Z -30 II

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Re. Investigation of the phases of construction of the church. Laboratory analyses of samples taken from the façade, *prothesis* and north corridor.

April 2008 Mission - Report.

1. Materials and methods

On the basis of the results obtained during the first phase of the study carried out on site with the aid of a portable stereo-microscope during the month of April 2008, Luigi De Cesaris and Alberto Sucato assisted us in selecting the most representative and significant samples for more in-depth analysis in the laboratory.

We decided to analyze sample ICO-3, taken from the north side of the facade, second tier, from the right side of the arch beside the impost painted with blue geometric motifs. The main aim of analysing this sample was to identify the blue pigment and understand the technique used to apply it.

The other samples were chosen from amongst those taken from the *prothesis* and the north corridor. In this instance, the analyses were intended both to ascertain the characteristics of the plaster types in order to compare them with other samples taken from the ground floor of the triconch and to investigate the painting technique.

All the samples taken were examined firstly under the stereo-microscope and subsequently prepared for in-depth study.

The preliminary examination under the stereo-microscope was crucial to the selection of those fragments most suitable for the tests to follow, namely: micro-stratigraphic analysis on a thin section, supplemented by micro-chemical and histo-chemical tests carried out directly on the section; chemical and mineralogical investigation using Fourier Transform Infrared Spectroscopy (FT-IR) and in one case, optical mineralogical tests under reflected and polarized light.

The following histo-chemical and micro-chemical tests were carried out on the thin sections:

- *Fuchsine*: to highlight proteins, particularly animal glues and gelatine;
- *Amido Black*: to identify proteins, especially egg;
- *Sudan Black* to identify lipids in a liquid state (oils);
- Test to identify *saponifiable substances* (oils, waxes and others);
- The micro-chemical tests included empirical tests to identify *carbonates, iron, copper and lead*.

The methods of analysis used were evaluated on the basis of the best result and therefore the greatest amount of information that could be obtained whilst containing overall costs.

However, during the course of this study, we encountered problem samples requiring closer investigation in the form of further tests and/or the use of techniques involving more sophisticated instruments ⁽¹⁾.

The main aims of the analyses were as follows:

- to study the sequence of layers in the sample and the stratigraphic relationships between them;
- to define the structure and general composition of the various layers;
- to analyze the mortar types used to make the plaster;
- to study the technique of the original paintings;
- to identify the number of instances of repainting by defining the general composition.

The investigations comprising this work were carried out in accordance with the recommendations contained in UNI – Normal documentation and the directions issued in scientific journals published by national and international institutions working in the field of heritage conservation such as the ICR, ICCROM and ICOM.

The results of the analyses are presented in analysis sheets in which the formulation and interpretation of the data is set out together with graphics and photographs.

Finally, we wish to point out that the colors appearing in the micro-photographs may differ from those seen during visual examination of the painted surfaces. At a microscopic scale the individual colors of the various components (pigments, charge and binder) are visible that together, at macroscopic scale, give each layer its overall color.

Rome, 25 November 2008

Domenico Poggi, Geologist



¹ The methods of analysis used supply general indications with regard to the nature of the binders, pigments and plaster types.

For more in-depth study and, on occasion, for the definite identification of particular components, other investigations were required in addition to the micro-stratigraphic analyses of thin sections, such as SEM-EDS elemental microanalysis, micro FT-IR spectrophotometric tests etc.)

Sample ICO 3

Origin of sample and its characteristics

Facade, north side, second tier, arch, right side, beside impost painted with geometric motifs. The sample was taken from a blue background.



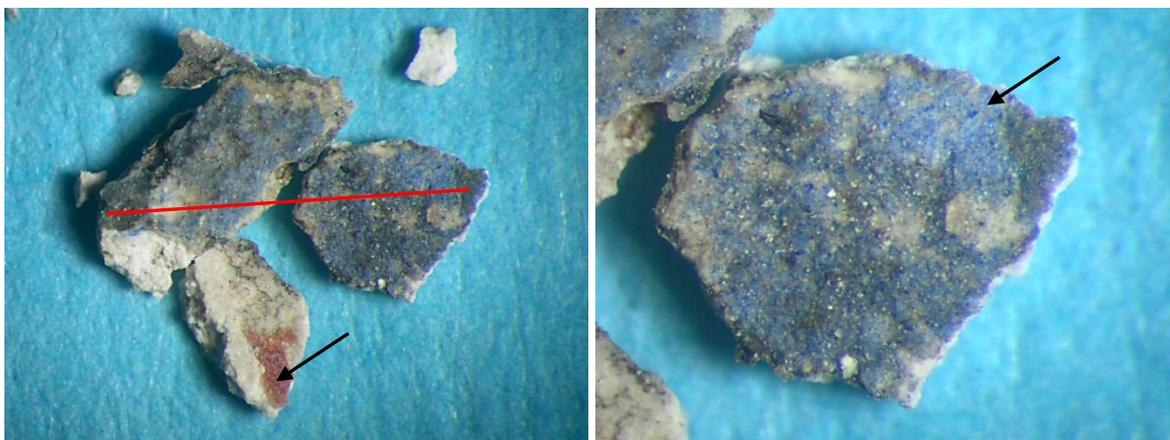
Type of analysis carried out

Micro-stratigraphic analysis of thin section supplemented by histo-chemical and micro-chemical tests.

Aims of laboratory investigations

To analyze the base plaster (on the basis of the model supplied in UNI-Normal document 12-83) and identify the number, type and nature of the layers applied over it.

Preliminary examination under stereo-microscope

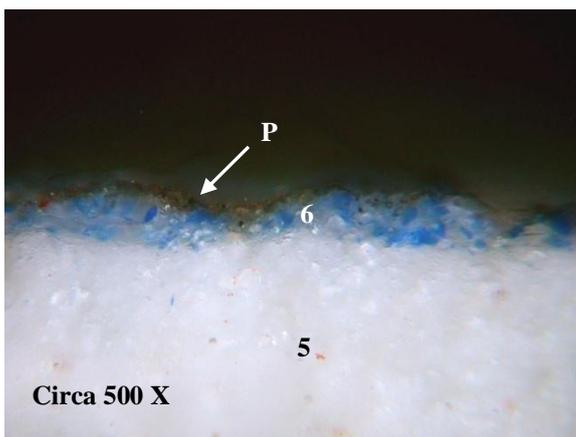
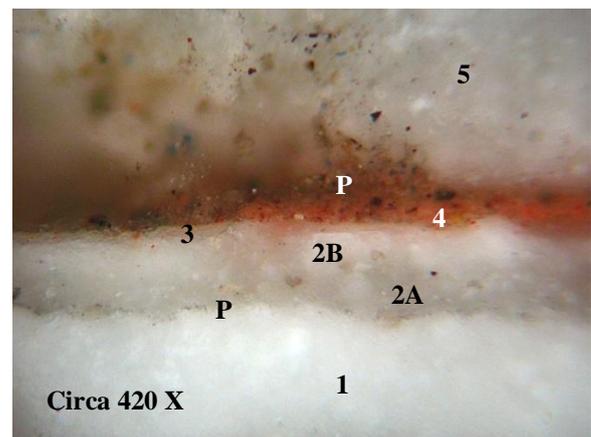
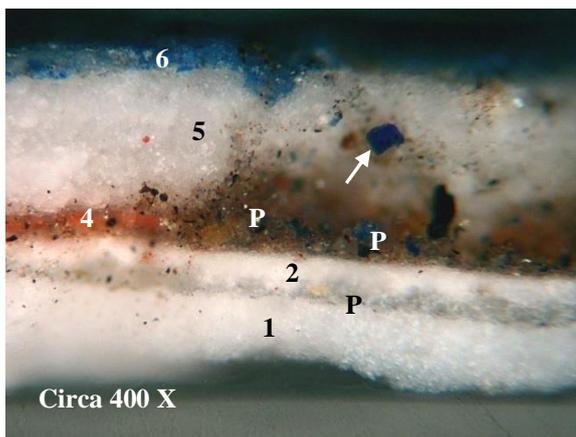
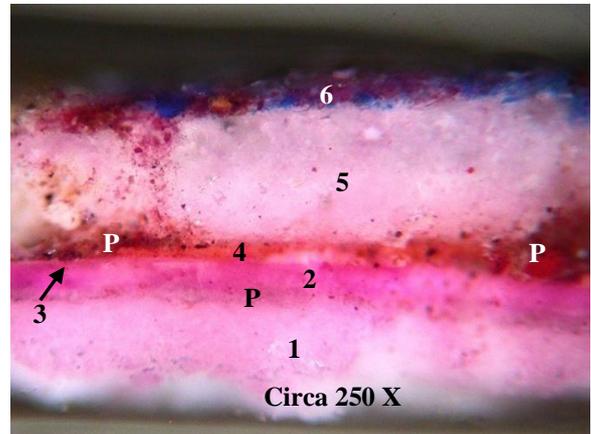
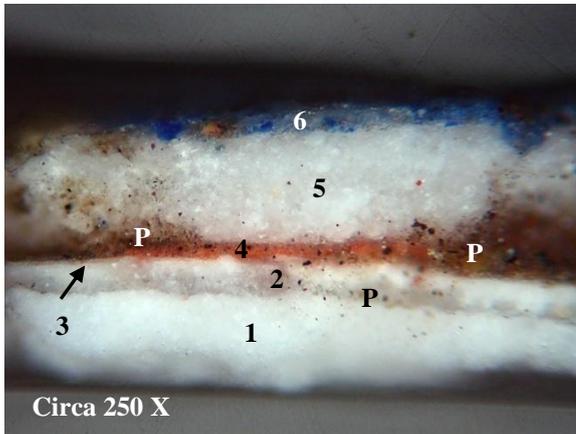


Stereo-microscope reflected light, enlargement approximately 18 (a sx) and 40 X respectively.

The image on the left shows all the tiny fragments comprising the sample. The fragment at the bottom, taken from the inside ‘face’ shows how beneath the whitish preparation over which the blue paint layer was applied, there is another pale red paint layer (see arrow). The picture on the right, greatly enlarged, shows the surface of one of the fragments, revealing the structure of the blue paint layer. Within it, minute angular blue particles (see arrow) can be made out; these are granules of lapis lazuli. On the upper part there are traces of particulate matter possibly mixed with the residue of an organic protective agent (P) [*sic*]. The red line indicates roughly the line along which the thin section was cut for the micro-stratigraphic analysis described in the following pages.

Micro-stratigraphic analysis on a thin section supplemented by micro-chemical and histo-chemical tests

Analysis sheet compiled in accordance with the directions contained in UNI-Normal 12/83 documentation



Thin section, reflected light.

The two images above show virtually the entire surface of the section. The image on the right was taken after the histo-chemical test with fuchsin was carried out in order to identify and locate protein compounds (particularly animal glue and gelatine) within the stratigraphy. The other images, which are greatly enlarged, each illustrate a detail of the stratigraphic sequence by showing the features of the various layers. The innermost layer (no. 1) comprises the plaster layer. On its surface, which is slightly uneven, there is a thin layer of particulate matter (P) made up of very fine micrometrical granules of lamp

black. The presence of this layer indicates that a certain period of time elapsed before the application of the next layer (no. 2). This was applied in two coats (2A and 2B) that are made up of hemidrate gypsum (or anhydrite) and animal glue or gelatine.

The sequence continues with a thin, intermittent, translucent layer of a whitish color (no. 3) that is a protein-based primer applied to the underlying preparation while it was still wet, and a thin and patchy orange-red paint layer (no. 4) produced by dispersing red ochre (hematite) in a protein binder. At the edges of the orange-red paint layer there are pockets of particulate matter (P) which have been deposited in the gaps between the layers.

The particulate matter also contains a number of granules of lapis lazuli that probably became detached from the upper layer (no. 6) and penetrated the irregularities of the stratigraphic sequence (see for example the white arrow in the center left photo).

Layers nos. 5 and 6 represent the last paint layers identified in the sample. The first (no. 5) is relatively thick and was applied as a preparation containing hemidrate gypsum. Within the layer there are also traces of calcium carbonate which may be the result of impurities in the raw material from which the gypsum was obtained or perhaps the intentional addition of slaked lime to act as an inert.

Over this whitish preparation there is a thin blue lapis lazuli paint layer (no. 6). Although given the data acquired, we cannot be certain that the layer does not contain protein compounds, we must bear in mind the possibility that the lapis lazuli was applied to the preparation while it was still wet using a technique similar to that documented in Spain in wall paintings of the 14th-16th centuries. This is the so-called 'false fresco' technique that involved applying the pigment to plaster or a gypsum-based preparation while the latter was still wet.

The stratigraphic sequence concludes with a thin brown layer (no. 7) composed of fine carbon particles with intermittent ochreous particles consistent with the deposition of particulate matter ('dirt'). This layer is only visible in the lower left-hand image.

There follows a detailed description of all the layers.

1) Whitish gypsum-based layer of plaster⁽²⁾

Thickness: between 0.05 and 0.08 mm; it is possible that the sample does not represent the entire thickness of the layer.

Given the results of the histo-chemical tests we cannot exclude the presence of animal glue in the layer⁽³⁾.

- *Type of contact between the layers:* clear-cut, slightly uneven, characterized by the presence of small amounts of fine carbon-based particulate matter made up of lamp black ('dirt').

2) Layer comprising two coats of gypsum and animal glue or gelatine applied in rapid succession, giving it an overall whitish color

Thickness: fairly regular, varying between 0.04 and 0.05 mm. The two coats are similar in thickness.

The lower layer (2A) is more transparent than the layer overlying it.

The other layer (2B), is whiter and much thicker and gives better cover.

The entire layer is intended to be a preparatory one.

- *Type of contact between the layers:* poorly defined with good adhesion.

² The layers are described in order of application.

³ The colorimetric test with fuchsine gave a weak positive result. However, the color that developed may be a function of physical absorption by the porous structure of the gypsum rather than a chemical reaction between the fuchsine and any protein compounds (essentially, animal glue or gelatine) present within the layer.

3) Intermittent, thin, translucent layer, whitish in color; probably a protein-based primer applied to the underlying preparation while the latter was still wet

Thickness: less than 0.01 mm.

- *Type of contact between the layers:* clear-cut with reasonable adhesion.

4) Thin and patchy orange-red paint layer produced by dispersing red ochre (hematite) in a protein binder

Thickness: varies between 0.010 and 0.015 mm.

The micro-chemical test to identify lead proved negative, indicating that at least in the small remaining areas of the paint layer there are no lead-based pigments. The optical morphological characteristics of the particles, although only insofar as they can be seen under reflected light, are compatible with the presence of red ochre (hematite) ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ - Fe_2O_3).

The presence of the protein binder is indicated by the data obtained from the histo-chemical tests given the physical characteristics of the layer and the nature of the preparatory layers.

Comments

A blue-gray layer containing granules of ochre and particulate matter and a few granules of lapis lazuli can be seen at the edges of the orange-red paint layer, in direct contact with the underlying preparation. This is particulate matter ('dirt') deposited over time in the cavities and gaps between the layers.

- *Type of contact between the layers:* clear-cut with reasonable adhesion.

5) Thick, whitish gypsum-based layer applied as a preparation

Thickness: varies between 0.12 and 0.15 mm.

The layer also contains calcium carbonate (calcite) diffused within its mass. The calcite could be traced back directly to the raw material (gypsum or selenite) used to make the hemihydrated gypsum (hemihydrated calcium sulphate) for the production of the layer. In addition to bihydrated calcium sulphate, the gypsum could actually contain calcite and other compounds. Consequently, if the gypsum is not thoroughly refined before burning, it is possible that the final product could contain a certain percentage of calcite.

Theoretically, the calcite could also derive from the use of a bastard mortar made of lime and gypsum or from the addition of slaked lime as an inert. In this context, the first of these two hypotheses is deemed to be unlikely.

- *Type of contact between the layers:* from clear-cut to poorly defined with good adhesion.

6) Blue lapis lazuli-based paint layer applied to the underlying preparation while still wet; pigment possibly mixed with a protein binder

Thickness: varies between 0.03 and 0.05 mm.

The various histo-chemical tests carried out proved negative or inconclusive. Only the fuchsine test, used to identify animal glue or gelatine in particular, produced a coloration that can be considered positive. However, we must consider the possibility that a glue-based protective agent applied during maintenance operations may be present within the paint layer.

(Contd.)

The relationship between the paint layer and the underlying preparation further suggests that the two coats were applied at the same time, 'fresco on fresco'. Some of the granules of lapis lazuli show a tendency to 'run' into the middle of the preparation itself, across the line between the two layers.

One of the hypotheses to consider with regard to the painting technique used is the possibility that paint was applied to the wet gypsum preparation or plaster finish using the gypsum itself as a binder. This technique, known as 'false fresco' is documented in Spain in ecclesiastical wall paintings of the 14th to 16th centuries.

- *Type of contact between the layers*: from clear-cut to poorly defined with good adhesion.

7) Thin brown layer composed of fine carbon particles and intermittent ochre-colored particles consistent with a deposit of particulate matter ('dirt') possibly mixed with the traces of an organic protective agent

Thickness: less than 0.005 mm.

On the basis of the data supplied by the fuchsine test, the protective agent could be based on animal glue or gelatine (compare with the micro-photographs).

Sample PRO 9

Origin of sample and its characteristics

North Corridor, wall decorated with concentric circles, left side, from the band painted with a multicolored braid. Sample taken from a portion with a green coat applied over a yellow one.



Type of analysis carried out

Micro-stratigraphic analysis on a thin section supplemented by histo-chemical and micro-chemical tests.

Chemical and mineralogical analysis using Fourier Transform Infrared spectrometry (FT-IR).

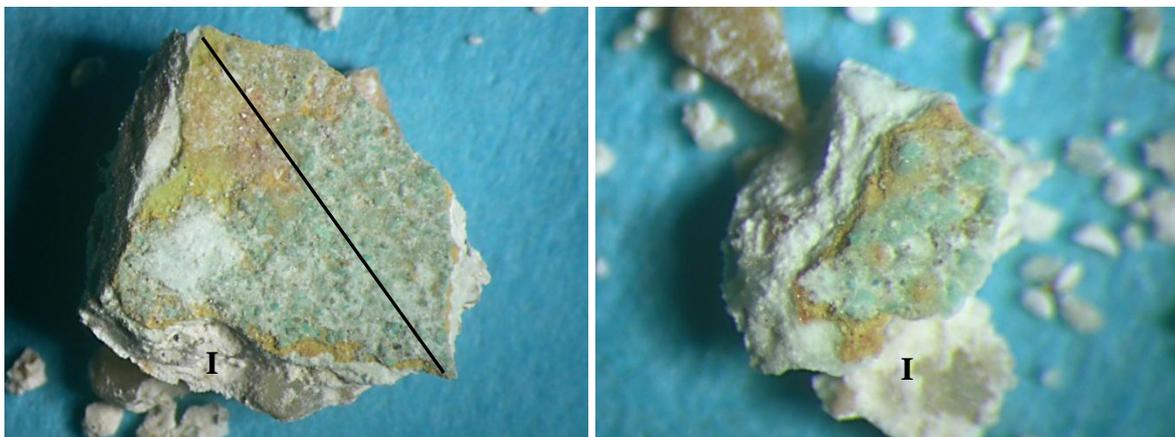
Optical and mineralogical analysis using microscopy under polarized transmitted and reflected light.

Aims of laboratory investigations

To analyze the base plaster (on the basis of the model supplied in UNI-Normal document 12-83) and identify the number, type and nature of the layers applied over it.

To identify the pigments, binders and any modifying products present in the two coats of green and yellow paint.

Preliminary examination under stereo-microscope



Stereo-microscope, reflected light, enlargement approximately 10 (a sx) and 40 X respectively

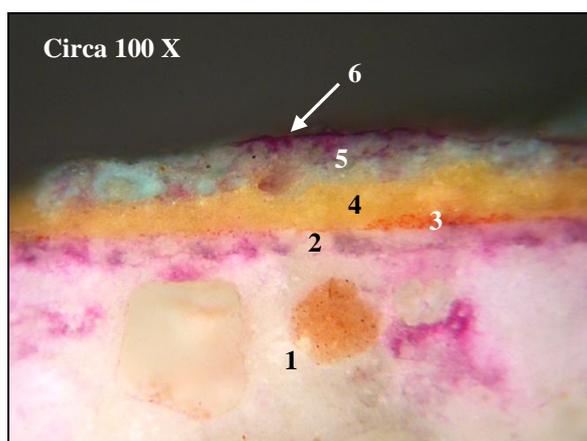
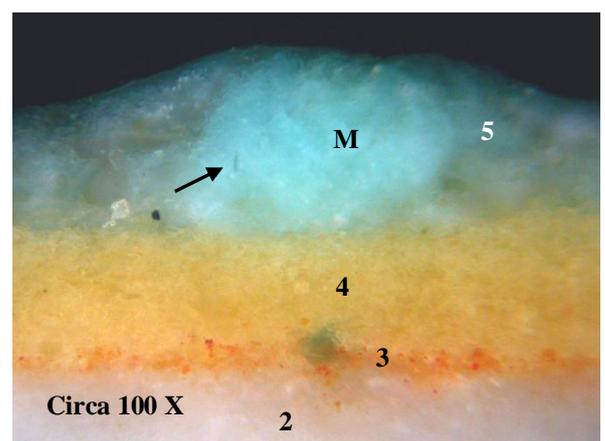
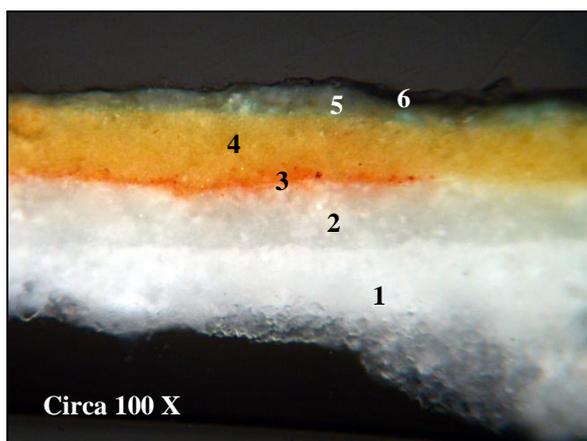
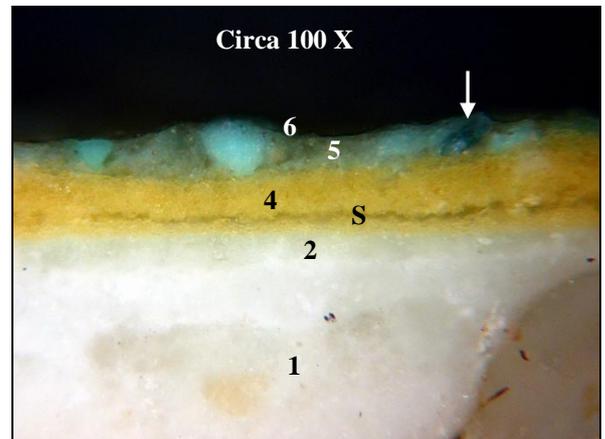
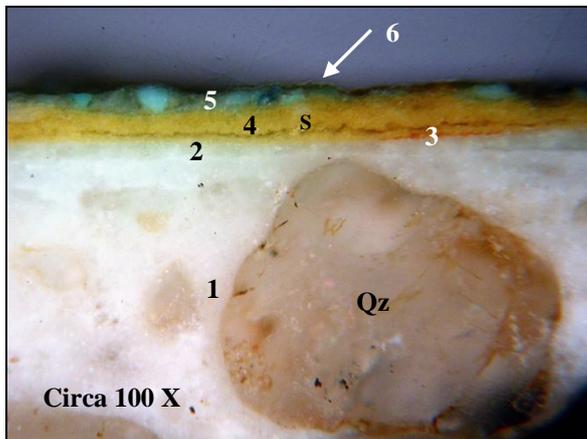
The image on the left shows the upper part of the fragment used to provide the thin section used in the micro-stratigraphic study (see the images shown on the following pages⁴). The paint layer, comprising two coats of greenish yellow and green paint was applied over a light-colored lime and sand plaster (I).

The image on the right, greatly enlarged, shows the surface of another of the flakes of plaster included in the sample. The granular structure of the green paint layer is clearly visible in the photograph. The small green masses visible in the image were found to be composed of two pigments mixed together, one white and one green (see the results of the microscopic and FT-IR analyses set out on the following pages).

⁴ The black line indicates approximately the line along which the thin section used for the micro-stratigraphic analysis was cut.

Micro-stratigraphic analysis on a thin section supplemented by micro-chemical and histo-chemical tests

Analysis sheet compiled in accordance with the directions contained in UNI - Normal 12/83 documentation



Thin section, reflected light.

The top left-hand image, at a relatively low magnification, shows a good part of the section and the entire stratigraphic sequence. The other, more highly magnified images show other details of the layers contained in the sample. In particular, the bottom left-hand image was taken after the histo-chemical test with fuchsine aimed at identifying and locating protein compounds within the stratigraphy (especially animal glue or gelatine).

The finishing coat of plaster (n. 1), made of slaked lime and quartz-based (Qz) sand,

has been carefully smoothed and pressed with a float or trowel. Next, a preparatory layer of plaster (no. 2) was applied on which the preparatory design (no. 3) was sketched immediately in red ochre (hematite). Then the coats that constitute the paint layer (layers nos. 4 and 5) were applied. Both used tempera colors, made by dispersing (probably in a protein-based binder) respectively natrojarosite (no. 4), and roundish light-green grains (M) obtained by mixing gypsum with a copper pigment that is probably atacamite (arrow at bottom right).

A few granules of Egyptian Blue can be seen within the light-green layer (arrow in top right image).

The stratigraphic sequence concludes with a thin and intermittent brown layer (no. 6) that is probably a protein-based protective agent (most likely made of animal glue or gelatine). The layer is particularly visible in the lower left-hand image where it is highlighted by the fuchsia color produced by the reaction with the fuchsine. However, the colorimetric reaction produced inconclusive results in the other layers.

All the layers are described in detail on the following pages and the results of the FT-IR analyses and the optical mineralogical examination are also set out.

1) Light-colored finishing plaster made of slaked lime and well-graded sand composed principally of silicates (mostly quartz) and a smaller proportion of grains of alabastrine limestone

Thickness: reaches a maximum of 1.0 mm.

Grain size: varies between that equivalent to very fine sand (0.10 mm) and that typical of coarse sand (0.82 mm).

Degree of uniformity of grain sizes: good.

Estimated original volumetric ratio of binder to aggregate: 1:2.

Characteristics of the mix

Mortar made of lime (slaked) and well-graded sand composed principally of silicates and a smaller proportion of alabastrine limestone. The latter appears in the form of intermittent sub-spherical grains. The silicate components are represented essentially by rounded grains of quartz, sometimes with oxidized edges (desert varnish) and solid inclusions.

The porosity of the mix is average (estimated to be in the region of 30-35%), determined by the presence of cracks, mostly caused by the desiccation of the lime. Cracks produced by physico-mechanical stress can be seen towards the surface of the layer, possibly caused when the sample was taken.

Comments

The surface of the plaster is very regular. It has been pressed and smoothed with an appropriate tool.

The plaster is the same as that taken in sample PRO-11B. However, it differs from plaster types taken from various parts of the first tier of the triconch and analyzed during earlier missions. These plaster types were made using a mortar comprising slaked lime and fragments of alabastrine limestone obtained by crushing the rock.

Type of contact between the layers: clear-cut with good adhesion.

2) Whitish gypsum-based layer applied as a preparatory coat

Thickness: in the region of 0.04 - 0.06 mm.

Parts of the layer are a pale greenish color possibly as a result of the penetration of the dissolved green pigment.

- *Type of contact between the layers:* poorly defined with good adhesion.

3) Thin and highly intermittent red hematite-based layer ((Fe₂O₃), probably a sort of sinopia used for the preparatory design

Thickness: less than 0.01 mm.

The layer seems to have been applied to the underlying coat while it was still wet.

- *Type of contact between the layers:* poorly defined with good adhesion.

4) Yellow paint layer based on jarosite dissolved in an organic, probably protein-based, medium

Thickness: in the region of 0.05 - 0.06 mm.

See the description of the FT-IR analysis below with regard to the characteristics of jarosite. The IR (infrared spectrum) results also indicate that the paint layer is rich in calcium oxalates whose presence is associated with the almost total mineralization of the original organic binder.

In some areas of the paint layer there are long longitudinal cracks that tend to separate the layer into two parts.

- *Type of contact between the layers:* clear-cut with good adhesion.

5) Light-green paint layer based on gypsum and a green copper pigment, most likely atacamite, dispersed in a medium that is probably organic in nature

Thickness: varies between 0.06 and 0.08 mm.

The information contained in the description of the previous layer concerning mineralization into calcium oxalate also applies to the organic binder.

The presence of the gypsum and atacamite was ascertained on the basis of data acquired using spectrophotometric and optical mineralogical methods (see below).

- *Type of contact between the layers:* clear-cut with good adhesion.

6) Traces of a thin brown layer resulting from the application of a protein-based organic protective agent (most likely based on animal glue or gelatine)

Thickness: varies between 0.06 and 0.08 mm.

The protein-based nature of the layer was suggested by the positive result of the histochemical test with fuchsine (see micro-photographic documentation).

Fourier transform infrared spectroscopy (FT-IR) analysis

Preparation of sample and method of analysis

A flake of submillimetric dimensions comprising the paint layer and traces of the underlying whitish preparatory layer was used for the FT-IR analysis. As has been well documented in the micro-stratigraphic analysis (see preceding pages), the paint layer is made up of two coats, one yellow and one light green. The diminutive proportions of the fragments, their relative fragility and the good adhesion between the two paint layers meant that it was impossible to separate the two coats in order to analyze them independently.

The submillimetric flake was finely ground with KBr in an agate mortar and analyzed without further treatment using a Shimadzu 8400 – S FT-IR spectrophotometer (DRIFT method).

The FT-IR spectrum obtained from the analysis was interpreted by comparing it with the laboratory data base and others published in various scientific journals⁵. In particular, the assignments were made on the basis of the vibrational frequencies of pure or mixed reference standards at particular matrices (calcite, gypsum, animal glue, etc.) recorded under the same experimental conditions.

Results and interpretation thereof

Study of the IR spectrum obtained from the analysis enabled us to establish that the sample comprises the following crystalline phases, listed in order of relative abundance.

- *Natrojarosite* [Na(Fe³⁺)₆(SO₄)₄(OH)₁₂]. Principal absorption bands: 3355, 1629, 1191, 1099, 1026, 1012, 636, 514, 482 cm⁻¹.
- *Calcium oxalates* probably represented by the sole bihydrate phase (*weddellite*: CaC₂O₄·2H₂O). Principal absorption bands: 3062, 1650, 1317, 781 cm⁻¹.
- *Calcium sulphate (gypsum)* probably represented by both the hemihydrate phase (CaSO₄·0,5H₂O) and the anhydrous phase (CaSO₄: anhydrite). Principal absorption bands: 3433 (?), 1142, 1157, 676, 659, 597 cm⁻¹.
- *Calcite* (CaCO₃). Principal absorption bands: 2509, 1793, 1456, 877 cm⁻¹.
- *Nitrates* (XNO_y). The only principal band is visible at 1382 cm⁻¹.
- Slight traces of *organic compounds*, shown by a single weak band at 2929 cm⁻¹.

Certain absorption bands corresponding to peaks in the IR spectrum could be partially caused by the presence of *atacamite* [Cu₂(OH)₃Cl]. These bands are found in areas of the spectrum in which the effects of absorption produced by *natrojarosite* (514, 482 cm⁻¹) and *calcium sulphate* (3433, 597 cm⁻¹) are also found. Therefore, owing to the interference caused by both *natrojarosite* and *calcium sulphate*, on the basis of the data acquired from the spectrum study, we cannot be certain that *atacamite* is present.

Natrojarosite is the pigment used in the yellow coat forming the first stratum of the paint layer included in the sample.

Calcium oxalate dihydrate is produced by the mineralization of the original organic binder (presumably protein-based) used in painting⁽⁶⁾.

Calcite, present in small quantities, could represent an impurity present in the other pigments. It could also have been added deliberately to the paint layer as a charge or white pigment (for example, the white slaked lime known as *Bianco San Giovanni*).

⁵ These include, inter alia:

- *Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures*. H.W van der Marel; H. Beutelspacher. Elsevier Scientific Publishing Company – Amsterdam – Oxford – New York 1976.
- Janice L. Bishop and Enver Murad (2005). The visible and infrared spectral properties of jarosite and alunite. In *American Mineralogist*, vol. 90, pages 1100 – 1107, 2005, Ed. Mineralogical Society of America.

⁶ See the proceedings of the following conventions for hypotheses relating to the origin of the oxalates:

- AA. VV., 1989. *The Oxalate Films: origin and significance in the conservation of works of art*, Milan, 25 – 26 October 1989. Ed. C.N.R. “Gino Bozza” – Politecnico di Milano.
- AA. VV., 1996. *The oxalate films in the conservation of works of art*, Milan, 25 – 27 March 1996. Ed. C.N.R. “Gino Bozza” – Politecnico di Milano.

The *calcium sulphate* (both in the *hemidrate* and *anhydrate* stage could be present either within the paint layer or in the whitish preparatory layer of which there were traces in the small flake analyzed (see the paragraph on the preparation of the sample). In particular, it is possible that calcium sulphate forms the ‘main body’ of the light green grains contained within the green paint layer (compare with the results of the micro-stratigraphic analysis).

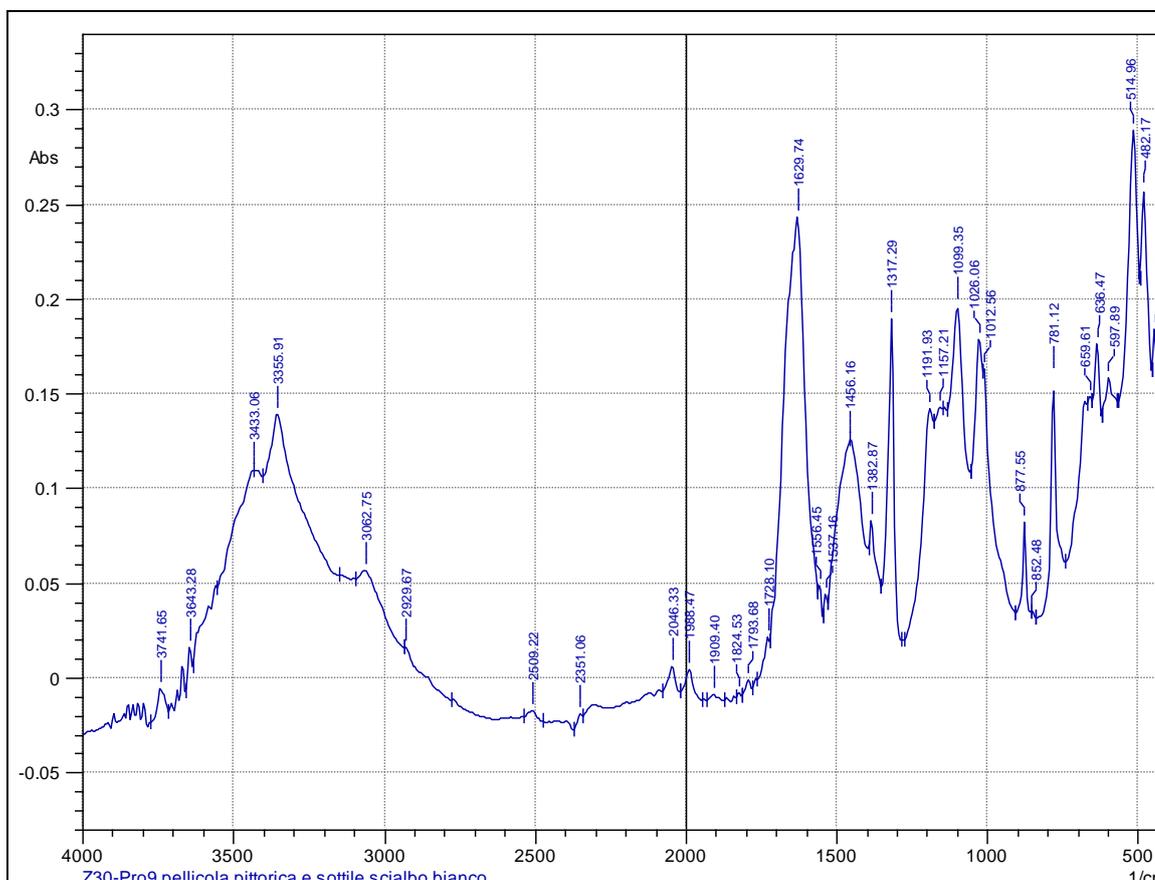
Nitrates are soluble salts that can easily accumulate in the paint layer of paintings in an environmental and climatic context such as that of the Red Monastery.

It is difficult to formulate a hypothesis with regard to the slight traces of *organic compounds* present. Are these residues of the original binders or fixatives applied during the course of maintenance work that have not been transformed entirely into calcium oxalate or are they perhaps compounds produced by unintentional contamination of the painted surfaces?

Atacamite, should its presence be confirmed by more in-depth analysis (for example, by analyzing a few tens of milligrams of dust selectively taken from the green layer alone with an FT-IR or XRD), may be the pigment used in the outermost paint layer. Atacamite has also been encountered in ancient Egyptian paintings⁽⁷⁾

During the course of the IR spectrum study, particular attention was paid to the presence of other copper pigments used in Egypt such as *malachite* and *chrysocolla*. However, no absorption band that could be attributed to either one of these two pigments was found.

⁷ See for example S. Colinart, E. Delange and S. Pagés (1996), *Couleurs et pigments de la peinture de L’Egypte Ancienne* [Colors and pigments used in Ancient Egyptian paintings], in *Techne* n. 4, 1996, pp. 29 – 45.



FT-IR Spectrum.

Optical mineralogical analysis aimed at identifying the pigments present in the paint layer

A submillimetric fragment of the paint layer including both the yellow and green coats was used to furnish the sample. Observations were made under reflected light and, in particular, an optical mineralogical study was carried out under transmitted polarized light.

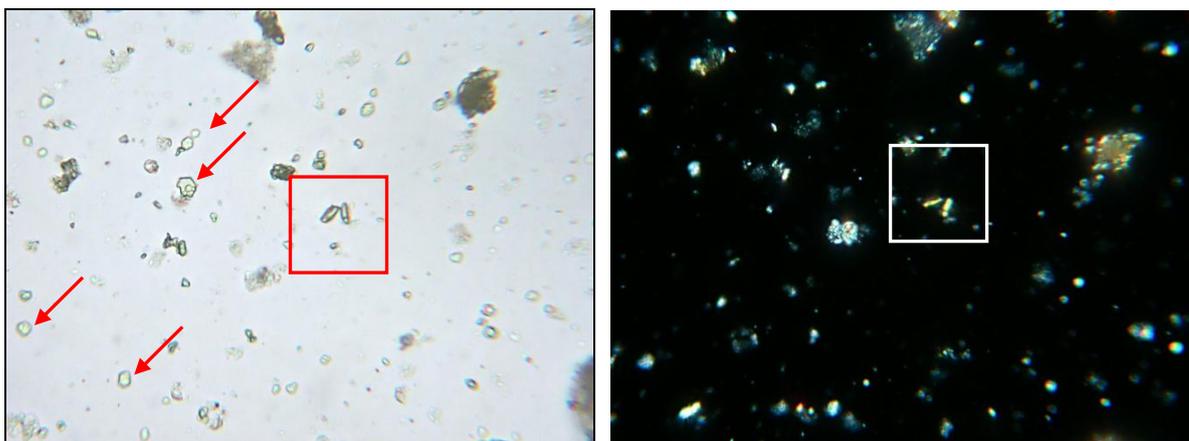
The microscopic examination enabled us to identify the constituents listed below in descending order of abundance:

- Very numerous *jarosite* crystals with the typical crystalline habitus characterized by a marked tendency to flake off according to 0001. They show an average relief, pleochroism varying from colorless to pale greenish yellow, low birefringence with interference colors on the light gray of the first order.
- Various small rounded light green masses made up of a fine matrix of *micro* to *cryptocrystalline* gypsum surrounding several crystals of acicular prismatic habit of dimensions in the range of 1 to 5 micrometers. These crystals have average to high relief, perpendicular extinction and strong birefringence with high interference colors.

(Contd.)

Of the copper pigments used in Egypt⁽⁸⁾, *atacamite* is the one that displays comparable optical characteristics. However, in order to identify it with certainty it would be useful to carry out complementary analyses such as the diffraction of X rays on powder.

- a few particles of *red ochre – ematite* ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O} - \text{Fe}_2\text{O}_3$)
- a few granules of monocrystalline *quartz*
- a few crystals of *microsparitic and sparitic calcite* (dimensions less than or slightly larger than 0.01 mm), sometimes in aggregates of two or more crystals.



Slide, transmitted light, enlarged circa 500 X (both images). Right-hand photo, polarizer only; sx photo, crossed Nicol.

The two images represent the same frame taken under different optical conditions. The left-hand image shows several jarosite crystals, distinguished by a polyhedral habit and very pale greenish yellow color. Inside the red box there are two prismatic crystals whose optical characteristics enable us to identify them as atacamite. In the image on the right the high birefringence of the two crystals (white box) can clearly be seen by comparison with the very weak birefringence of the jarosite (the jarosite crystals are hardly visible under these optical conditions).

⁸ Chrysocola, Malachite, Paratacamite, Plancheite, Sampleite and Verdigris (cf. In S. Colinart, E. Delange and S. Pagés, 1996, op. cit.)

Sample PRO 11A

Origin of sample and its characteristics

North corridor, wall decorated with concentric circles, left side, from a dark red background within the band decorated with a multicolored braid.



Type of sample taken

The sample included the paint layer, a white preparatory layer and traces of the underlying base plaster. Owing to the poor adhesion between the finishing plaster and the overlying preparation, it was not possible to include in the sample a fragment of plaster large enough to allow any meaningful definition. Therefore we had to take another two samples (11B and 11C) from the finishing plaster underlying the preparatory and paint layers and the base plaster adhering to the masonry respectively. The results of the analyses of these two samples are provided in two separate analysis sheets.

Type of analysis carried out

Micro-stratigraphic analysis on thin section supplemented by micro-chemical tests.
Chemical and mineralogical analysis using Fourier Transform Infrared Spectroscopy (FT-IR).

Aims of the laboratory investigations

To analyze the base plaster (based on the model supplied in UNI-Normal document 12-83) and identify the number, type and nature of the layers applied over it.
To identify the pigments, binders and any modifying products present in the red paint layers.

Preliminary examination under stereo-microscope



Stereo-microscope, reflected light, enlarged circa 16 X.

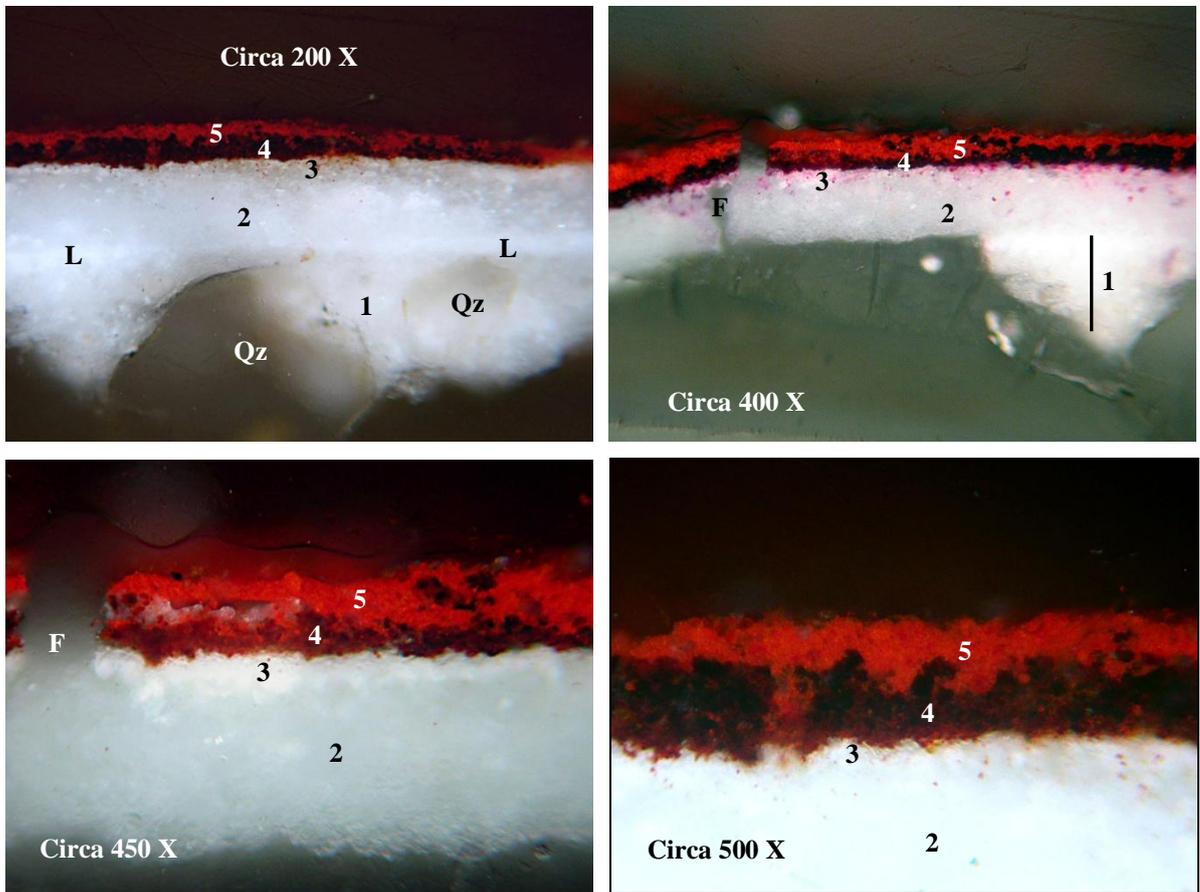
The image shows one of the small flakes included in the sample. The purplish red paint layer can be seen on top of the plaster (I), which is very well smoothed and compacted. Below the purplish red level there is also a thin blackish layer which can be identified, on the basis of the data acquired from the micro-stratigraphic analysis (see below), as an altered lead pigment.

The paint layer is almost entirely supported by the base plaster.

The white line indicates roughly the line along the thin section was cut for the micro-stratigraphic analysis described below.

Micro-stratigraphic analysis on thin section supplemented by micro-chemical and histo-chemical tests

Analysis sheet drawn up in accordance with the directions provided in Doc Normal 12/83.



Thin section, reflected light.

The four images, representing different enlargements, show a good part of the section and enable us to describe the entire stratigraphic sequence.

Starting from the bottom we can see: 1) traces of the finishing plaster based on carbonized lime and sand with a high quartz (Qz) content; 2) whitish gypsum-based layer applied as preparation; 3) thin and intermittent white layer based on white lead applied to the preparation while the latter was still wet. The pigment was possibly dissolved in a protein-based binder. The layer may have been applied as a primer or base coat; 4) paint layer now a dark purplish red color, tending to black, composed of a lead pigment that has become darker as a result of chemical alteration. This layer may have been produced by dissolving lead minium in a protein medium and applying it as a base color; 5) red, hematite-based (Fe_2O_3) paint layer finely dispersed, most likely in a protein-based medium, and now completely mineralized into calcium oxalate.

All the layers are described in detail below, together with the results and their interpretation.

1) Traces of light-colored plaster composed of slaked lime and sand with a high silicate content

Thickness: reaches a maximum of 0.27 mm.

The diminutive size of the fragments of plaster taken in the sample do not permit a definition with a minimum statistical value as set out in UNI-Normal 12-83 documentation. We can only state that the surface of the plaster is very regular and has been carefully compacted and smoothed with a float or trowel. This action has probably caused the lime in the binder to effloresce on the surface, forming a thin, more compact layer (approximately 0.02 mm thick) that can be seen clearly on top of the plaster (see the images on the previous page).

- *Type of contact between the layers:* characterized by poor adhesion; the two layers tend to separate easily.

2) Whitish gypsum-based layer applied as a preparation

Thickness: very regular, varies from approximately 0.07 to 0.08 mm.

- *Type of contact between the layers:* clear-cut with good adhesion.

3) Thin and intermittent white layer based on white lead applied to the preparatory layer whilst the latter was still wet. The pigment may have been dissolved in a protein-based binder.

This layer may have been intended to act as a primer.

Thickness: reaches a maximum of 0.01 mm.

The lead identification test proved positive, indicating that the layer contains white lead. The carbonate identification test showed a weak positive result, indicating that in all likelihood, ceruse [$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$] was used as a pigment.

The various histo-chemical tests carried out gave negative or inconclusive results. Only the fuchsine test, particularly useful in identifying animal glue or gelatine, produced a color that could be interpreted as positive.

The relationship between the paint layer and the underlying preparatory layer further suggests that the two coats were applied 'fresco on fresco' whilst the first was still wet. Some of the grains of white lead display a tendency to 'run' into the preparatory layer, across the line between the two layers.

One hypothesis to be examined with regard to the painting technique is that paint was applied directly to the still wet preparatory layer or *intonachino*, using the plaster itself as a binder. This technique, known as 'false fresco' is documented in wall paintings in Spanish churches of the 14th-16th centuries.

- *Type of contact between the layers:* clear-cut with good adhesion.

4) Paint layer now a dark purplish red, tending to black, composed of a lead pigment that has become darker as a result of chemical alteration

Thickness: approximately 0.03 mm.

The presence of lead was ascertained by means of a specific micro-chemical test ($\text{HNO}_3 + \text{KI}$) carried out directly on the section. Owing to the dark color of the layer, the histo-chemical tests proved unsuccessful.

However, on the basis of our observations we can conjecture that this layer and the next were painted using a protein-based binder.

On the other hand, it is difficult to understand the original nature of the lead pigment now chemically altered and darkened into lead oxide (plattnerite). Given the coloration of some parts of it and on the basis of comparison with Spanish and Italian Renaissance painting techniques, we can speculate that the original pigment used in the paint layer was minium – lithargirium ($\text{Pb}_3\text{O}_4 - \text{PbO}$).

In this case, the layer could have been intended to act as a base color applied to modulate or highlight the color applied in the successive paint layer.

- *Type of contact between the layers:* from poorly defined to clear-cut, uneven, with good adhesion.

5) Red hematite-based (Fe_2O_3) paint layer finely dispersed in a medium that is probably protein-based, now completely mineralized into calcium oxalate.

Thickness: varies between 0.01 and 0.03 mm.

The hematite was identified both on the basis of the special optical and morphological characteristics of the pigment particles (even under reflected light) and the positive result of the micro-chemical test for iron.

The mineralization into calcium oxalate of the original organic binder was indicated by the results of the FT-IR analysis (see below). The theory that the original binder was protein-based was advanced on the basis of stratigraphic, optical and morphological data obtained from the study of the section.

Fourier Transform Infrared Spectroscopy (FT-IR) analysis

Preparation of the sample and methods of analysis

A flake of submillimetric dimensions comprising solely the paint layer was used for the FT-IR analysis. As was well documented in the micro-stratigraphic analysis (see preceding pages) the paint layer is made up of three layers that are white, dark purplish red and red respectively. The tiny size of the fragments, their relative fragility and the good adhesion between the paint layers made it impossible to separate the layers in order to analyze them independently.

The submillimetric flake was finely ground in an agate mortar with KBr and analyzed without further treatment using a Shimadzu 8400-S (DRIFT method) FT-IR spectroscope.

The FT-IR spectrum obtained from the analysis was interpreted by comparing it with the laboratory data base and others published in various scientific journals⁽⁹⁾. In particular, the assignments were made on the basis of the vibrational frequencies of pure or mixed reference standards at particular matrices (calcite, gypsum, animal glue, etc.) recorded under the same experimental conditions.

Results and interpretation thereof

The IR spectrum study obtained from the analysis (see following page) enabled us to ascertain that the sample comprises the following crystalline phases, listed below in order of relative abundance.

- *Calcium oxalates* probably represented by the single bihydrate phase (*weddellite*: CaC₂O₄·2H₂O). Principal absorption bands: 3440 (?), 3340, 3062, 1643, 1317, 781, 516 cm⁻¹.
- Probably *barium sulphate* (barite: BaSO₄). Principal absorption bands: 1176, 1137, 1087, 989, 642, 617 cm⁻¹. For absolutely certain identification the barium should be identified using ED-XRF (X-ray fluorescence) or SEM (Scanning Electron Microscopy) supplemented by X-ray microsound (EDS system). Many of the absorption bands encountered actually have a position slightly different to those in library reference standards.
- *Calcite* (CaCO₃). Principal absorption bands: 1454, 875 cm⁻¹.
- *Nitrates* (XNO_y). Only the principal band is visible at 1382 cm⁻¹.
- Probably *phyllosilicates* (silicates and silicon aluminate, hydrates of calcium, potassium and sodium and other metal ions. Absorption bands: 1035, 1010, 912 cm⁻¹.

A single absorption band at 453 cm⁻¹ can be linked with the presence of *minium* (Pb₃O₄). Of those bands visible in the analytical interval (4000 – 400 cm⁻¹) possible when using the standard instrument, the only one missing is that at 527 cm⁻¹ which may have been covered in any case by the effect at 516 cm⁻¹ caused by the bihydrate calcium oxalate.

The *bihydrate calcium oxalate* derives from the mineralization of the original organic binder (presumably protein-based) used in painting⁽¹⁰⁾.

Although its presence was ascertained by identifying the barium and sulphur in the paint layer, the *barium sulphate* could have been used as an inert carrier within the paint layer (most easily in the red surface layer). The use of barium sulphate in painting is documented in Italy and Europe from the beginning of the 19th century⁽¹¹⁾. However, the abundance of this mineral in Egypt⁽¹²⁾ could have led to the local use of the compound.

Calcite, present in small quantities, could be an impurity in other pigments.

⁹ See contents of sheet for sample PRO9, paragraph concerning the FT-IR.

¹⁰ See preceding note.

¹¹ G. Montagna, 1993. *I pigmenti, prontuario per l'Arte e il restauro*, Scheda n. 36, [Pigments: a Handbook for Art and Restoration, Sheet 36] Ed. Nardini, Florence, 1993.

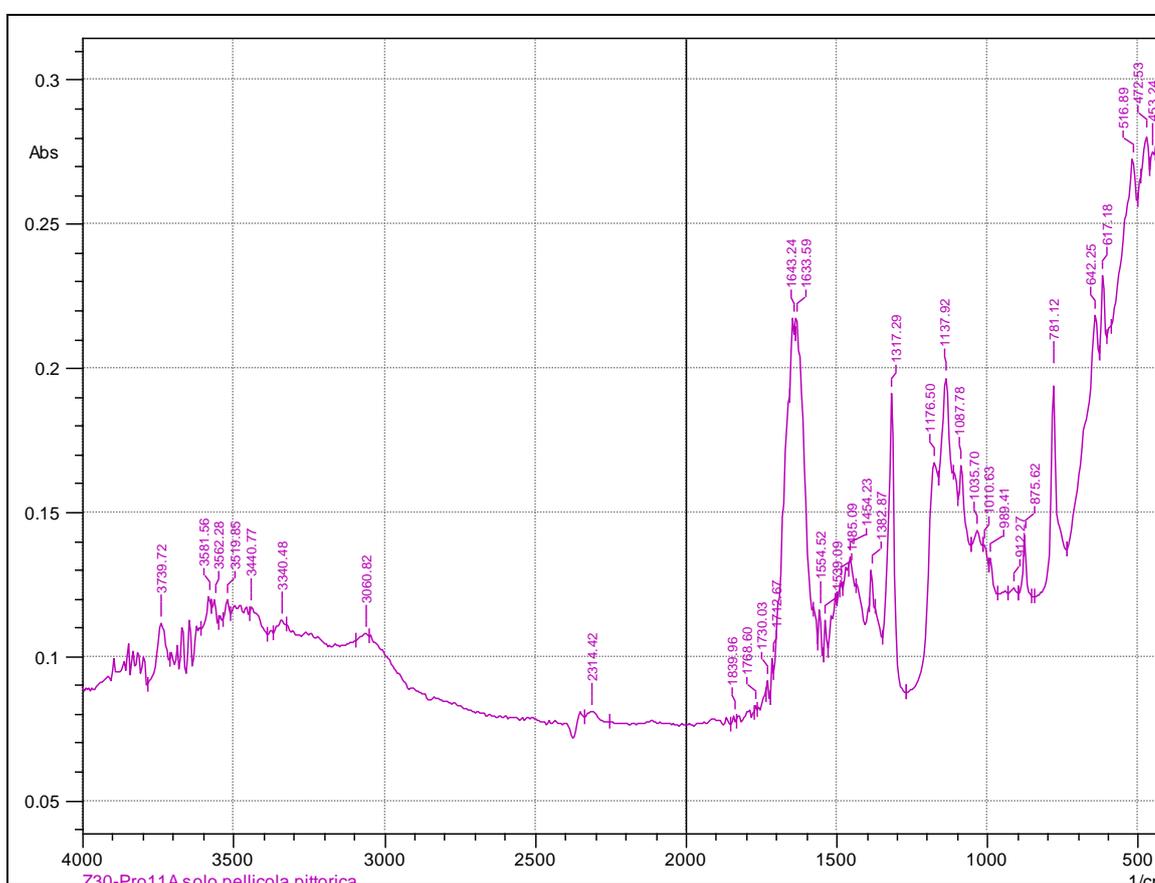
¹² See for example Wetait, M. *Barite mineralisation in the south Um Monqul area, North Eastern Desert, Egypt*, Journal of African Earth Sciences, vol. 25, issue 3, pp. 485-489, 10/1997.

It could also have been added deliberately to the paint layer as a carrier or white pigment (for example, slaked lime of the Bianco San Giovanni type).

Nitrates are soluble salts that could easily accumulate in the paint layer of paintings in a climatic and environmental context similar to that of the Red Monastery.

The *phyllosilicates* can be associated with hematite which derives from the refining, and often the calcination, of earth pigments, a raw material normally distinguished by the presence of argillaceous and micaceous minerals.

In the spectrum no absorption bands for hematite were observed owing to the strong interference of the other substances. The main peak for hematite at approximately 600 cm⁻¹ was interfered with by that of barium sulphate.



FT-IR Spectrum.

Sample PRO 11B

Origin of sample and its characteristics

North corridor, wall decorated with concentric circles, left side, from a dark red background (area stratigraphically beneath sample 11A) within the band decorated with a multicolored braid.



Type of sample taken

The sample included several fragments of finishing plaster underlying the preparatory and paint layers (compare with sample 11A).

Type of analysis carried out

Micro-stratigraphic analysis on thin section supplemented by histo-chemical and micro-chemical tests.

Aims of laboratory investigations

Identification of the base plaster (on the basis of the model provided in UNI – Normal 12-83 documentation) and identification of the number, type and nature of the layers applied over it.

Preliminary examination under stereo-microscope



Stereo-microscope, reflected light, enlargements approximately 10 (sx) and 16 X.

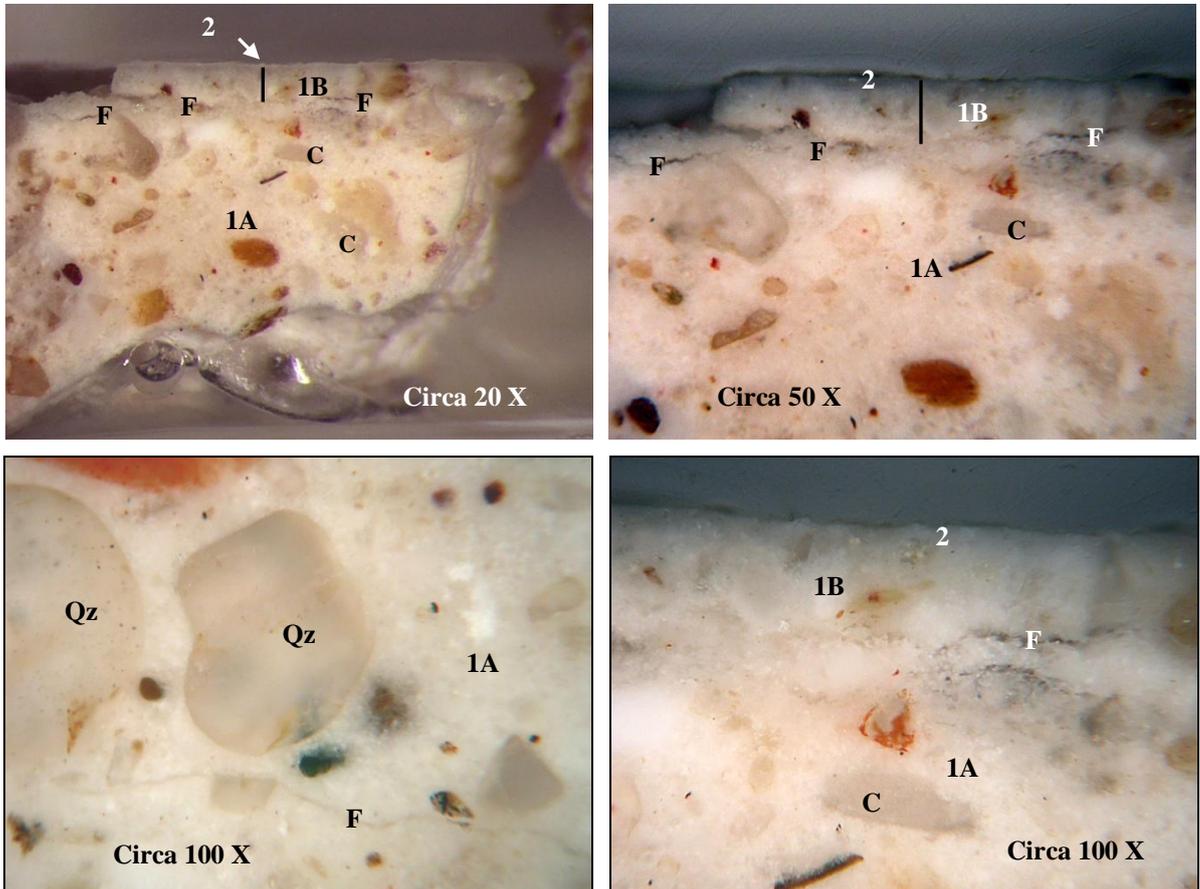
The image on the left shows the flakes of finishing plaster included in the sample. The lower flake shows the surface of the plaster. However, this is more clearly shown in the enlarged image on the right.

It appears that a thin layer of lime (C) has been applied over the plaster which has been well smoothed and pressed with a float or trowel.

The black line indicates roughly the line along which the thin section was cut for the micro-stratigraphic analysis described in the following pages.

Micro-stratigraphic analysis on thin section supplemented by micro-chemical and histo-chemical tests

Analysis sheet drawn up in accordance with the provisions of UNI - Normal 12/83 documentation.



Thin section, reflected light

The top left-hand image shows a good part of the surface of the transverse section of one of the two fragments used for the microscopic study. The image shows the structure of the finishing plaster which is a mortar of slaked lime and well-graded sand composed mainly of silicates (mostly quartz: Qz) and, to a lesser extent, fragments of alabastrine limestone. A longitudinal crack (F), located approximately 0.25 mm below the surface of the plaster tends to separate it into two portions: 1A and 1B.

The crack, caused by small physical and mechanical stresses, may have been encouraged by a pre-existing latent break where one layer overlaid the other. The plaster may in fact have been applied in two coats at one time.

Above the plaster there is a compact, thin layer, whitish in color, made of carbonated lime (no. 2).

This layer may be the result of the efflorescence on the surface of the plaster of a small amount of the lime from the binder caused by the actions of smoothing and compacting the plaster itself.

The other images show further details of the stratigraphy that will be described in detail on the next page.

1) Light-colored finishing plaster made of slaked lime and well-graded sand composed principally of silicates (mostly quartz) and, to a lesser extent, fragments of alabastrine limestone

Thickness: does not exceed 2.5 mm.

Grain size: varies from the equivalent of fine sand (0.15 mm) to that of very coarse sand (1.9 mm).

Degree of uniformity of grain size: moderate to good.

Estimate of original volumetric ratio between binder and aggregate: 1:2 or slightly more

Characteristics of the mix:

Mortar made using slaked lime and well-graded sand, composed principally of silicates and, to a lesser extent, fragments of alabastrine limestone.

These latter are represented by intermittent grains, both angular (markedly prevalent) and rounded in shape. The silicate components are represented essentially by rounded grains of quartz, sometimes distinguished by oxidized edges (of the desert varnish type) and solid inclusions.

The porosity of the mix is average (estimated to be around 30%), owing to the presence of cracks produced as the lime dried out and bubbles resulting from the fact that the mortar was not mixed to a perfect consistency.

Within the mix there are also cracks caused by physical and mechanical stresses.

Comments

The surface of the plaster is very regular. It has been carefully compacted and smoothed with a trowel or float.

Approximately 0.25mm below the surface of the plaster a long crack displays a tendency to isolate a fragment parallel to the surface. The crack, caused by small physical and mechanical stresses, may have been encouraged by a pre-existing latent break where one layer overlaid the other. The plaster may in fact have been applied in two coats at one time (1A and 1B).

The plaster is the same as that in sample PRO-9. However, it is not the same as that taken from various areas of the first tier of the triconch and analyzed during the earlier missions. These plaster types used a mortar made with slaked lime and fragments of stone obtained by crushing alabastrine limestone.

- *Type of contact between the layers:* poorly defined with excellent adhesion.

2) Thin, compact whitish layer, based on carbonated lime

Thickness: less than 0.05 mm.

This layer seems to be the result of the application of a 'coat' of lime, very well smoothed with a float or trowel, rather than the efflorescence on the surface of the plaster of a small amount of the lime in the binder (see the stereo-microscope images).

Sample PRO 11C

Origin of sample and its characteristics

North corridor, wall decorated with concentric circles, left side, from a dark red background (area stratigraphically beneath samples 11A and 11B) within the band decorated with the multicolored braid.



Type of sample taken

The sample included several fragments of the base plaster, underlying both the finishing plaster and the preparatory and paint layers.

Type of analysis carried out

Micro-stratigraphic analysis of thin section supplemented by micro-chemical tests.

Aims of the laboratory investigations

Analysis of the plaster on the basis of the model supplied in UNI – Normal 12-83 documentation.

Preliminary examination under stereo-microscope

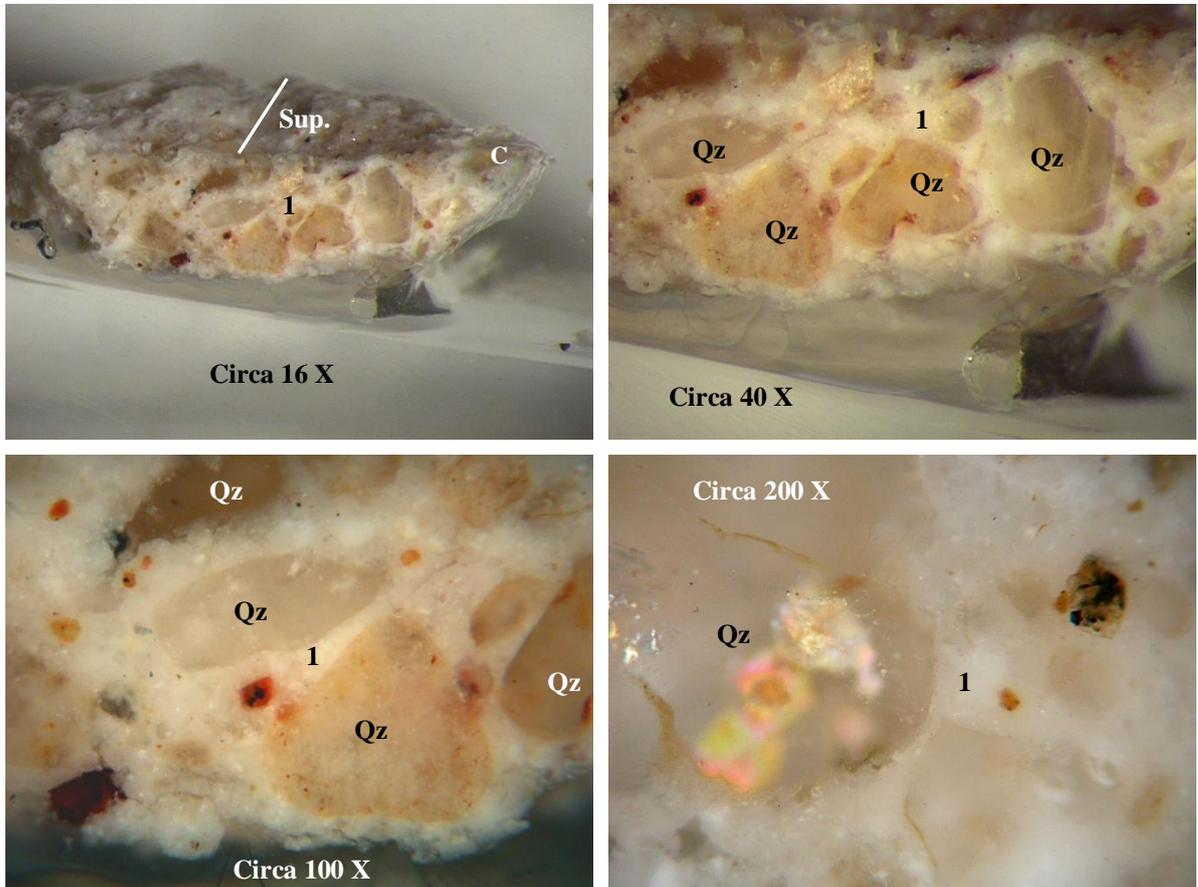


Stereo-microscope, reflected light, enlargement approximately 8 X.

The image shows the two fragments of plaster from which the thin section was taken for the micro-stratigraphic analysis. The black line indicates roughly the line along which the thin section was cut.

The results of the micro-stratigraphic analysis of the plaster are set out on the following page.

Micro-stratigraphic analysis of thin section supplemented by micro-chemical tests
Analysis sheet drawn up in accordance with the directions provided in UNI-Normal 12/83 documentation.



Thin section, reflected light.

The top left-hand image is a relatively low enlargement and shows a good part of the surface of the transverse section of one of the two fragments used to prepare the thin section for the microscopic study. The image shows the structure of the finishing plaster (no. 1) which comprises a lime mortar (slaked lime) and well-graded sand, principally made up of silicates (especially quartz) and to a lesser extent, fragments of alabastrine limestone (C).

Owing to the considerable depth of field in the image the external surface of the plaster (Sup) is also partially visible and in focus.

The other images are more greatly enlarged and show how the appearance of the numerous grains of quartz (Qz) in the aggregate differs, depending on the number of inclusions or oxides they contain.

The two uppermost images enable the viewer to see the volumetric ratio of binder to aggregate which is lower than that of the overlying finishing plaster (1:3 as against 1:2).

All the layers are described in detail on the following pages.

1) Light-brown base plaster made of slaked lime and well-graded sand, principally comprising silicates (basically quartz) and to a lesser extent, fragments of alabastrine limestone.

Thickness: reaches a maximum of 1.25 mm.

Grain size: varies between the equivalent of very fine sand (0.10 mm) and coarse sand (0.85 mm).

Degree of uniformity of grain size: good.

Estimate of original volumetric ratio between binder and aggregate: 1:3.

Characteristics of the mix

Mortar made with slaked lime and well-graded sand principally comprising silicates and, to a lesser extent, fragments of alabastrine limestone. The latter appear as intermittent grains with an angular shape. The silicate components appear essentially as rounded grains of quartz, often with oxidized edges (of the desert varnish type) and solid inclusions.

The porosity of the mix is average (estimated to be in the region of 30%), determined essentially by the presence of cracks produced as the lime dried out.

Comments

The mix differs from that used for the overlying finishing plaster (sample 11B) in that it contains a greater proportion of sandy aggregate (a 'poorer' mortar).

The sandy aggregate used to make the mortar in the sample under examination is further distinguished by its darker color (a reddish tinge) caused by the presence of iron oxides (and possibly manganese too) within or on the edges of the grains of quartz.

No substantial differences are apparent between the base plaster (sample 11C under examination) and the overlying finishing plaster (11B) with regard to the composition of the sandy aggregate.

Sample PRO - 14

Origin of sample and its characteristics

Prothesis, vault, wall with Madonna and Saint, from the area above the point of the cross, from the edge of the large gap in the plaster layers.



Type of sample taken

The sample included the entire thickness of the base plaster and all the layers overlying it.

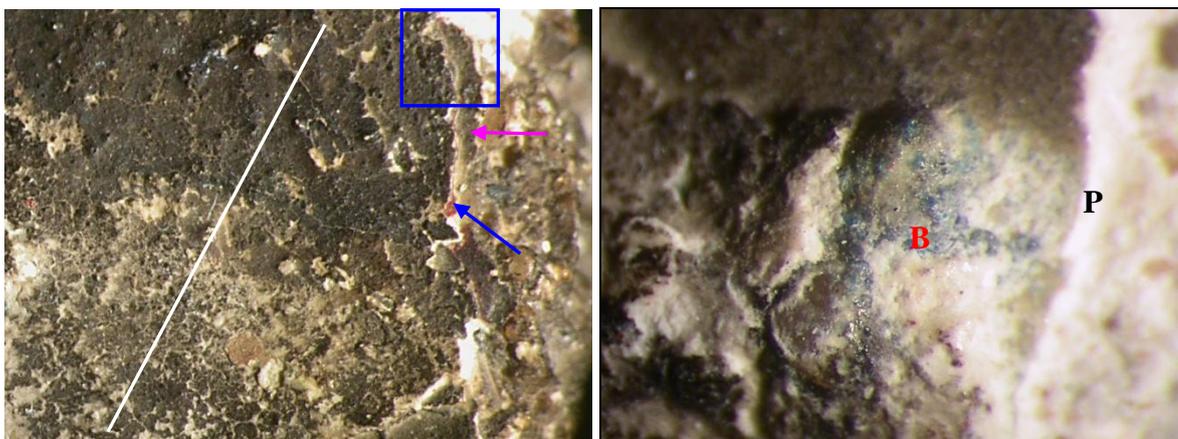
Type of analysis carried out

Micro-stratigraphic analysis on thin section supplemented by histo-chemical and micro-chemical tests.

Aims of the laboratory investigations

Analysis of the base plaster (on the basis of the model provided in UNI – Normal 12-83 documentation) and identification of the number, type and nature of the layers overlying it.

Preliminary examination under stereo-microscope



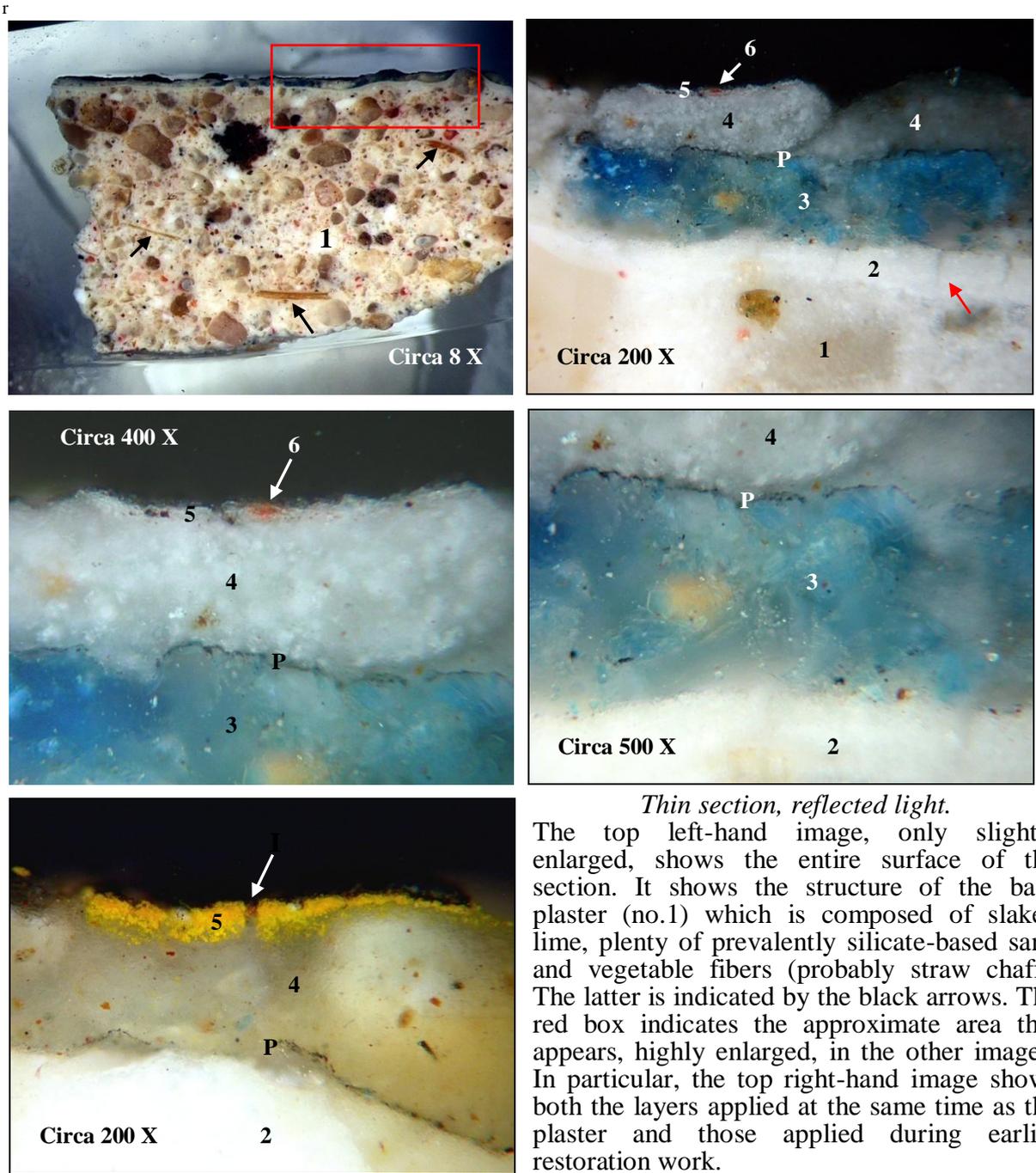
Stereo-microscope, reflected light, enlargement approximately 12 (sx) and 35 X respectively.

The left-hand image shows a portion of the surface of the sample fragment. Along the edge of the fragment there are traces of a red layer (blue arrow) that is in turn overlying a well-smoothed surface covered with blackish particulate matter (pink arrow). The right-hand

image shows an enlarged detail of the blue square visible in the previous image. The plaster is overlaid by a white layer (P) and a blue paint layer (B).

Micro-stratigraphic analysis of thin section supplemented by micro-chemical and histo-chemical tests

Analysis sheet drawn up in accordance with the directions contained in UNI- Normal 12/83 documentation.



Thin section, reflected light.

The top left-hand image, only slightly enlarged, shows the entire surface of the section. It shows the structure of the base plaster (no.1) which is composed of slaked lime, plenty of prevalently silicate-based sand and vegetable fibers (probably straw chaff). The latter is indicated by the black arrows. The red box indicates the approximate area that appears, highly enlarged, in the other images. In particular, the top right-hand image shows both the layers applied at the same time as the plaster and those applied during earlier restoration work.

A whitish, lime-based preparation (no. 2) affected by typical drying cracks (arrow), and a thick blue paint layer (no. 3) based on Egyptian Blue, probably dissolved in a protein-based binder, have been applied over the plaster. The paint layer, now very patchy and broken up, does not display within it the drying cracks encountered in the underlying preparation.

The sequence continues with a thin layer of particulate matter composed of lampblack (P) that separates the older layers from those applied during earlier restoration work. These comprise a thick ivory colored gypsum-based layer (no. 4) applied as a preparation; a thin and patchy whitish layer based on white lead (no.5) applied over the underlying preparation whilst it was

still wet (the pigment was possibly dissolved in a protein-based binder), and traces of a red, hematite-based layer (no. 6).

The other three images are greatly enlarged and show details of the outermost layers. The lower left-hand image, taken after the micro-chemical test to identify lead was carried out, shows the lead itself only within layer no. 5 comprising white lead.

All the layers are described in detail on the following pages.

1) Nut-brown plaster with dark dots made by mixing slaked lime, plenty of silicate-rich sand and vegetable fibers (probably straw chaff)

Thickness: in the range 6.5 to 7.2 mm. The sample included the entire thickness of the base plaster.

Grain size: The size of the grains of sand varies between the equivalent of coarse silt (0.05 mm) and very coarse sand (1.6 mm). The size of the vegetable fibers varies between 1.0 and 2.0 mm approximately.

Degree of uniformity of grain size: moderate.

Estimated volumetric ratio between the binder and the aggregate: 1:3.

Characteristics of the mix

Mortar made of slaked lime, plenty of sand rich in silicates (principally quartz) and a smaller proportion of alabastrine limestone.

The latter appears as intermittent grains which may have an angular or rounded shape.

In addition to rounded grains of quartz, sometimes distinguished by oxidized edges of the desert varnish type, the silicate components comprise stone fragments rich in opaque minerals that can be identified, at a rough guess, as iron and/or manganese oxides, grains of pseudomorphic chlorite and occasional crystals of ferro-magnesium-based minerals.

The porosity of the mix is average (estimated to be in the region of 30%), determined by the presence of microscopic cracks, produced by the drying out of the lime and uniformly distributed throughout the interior of the binder.

Comments

Although the surface of the plaster has been smoothed, it is slightly undulating rather than smooth and flat.

The plaster is similar to that taken from the triconch during the first mission (end of 2003) and at that time linked with the second phase of execution.

- *Type of contact between the layers:* clear-cut with good adhesion.

2) White, lime-based layer applied as preparation

Thickness: varies between 0.05 and 0.12 mm.

The layer is affected by several transverse cracks caused by the drying out of the lime (drying cracks). These cracks do not penetrate the overlying paint layer. This shows that the blue paint layer was applied after the hardening of the lime-based preparation.

- *Type of contact between the layers:* clear-cut with good adhesion.

3) Thick but patchy azure blue paint layer of Egyptian Blue, probably dissolved in an organic medium

Thickness: varies between 0.12 and 0.14 mm.

The layer has been reduced to traces, sometimes detached from the underlying preparation and incorporated within the following layer (no. 4), applied during the course of earlier restoration rework.

The blue pigment identified as Egyptian Blue is made up of azure blue particles distinguished by a glassy sheen, medium relief and a fibrous to prismatic habit. Some particles have a marked pleochroism from colorless to blue even under reflected light. Their dimensions generally vary between 0.04 and 0.1 mm. They are often aggregated to form slightly larger masses. The masses and particles of pigment are resistant to cold HCl attack.

In addition to the Egyptian Blue, the paint layer also incorporates a few minute particles of carbon, ochre and even rarer whitish masses that may be gypsum used to modulate the color of the layer.

The paint layer is virtually free of carbonates (and therefore of carbonated lime), giving rise to the hypothesis that the *a secco* technique was employed, using an organic binder. On the other hand, all the histo-chemical tests carried out have produced negative results (possibly owing to the mineralization into oxalates of the lime in the organic binder).

- *Type of contact between the layers:* clear-cut, distinguished by a continuous blackish layer composed of minute carbon particles deposited on the surface over time (layer of particulate matter based on lamp black). Where the blue layer is patchy, the blackish layer separates layers nos. 2 and 4.

4) Thick ivory-colored gypsum-based layer applied as a preparation

Thickness: varies between 0.15 and 0.25 mm.

The layer also contains lime carbonate (calcite) diffused within the mass. The calcite could be derived directly from the raw material (gypsum or selenite) used to produce the hemihydrated gypsum (hemihydrated lime sulphate) used in the layer. Gypsum may also contain calcite and other compounds in addition to bihydrated lime sulphate. Therefore, if gypsum is not properly refined before burning, it is possible that the final product may contain a certain percentage of calcite.

Theoretically, the calcite could also derive from the use of a bastard mortar made of lime and gypsum or from the addition of spent lime as an inert.

Particles of pigments of various types can also be seen within the layer (Egyptian Blue, minium, litargirium and ochre). These have become detached from the underlying paint layers and incorporated in the preparation whilst the layer was being applied. The layer also contains lampblack.

Out of all the histo-chemical tests, only the fuchsine test produced a result allowing speculation about the presence of animal glue or gelatine within the layer.

- *Type of contact between the layers*: clear-cut distinguished by a continuous blackish layer.

5) Thin and patchy whitish layer based on white lead, applied to the underlying preparation whilst it was still wet. The pigment may have been dissolved in a protein-based binder.

Thickness: in the region of 0.01 to 0.015 mm.

The various histo-chemical tests carried out produced negative or inconclusive results. Only the fuchsine test, particularly useful in identifying animal glue or gelatine gave a color result which may be considered positive. However, the possible presence within the paint layer of a glue-based protective agent applied during maintenance work cannot be excluded.

The relationship of the paint layer to the underlying preparation suggests furthermore that the two layers were applied in rapid succession, fresco on fresco. In fact, several grains of lapis lazuli have run into the interior of the preparation.

One of the hypotheses to be evaluated with regard to the painting technique is the possibility that the paintings were executed on the gypsum preparation whilst it was still wet, using the gypsum itself as a binder. This technique, known as false fresco, is documented in the wall paintings of 14th- to 16th-century Spanish churches.

The layer also contains a few purplish black granules that are probably a lead pigment such as minium, blackened by chemical alteration.

The function of the layer could be similar to that of the priming layers used in painting on canvas and panel during the 14th to 16th centuries.

- *Type of contact between the layers*: poorly defined with good adhesion.

6) Traces of a red layer with a hematite (Fe₂O₃) base

Thickness: 0.005 mm.

The slight traces remaining make it impossible to conjecture about the technique used to apply the layer. However, like the layer below and those in the other samples analyzed, we assume the technique involved tempera and the use of protein-based binders.

Appendix

Images showing locations from which samples were taken

3.1 Church perimeter walls

3.1.1 *Painted plaster on the interior walls of the church*



Sample E-1.



Sample E-2.



Sample E-3.



Sample E-4.



Sample E-5.



Sample E-6.



Sample E-7.



Sample E-8.



Sample E-9.



Sample E-10.



Sample E-11.



Sample E-12.



Samples E-13A and E-13B.



Sample E-14.



Sample E-15.



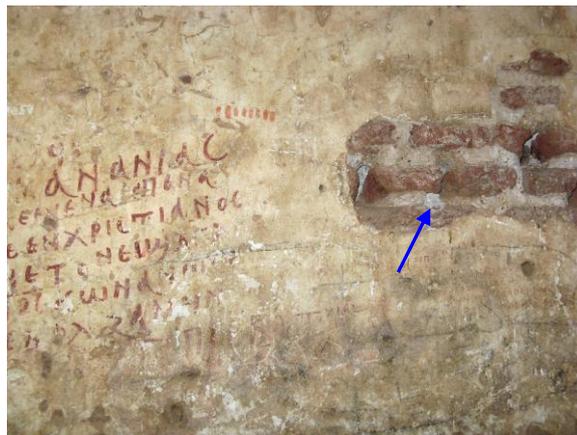
Sample E-16.



Sample E-17.



Sample E-18.



Sample E-19.



Sample E-20.



Sample E-21.

3.1.2 Doorway in the north west facade – finishing layers



Samples E-PO – 1A, 1B and 1C.



Sample E-PO – 2.



Sample E-PO – 3.



Sample E-PO – 4.

3.1.3 *External walls (south east and south west sides)*



Sample SE/SW – 1.



Sample SE/SW – 2.



Sample SE/SW – 3.



Sample SW/SE – 4.



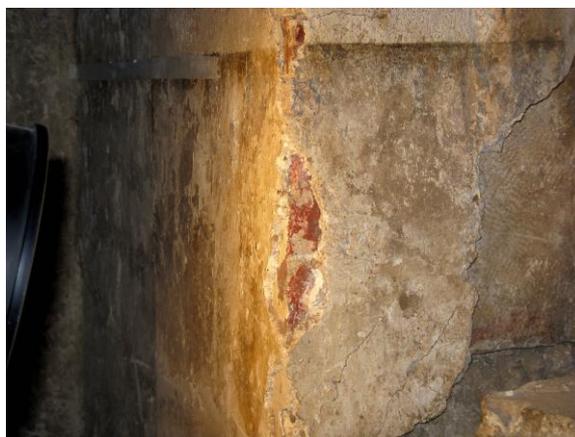
Sample SW/SE – 5.



Sample SW/SE – 6.

3.2 Interior of the church

3.2.1 *Facade*



ICO - 1.



ICO - 2.



ICO - 3.



ICO - 4.



ICO - 5.

3.2.2 North west wall, area surrounding the painting of the medieval knight on horseback



CAV - 1.

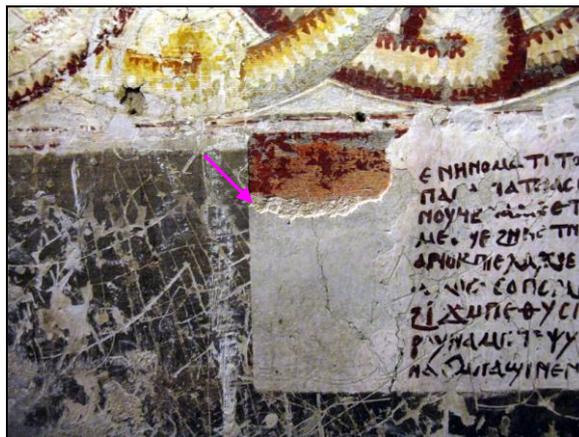


CAV - 2.

3.2.3 Prothesis – North Corridor



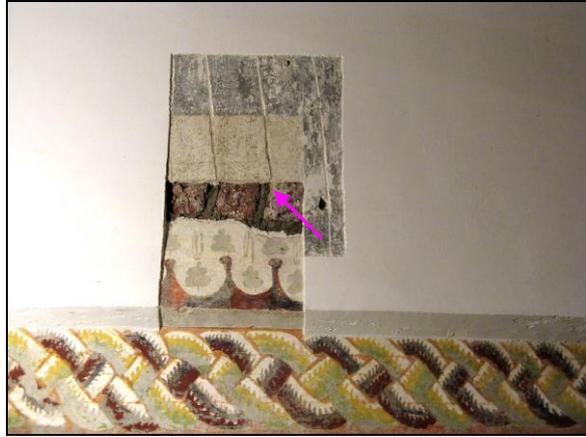
CN-A.



CN-B.



CN-C.



CN-D.



CN-E.



CN-G.



CN-H.



PRO-6.



PRO-7.



PRO-15.