GELATI MONASTERY (GEORGIA)
CHURCH OF THE NATIVITY
OF THE HOLY VIRGIN (1106 AD)

SCIENTIFIC INVESTIGATION
ON THE MURAL PAINTINGS
- PART II -

November 23th, 2022

CUSTOMER:

ASSOCIATION

GIOVANNI SECCO SUARDO

via Mazzini, 13

24050 Lurano (BG)

Report by

Dr. Geol. Davide Melica

Collaborators:

Dr. Manuel Jardón Cabezas

Dr. Llucia Bosch Rubio

1. INTRODUCTION

Upon the request of ASSOCIATION GIOVANNI SECCO SUARDO, a preliminary scientific investigation was carried out prior to restoration works of the mural paintings of the *Church of the Nativity of the Holy Virgin* in the Unesco World Heritage Site of *Gelati Monastery* (Georgia). This technical report is in addition to the previous one dated July 2021.

Despite the limitations of the analytical techniques employed, the aims of this study are:

- o to characterise the pictorial layers and to identify the executive technique of the paintings through the examinations of stratigraphic sequences and identification of pigments and binders;
- o to distinguish the original layers from possible overpaints;
- o to identify the decay products.

2. SAMPLE LIST AND PHOTOGRAPHIC DOCUMENTATION
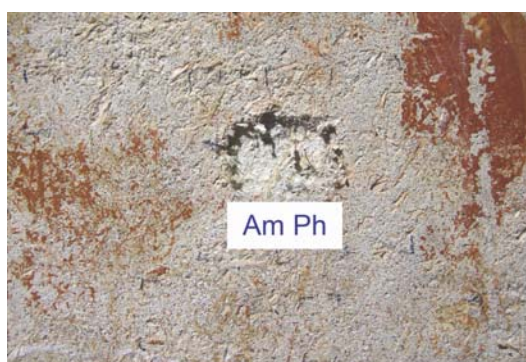
Samples are described in the following tables:

West arm

Code	Sample type	Sampling zone	Adopted analisys
UT	fragment of untreated plaster		
Am-Ox	fragment of plaster treated with Ammonium Oxalate	west arm, southern wall	OM-RL, micro-Raman, SEM-EDS
Am-Ph	fragment of plaster treated with Di-Ammonium Phosphate		
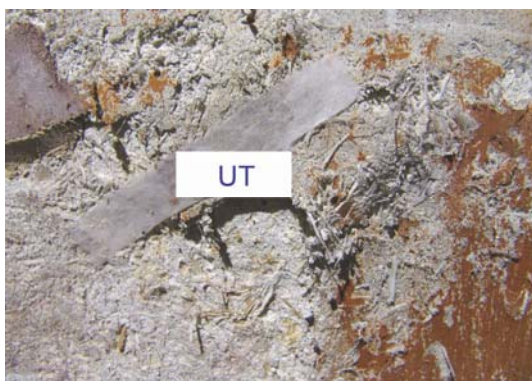
UT sampling point

Am-Ox sampling point

Am-Ph sampling point

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

Peeling test: untreated area

Peeling: treated area with Ammonium Phosphate

Peeling test: treated area with Ammonium Oxalate

West arm

Code	Sample type	Sampling zone	Adopted analisys
A1	gray pictorial fragment	west arm, western side (uncleaned zone)	ST, OM-RL, HT
A2	pale-yellow pictorial fragment with shiny appearance	west arm, northern side	ST, FT-IR
A3	gray pictorial fragment	west arm, western side (cleaned zone)	ST, OM-RL, HT
A4	red pictorial fragment with shiny appearance	west arm, northern side (uncleaned zone)	ST, FT-IR
A5	red pictorial fragment	west arm, northern side (cleaned zone)	ST, FT-IR

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

2

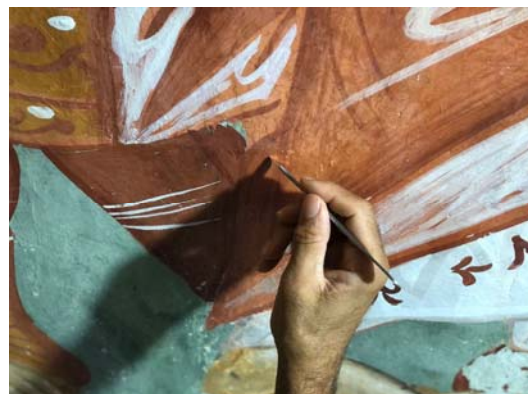| Code	Sample type	Sampling zone	Adopted analisys
31	blue pictorial fragment	west arm, western side, background	ST, XRF, OM-RL, HT
32	electric blue pictorial fragment	west arm, western side, background	ST, XRF, OM-RL, HT, FT-IR
33	gray pictorial fragment	west arm, western side	ST, OM-RL, HT
34	salt efflorescences	west arm, western side	FT-IR
35	blue pictorial fragment	west arm, southern side, left register, Saint's cloak	ST, XRF, OM-RL, HT, OM-TL, FT-IR
36	green pictorial fragment	west arm, southern side, left register	ST, OM-RL, HT
38	blue pictorial layer fragment	west arm, northern side, right register	ST, XRF, OM-RL, HT, FT-IR
39	blue pictorial fragment	west arm, vault, background of the cross	ST, XRF, OM-RL, HT
40	fibers	west arm, northern side	OM-TL
41	red pictorial fragment with shiny appearance	west arm, northern side, right register	ST, OM-RL, HT, FT-IR
42	white pictorial fragment	west arm, northern side, left register	ST, OM-RL, HT
43	grey pictorial fragment with shiny appearance	west arm, southern side, left register	ST, OM-RL, HT, FT-IR

A1 sampling point

A2 sampling point

A3 sampling point

A4 sampling point

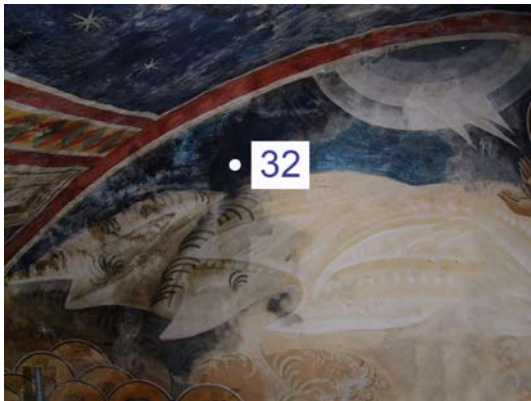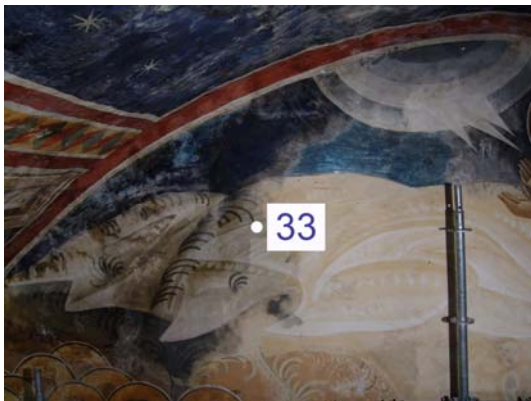Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

3

A5 sampling point

31 sampling point

32 sampling point

33 sampling point

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

4

34 sampling point
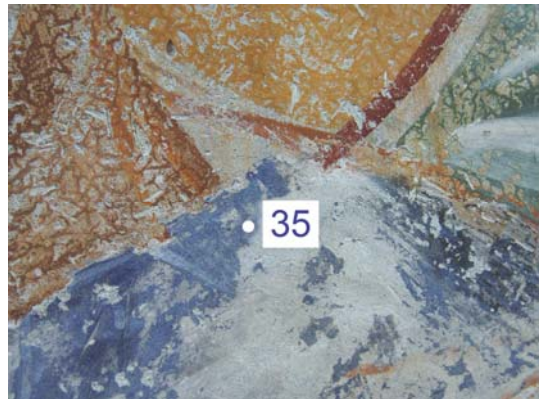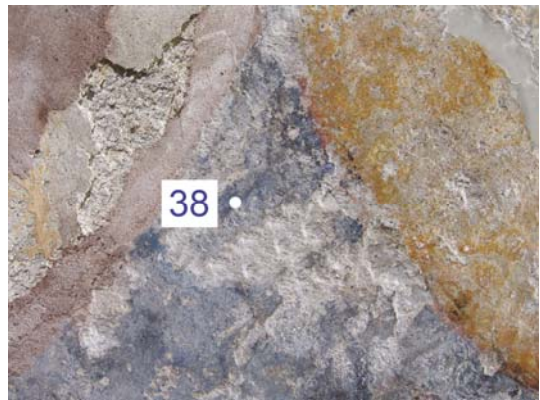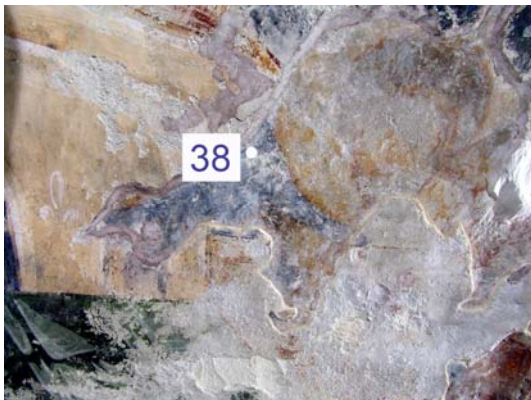

35 sampling point

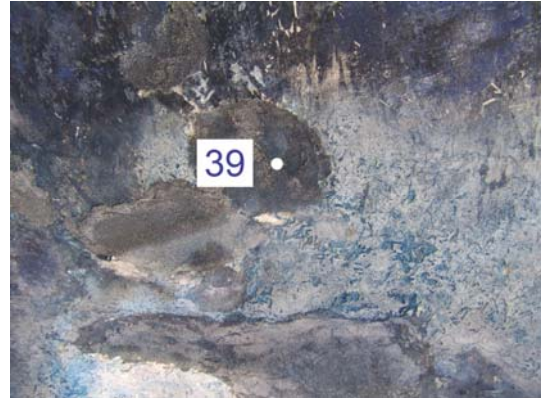36 sampling point

38 sampling point

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

5

39 sampling point

40 sampling point

41 sampling point
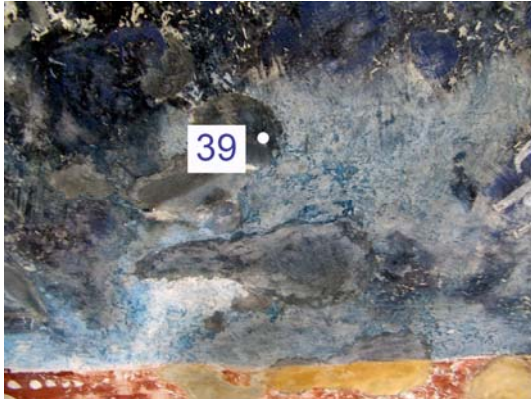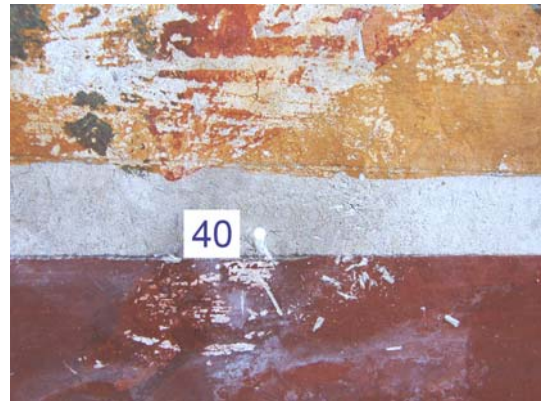

42 sampling point

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

6
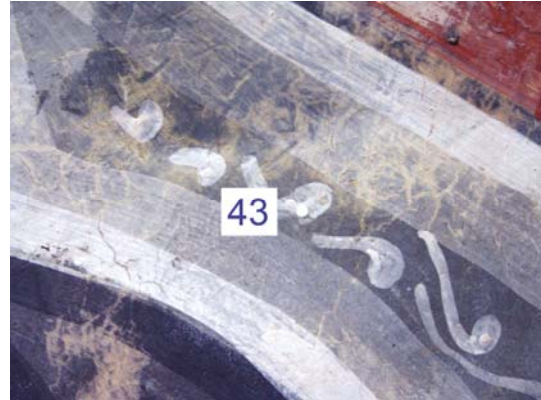
43 sampling point

West arm

Code	Sample type	Sampling zone	Adopted analisys
M1	fragment of white restoration mortar	west arm, southern side	
M2		west arm, southern side	
M3	fragment of reddish restoration mortar	west arm, northern side	
M4		west arm, northern side	
M5		west arm, vault	ST, OM-TL
M6	fragment of white restoration mortar		
M7	fragment of gray restoration mortar	west arm, vault	
M8	fragment of white restoration mortar		

M1 sampling point

M2 sampling point

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

7

M3 sampling point

M4 sampling point

M5, M8 sampling point

M6, M7 sampling point

North arm

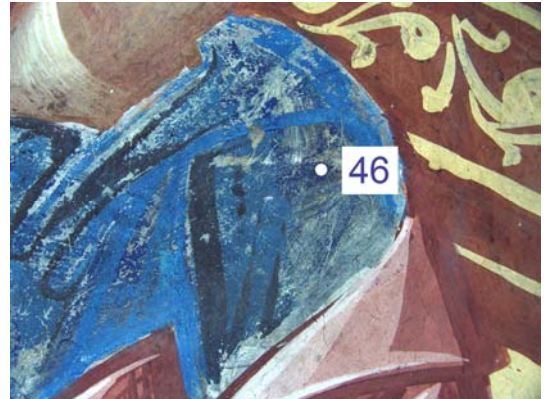| Code	Sample type	Sampling zone	Adopted analisys
44	green pictorial fragment	north arm, background of the vault	ST, OM-RL, HT, FT-IR
45	blue pictorial fragment	north arm, background of the vault	ST, OM-RL, HT, FT-IR
46	blue pictorial fragment	north arm, northern side, Apostle's cloak on right side	ST, XRF, OM-RL, HT, FT-IR
48	brown pictorial fragment	north arm, northern side, middle Apostle's hand	ST, XRF, OM-RL, HT

44 sampling point
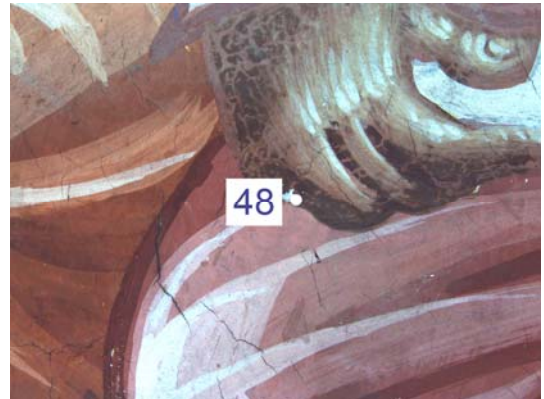
Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

8
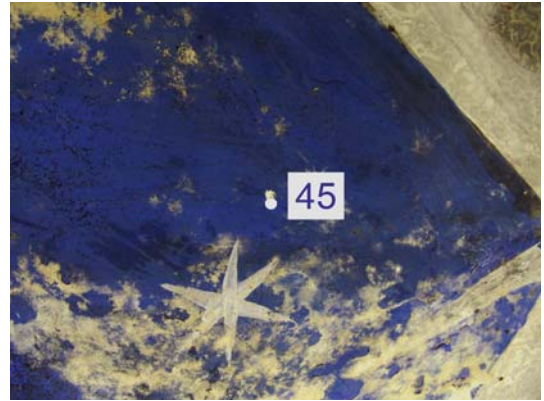
45 sampling point

46 sampling point

48 sampling point

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

9

3. ANALYTICAL TECHNIQUES

The adopted techniques are briefly described below:

- **peeling test (Peel)**: to assess on site the degree of surface cohesion of stone materials. A strip of adhesive paper, having known dimensions and weight, is pressed onto the surface; after detaching it, it is weighed again with an analytical balance; the difference in weight corresponds to the weight of the material that adhered to it after its detachment. This value is indicative of the degree of cohesion of the material;

- **optical stereoscopic microscopy (ST)**: to verify the representativity of the sample and to provide a descriptions of its superficial morphology (stereomicroscope *Zetaline* model, 60X max);

- **optical microscopy with polarized reflected light (OM-RL)**: sample is embedded in polyester resin block, which is grounded and polished to reveal a perpendicular section to the layer structure; this cross-section is observed under the optical polarizing microscope (Olympus, *BX51* model, maximum magnification 400X) in white and ultraviolet reflected light, in order to define the nature, the thickness and the sequence of the layers (*Normal 14/83*);

- **optical microscopy with transmitted light (OM-TL)**: the sample is embedded in polyester resin and then glued to a glass-slide to prepare a thin section to be examined using a polarizing microscope (*Olympus, BX51* model). The optical and morphological properties of the phases present are used to identify the mineral constituents of plasters, mortars and stones and their structural and textural features, including primary and secondary calcite, gypsum and any other recognizable substances. Thin sections are described according to UNI 11176 "Cultural Heritage - Petrographic descrizione of a mortar"). Thin sections are prepared according to italian standard method NORMAL 14/83 "Sezioni sottili e lucide di materiali lapidei. Tecnica di allestimento";

- **histochemical tests on cross-section (HT)**: specific tests using Black Starch (AB I, AB II), Acid Fucsin, Red Oil and Lugol, are used to define the class of possible natural organic compounds (protein, lipid or polysaccharide) contained in the paint layers (*Dimos I, modulo 3, 1978*);

- **infrared spectroscopy (FT-IR)**: this technique allows to recognize the natural and synthetic organic compounds and the inorganic compounds referable to constitutive or degradation materials. Spectrum are acquired by means of a Perkin Elmer spectrometer *Spectrum Two* model, in ATR mode (Attenuated Total Reflection), in the range 4000-400 cm^{-1}, with a 4 cm^{-1} resolution.
  Limits of the technique:
  - it is not possible to identify the sulphides, many of the oxides and the carbon based pigments of vegetable origin;
  - it is possible to determine the group to which the organic compounds belong (lipid, protein or polysaccharide), but not the specific compound (e.g. linseed oil, nut oil, etc.);
  - the compounds present in traces or whose signal is covered by other substances present in relevant quantities are not identified.

- **micro-Raman spectroscopy** using a Renishaw Raman Invia spectrometer interfaced to a Leica DMLM microscope (obj. 5x, 20x, 50x). Exciting source: Ar+ laser (514.5 nm). The system is

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

10

equipped with filters to eliminate excitating monochromatic radiation (edge filters), monochromators (1800 lines/mm, 1200 lines/mm), CCD detector. Operating conditions: numbers of accumulations 4, accumulation time 15 s, P_{out} 1.5 mW (5%), spectral range: 685-1585 cm^{-1} (static mode);

- **scanning electron microscopy (SEM) coupled to energy dispersive chemical elemental analysis (EDS)**, aimed at determining the penetration of the tested consolidation products. The observations were carried out with a Philips XL30 microscope, under vacuum (100 Pa), coupled to a Brucker EDS spectrometer. The parameters used were: Voltage: 25 kV, Filament current (W): 100 µA, Acquisition time: 30s. The images attached to this report were obtained in SEM-BSE mode (secondary electrons). Sample 43 was metallised with gold;

- **X-Rays fluorescence spectroscopy (XRF)**: this analysis provides the elemental composition of the paint layer. It is performed on the sample using a Bruker S1 Titan 800 device composed of an X-ray generator with an air-cooled Rhodium anode and a silicon detector (SDD) with Peltier cooling; the instrument allows the detection of elements from Magnesium (Z=12) to Uranium (Z=92). The device consists of a rhodium (Rh) anode X-ray tube, 6-50 kV, which provides an X-ray beam with a diameter of approximately 5 mm, and a CubeTM SDD detector with associated electronics. A microcamera to visualise the positioning of the incident beam on the sample is also included. The irradiation conditions were 15 kV, 45 µA with an acquisition time of 60 seconds.

  Límits of the technique:

  o elements with atomic numbers lower than Magnesium are not revealed (Z≤12), because they have very low fluorescence energies; therefore, it is not possible to identify all organic compounds (e.g. carbon blacks, lakes, indigo);

  o results obtained are purely qualitative because there are no valid reference standards to perform quantitative analyses on paint materials;

  o it is not possible to discriminate between the different paint layers, because of the penetration capacity of X-rays; the results obtained often refer to a thickness greater than that of the superficial paint layer;

  o it is not possible to directly determine the compounds to which the revealed chemical elements belong; these are identified interpreting possible associations and taking into account the colour of the sample or the colour of the surface being analysed.

REMARKS:

Results are reported in detail in the attached analytical sheets and they only refer to the samples examined.

The description of the layers starts from the outermost one.

The thicknesses and the micrometric determinations are expressed in millimetres or in microns (µm, 1 µm = 0.001 mm).

It should be noted that the colours of the paint layers reproduced in the microphotographs may differ from those perceived by the direct observation of the painted surfaces due to the color of their components (binders, pigments, mineral fillers) under the microscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

11

4. LIST OF ANALYSIS

Code	Peel.	Raman	SEM-EDS	XRF	ST	MO-RL	HT	MO-TL	FT-IR
					Type of analysis				
UT	X	X	X			X			
Am-Ox	X	X	X			X			
Am-Ph	X	X	X			X			
A1					X				
A2					X	X	X		
A3					X				
A4					X	X	X		
A5					X	X	X		
31				X	X	X	X		
32				X	X	X	X		X
33					X	X	X		
34									X
35				X	X	X	X		X
36					X	X	X		
38				X	X	X	X		X
39				X	X	X	X		
40								X	
41					X	X	X		X
42					X	X	X		
43		X			X	X	X		X
44					X	X	X		X
45				X	X	X	X		X
46				X	X	X	X		X
48					X	X	X		X
M1					X			X	
M2					X			X	
M3					X			X	
M4					X			X	
M5					X			X	
M6					X			X	
M7					X			X	
M8					X			X	
total	3	3	4	7	27	20	17	9	10

Legend:

Peel: peeling test
Raman: micro-Raman
SEM-EDS: scanning elecron microscopy
ST: stereoscopic microscopy

XRF: X-Ray Fluorescence
MO-RL: optical microscopy on cross-sections
HT: histochemical test
MO-TL: optical microscopy on thin sections

FT-IR: infrared spectroscopy

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

12

5. RESULTS

Based on the analytical results, the following can be established:

5.1. Consolidation treatments of the plaster

The efficacy of two consolidation treatments, respectively with *Di-Ammonium Phosphate (DAP)* and with *Ammonium Oxalate (Am-Ox)*, was evaluated by means of on-site peeling tests (Scotch Tape tests) and by means of molecular (Raman) and elemental (SEM-EDS) laboratory chemical analyses; the latter were conducted on plaster samples with a maximum thickness of 4 mm approximately.

The peeling tests, which allow an evaluation of the degree of superficial cohesion of the plaster, gave satisfactory results for both treatments; in fact, the weight of the treated material adhering to the strip was almost halved compared to that of the untreated material. Results obtained, expressed as weight (W) of material pasted on the scotch tape, are listed in the following table:

Area	W (gr.)
untreated	0,044
treated with Di-Ammonium Phosphate	0.025
treated with Ammonium Oxalate	0.028

Laboratory analyses, aimed to assess the distribution of the newly-formed compounds (calcium phosphates and calcium oxalates respectively) formed after the application of the products, yielded the following results:

- the untreated plaster is free of oxalates and phosphates, but contains gypsum, presumably of new formation, heterogeneously distributed; in some places this compound is present in traces while in others it is concentrated on the surface or within the plaster;

- the newly-formed calcium oxalate is found in the bi-hydrated form (weddellite) up to a maximum depth of 60-80 µm; the efficacy of the treatment must therefore be defined as "cortical", as already demonstrated by numerous literature data;

- regarding the presence and distribution of the newly-formed phosphates, it should be noted that the results of the micro-Raman analyses were not exhaustive; in fact, a secondary signal (1050 cm^{-1}) of two different calcium phosphates (hydroxyapatite and anhydrous calcium phosphate) was identified at all depths of the sample, but not their main signal (955-960 cm^{-1}). On the other hand, EDS analyses ascertained the presence of Phosphorus with a heterogeneous distribution; in some areas of the sample, this element is concentrated at the surface while in others it appears to be present throughout the thickness of the plaster and also associated with Magnesium.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

13

5.2. Paint layers

On the basis of the analytical results, it is believed that the technique used in the making of painting layers is that of lime-painting, also known as _mezzo fresco_ painting. Some of these layers (samples **35**, **38**, **43**, **44**) contain hydromagnesite, so it is possible that magnesium lime was used as a binder in their execution.

In addition to the composition of the binder (calcite), the executive technique was defined by the microscopic appearance of the interface between the plaster and the first paint layer, which is always quite clear, without the typical interpenetration of the _fresco_ technique. The carbonatated pictorial layer, even though it englobes the pigments, appears in fact differentiated from the underlying plaster, as it was applied subsequently to it.

The lime-painting technique foresees that the pigments, thinned in lime milk, are applied on the plaster when it reaches an advanced stage of drying and superficial carbonation; at the moment of the application of the colour the support could be wet in order to favour its adhesion. Compared to the _fresco_ technique, it involves a considerable saving of time, as it allows to work on much larger portions of plaster, retaining the same characteristic beauty but with less brightness of colours.

The ubiquitary presence of calcium and/or magnesium oxalates, strengthens the hypothesis that the lime binder was originally mixed with a natural organic additive, probably of lipidic nature, which is no longer identifiable as it is now almost completely mineralised.

A list of the pigments identified is summarised in the following table:

color	sample	location	pigments
blue	**31**	west arm, western side, background	Cobalt Chromite Blue or Cobalt Blu Spectral
	32		Smalt (on black background)
	35	west arm, southern side, left register, Saint's cloak	Smalt (on gray background)
	38	west arm, northern side, right register	Natural Ultramarine Blue (on gray background)
	39	west arm, vault, background of the cross	Cobalt Chromite Blue or Cobalt Blu Spectral (on black background)
	45	north arm, background of the vault	Artificial Ultramarine Blue
	46	north arm, northern side, Apostle's cloak	Azurite, Smalt
gray	**A1**	west arm, western side (uncleaned zone)	Carbon Black, Yellow Ochre
whitish/ pale gray	**33**	west arm, western side	3 superimposed layers of Carbon Black and Yellow Ochre in differents concentrations
	A3	west arm, western side (cleaned zone)	3 superimposed layers of Carbon Black and Yellow Ochre in differents concentrations

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

14

color	sample	location	pigments
white	42	west arm, northern side, left register	lime (on Yellow Ochre)
white	43	west arm, southern side, left register	lime (on whitish background conteining scarce Carbon Black and Yellow Ochre)
green	36	west arm, southern side, left register	Green Earth
green	44	north arm, background of the vault	Green Earth (on black background)
red	41	west arm, northern side, right register	Red Ochre
brown	48	north arm, northern side, middle Apostle's hand	Yellow Ochre, Red Ochre, Carbon Black, (Bone Black?)

Insight into the blue tone represented by the samples 31 and 39 (blue shade)

XRF analysis performed on the blue layer led to the identification of Cobalt, Chromium and traces of Zinc. The co-presence of Chromium and Zinc identifies one of the pigments with a modified chemical formula well-known from late 1960s, such as cobalt green and chromium aluminium cobalt oxide (e.g. chromium aluminium cobalt oxide greenish-blue $CoO*2Al_2O_3*Cr_2O_3*ZnO$) which represents a valuable temporal marker in the examination of paintings.

However, it could also be *Cobalt Chromite Blue* [$Co(Al,Cr)_2O_4$], a pigment currently marketed by Kremer (product code Z-C0040, colour index PB36) or *Cobalt Blu Spectral* ($Co_2SiO_4*Zn_2SiO_4$), according to a study by S. Pisareva, a pigment synthesized in 1956 and introduced in the soviet market as an oil painting pigment for the first time in 1961. In the latter case it is a cobalt-doped willemite mineral (Zn_2SiO_4 - zinc silicate which is normally white), in which one zinc atom is substituted by cobalt, responsible for the characteristic blue color, in order to minimize the use of toxic cobalt and the production costs.

5.3. Fibres

In addition to straw, the plaster on the north side of the west arm contains fibres (sample **40**) of animal origin, classified as wool, and others of plant origin probably attributable to hemp; however, the correct identification of these latter requires further analysis. Wool is obtained from the fleece of sheeps.

5.4. Decay products

Calcium (weddellite, $CaC_2O_4*2H_2O$) and/or magnesium oxalates (glunshinskite, $MgC_2O_4*2H_2O$) have been found in many paint film samples. Salts efflorescence removed from the western side of the west arm (sample **34**) are composed of potassium nitrate (KNO_3).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

15

5.5. Products applied in previous interventions

5.5.1. Synthetic resins

Pictorial fragments collected from the west arm and characterised by a glossy appearance (samples **A2**, **A4**) present a surface film consisting of <u>acrylic resin</u>, most probably referable to a poly-ethyl acrylate. In an area that has already been cleaned with acetone (sample **A5**) this compound is found in very small quantities, demonstrating the effectiveness of this procedure.

5.5.2. Mortars

Most of the samples analysed consisted of carbonated aerial lime and pozzolan, an aggregate of pyroclastic volcanic origin that gives the mortar a hydraulic character and mechanical strengths superior to those of common aerial mortars.

Two gypsum mortars without aggregate were also recognised.

The compositional and textural features of the restoration mortars, obtained from the petrographic examination, are summarised in the following table:

sample code	sampling zone	Binder (B)	Aggregate (A)	grain size (mm)	B:A ratio (by volume)
M1	west arm	gypsum and anidride	-	-	-
M6	west arm	gypsum		-	
M2 **M3**	west arm	air-hardening lime	65% pozzolan 35%fluvial sand	0.03-0.8 main 0.2-0.4	1:3
M4 outer	west arm	air-hardening lime	55% pozzolan 45% limestone crushed sand	0.03-0.68 main 0.125-0.25	1:3
M4 inner			65% pozzolan 35%fluvial sand	0.03-0.8 main 0.2-0.4	1:3
M5 **M8**	west arm	air-hardening lime	pozzolan	0.03-1 main 0.15-0.35	1:3.5
M7	west arm	air-hardening lime	fluvial sand	0.03-1 main 0.1-0.25	1:3

November 23th, 2022

Report by

Dr. Davide Melica

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

16

References

AA.VV., 1995: *La fabbrica dei colori. Pigmenti e coloranti nella pittura e nella tintoria,* Il Bagatto editore;

Arnold A., Zender K. 1988: *Decay on stony materials by salts in humid atmosphere.* Proceedings of the VI International Congress on Deterioration and Conservation of Stone. Torun;

Ashok R. (Ed.), 1993: *Artists' pigments. A handbook of their history and characteristics*, vol. 2 National Gallery of Art, Oxford University Press, Washington, New York;

Berrie B. H., 2007: *Artist's Pigments. A handbook of their history and characteristics*, vol. 4, National Gallery of Art, Washington, Archetype Pubblications, London;

Derrick M., Stulik D., Landry J.M., 1999: *Infrared Spectroscopy in Conservation Science*, The Getty Conservation Institute;

Feller R. L. (Ed.), 1986: *Artists 'pigments. A handbook of their history and characteristics*, vol. I National Gallery of Art, Oxford University Press, Washington, New York;

Folk, R.L.,1965: *Some aspects of recrystallization in ancient limestones.* In: Pray, L.C. and Murray, R.C., Eds.: *Dolomitization and Limestone Diagenesis*, Vol. 13, Society for Sedimentary Geology, Special Publications,

Franzoni E., Sassoni E., Graziani G., 2015: *Brushing, poultice or immersion? Role of the application technique on the performance of a novel hydroxyapatite-based consolidating treatment for limestone.* Journal of Cultural Heritage, 16 173–184;

Gettens R. J., Stout G. L, 1966: *Painting Materials, A Short Encyclopedia.* Dover Publications, New York;

Graziani G., Sassoni E., Franzoni E., 2015: *Consolidation of porous carbonate stones by an innovative phosphate treatment: mechanical strengthening and physical-microstructural compatibility in comparison with TEOS-based treatments.* Heritage Science. Research Article, Open access;

Kadikova I., Pisareva S., Grigorieva I., Lukashova M., 2020: *Conservation of Modern Oil Paintings.* Springer;

Lalli C., 1999: *Analisi stratigrafiche su campioni in sezioni lucide e sezioni sottili.* In OPD Restauro, n. 11, Firenze;

Martin-Gil J., Ramos-Sanchez M. C., Martin-Gil F. J., 1999: *Ancient pastes for stone protection against environmental agents.* In: Studies in Conservation, 44;

Matteini M., Moles A., 2002: *La chimica nel restauro*, Nardini Editore, Firenze;

Matteini M., Rescic S., Fratini F., Botticelli G., 2011: *Ammonium phosphates as consolidating agents for carbonatic stone materials used in architecture and cultural heritage: preliminary research.* International Journal of Architectural Heritage, 5: 717–736, 2011;

Matteini M., Colombo C., Botticelli G., Casati M., Conti C., Negrotti R., Possenti E.; Realini M., 2013: *Ammonium phosphates to consolidate carbonatic stone materials: an inorganic-mineral treatment greatly promising.* Built Heritage 2013 Monitoring Conservation Management;

Meilunas, R.J., Bentsen, J.G., Steinberg, A., 1990: *Analysis of aged paint binders by FTIR spectroscopy. Studies in Conservation 35;*

Newman R., 1979: *Some applications of infrared spectroscopy in the examination of painting materials*, JAIC vol. 19, number 1, article 6;

Pinna, D., Galeotti, M., Mazzeo, R. (Eds.), 2009: *Scientific examination for the Investigation of Paintings. A Handbook for Conservator-restorers.* Centro Di, Firenze;

Piovesan R., Mazzoli C., Maritan L., Cornale P., 2012: *Fresco and lime-paint: an experimental study and objective criteria for distinguishing between these painting techniques.* In Archaeometry 54, 4, pp. 723-736;

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

17

Pisareva S., 2005: *A note on Cobalt Specral.* In Studies in Conservation, 50 (3), pp.190-192;

Rampazzi L., Corti C., 2019: *Are commercial pigments reliable references for the analysis of paintings? In* International Journal of Conservation Science, Alexandru Ioan Cuza University Publishing House;

Realini M., Toniolo L., 1996: Proceedings of the *International Symposium on the oxalate films in the conservation of works of art.* Editeam, Bologna;

Sassoni E., Graziani G., Franzoni E., 2015: *Repair of sugaring marble by ammonium phosphate: Comparison with ethyl silicate and ammonium oxalate and pilot application to historic artifact. In* Materials and Design 88, pp. 1145–1157, Elsevier;

Seccaroni C., Moioli P., 2004: *Fluorescenza X, Prontuario per l'analisi XRF portatile applicata a superfici policrome.* Nardini Editore, Firenze;

Tiano P., Pardini C. (a cura di), 2005: *Le patine: genesi, significato, conservazione.* Nardini Editore, Firenze;

West FitzHugh, E. (Ed), 1997: *Artists' pigments. A handbook of their history and characteristics*, Vol. 3, National Gallery of Art Washington, Oxford University Press, New York, Oxford University Press.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

18

SAMPLE SHEETS

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

19

![Consulenza e Diagnostica per il Restauro e la Conservazione logo]

ON-SITE EVALUATION OF THE EFFECTIVENESS OF CONSOLIDATION TREATMENTS BY MEANS OF PEELING TESTS

Results obtained in the **Untreated Area**			
Code	W_i (gr)	W_f (gr)	ΔW (gr)
1	0,772	0,783	0,011
2	0,760	0,789	0,029
3	0,775	0,786	0,011
4	0,774	0,777	0,003
5	0,779	0,826	0,047
6	0,800	0,805	0,006
7	0,785	0,811	0,026
22	0,792	0,862	0,070
23	0,800	0,909	0,110
24	0,781	0,817	0,036
25	0,787	0,800	0,014
26	0,927	0,983	0,056
27	0,948	0,961	0,012
28	0,954	1,012	0,058
		average	**0,044 gr**

Results obtained in the area treated with **Ammonium Phosphate**			
Code	W_i (gr)	W_f (gr)	ΔW (gr)
8	0,805	0,822	0,017
9	0,809	0,822	0,013
10	0,806	0,842	0,037
11	0,806	0,830	0,024
12	0,790	0,804	0,015
13	0,787	0,798	0,011
14	0,804	0,813	0,009
29	0,951	0,952	0,001
30	0,938	0,951	0,014
31	0,941	0,950	0,009
32	0,954	0,974	0,020
33	0,955	0,972	0,018
34	0,945	0,946	0,001
35	0,919	0,952	0,033
		average	**0.025 gr**

Results obtained in the area treated with **Ammonium Oxalate**			
Code	W_i (gr)	W_f (gr)	ΔW (gr)
15	0,782	0,785	0,004
16	0,802	0,806	0,005
17	0,806	0,824	0,018
18	0,800	0,813	0,013
19	0,796	0,807	0,012
20	0,774	0,820	0,046
21	0,792	0,807	0,015
36	0,946	0,976	0,030
37	0,962	0,987	0,025
38	0,930	0,972	0,042
39	0,942	0,965	0,023
40	0,923	0,932	0,008
41	0,922	0,947	0,025
42	0,970	0,980	0,010
		average	**0.028 gr**

W_i= initial weight of the scotch tape;

W_f= final weight of the scotch tape after removal from the plaster;

ΔW= W_f-W_i = weight of the adhering material on the scotch tape.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

20

Code	Sample type	Sampling zone	Adopted analisys
UT	fragment of untreated plaster	west arm, southern wall	OM-RL, micro-Raman
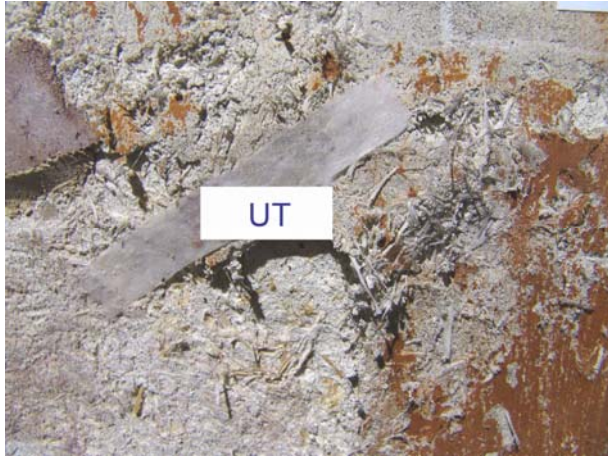
UT sampling point

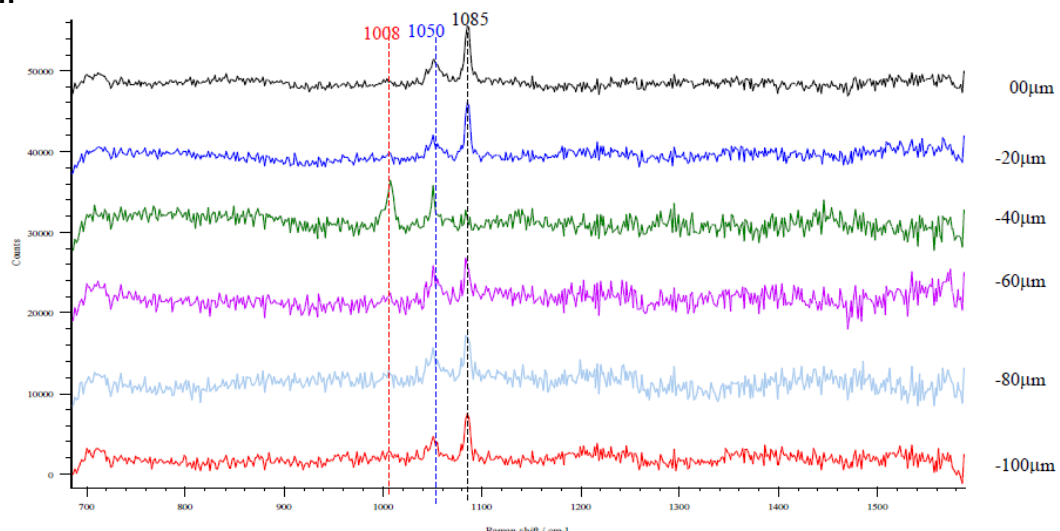sample UT: cross-section photograph
(white reflected light).

The sample belongs to the outermost layer of the plaster having a maximum thickness of 5 mm; it has and has weak cohesion.

Micro-Raman analysis

Analyses were performed along 3 different line-scans, with different steps, oriented orthogonally to the sample surface. The signals at 1085 cm-1 and 1003 cm-1 belong to calcite and gypsum, respectively.

Line-scan n.1

Raman spectra at different dephts

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

21

Line-scan n. 2

Raman spectra at different dephts

Line-scan n.3

Raman spectra at different dephts

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

22
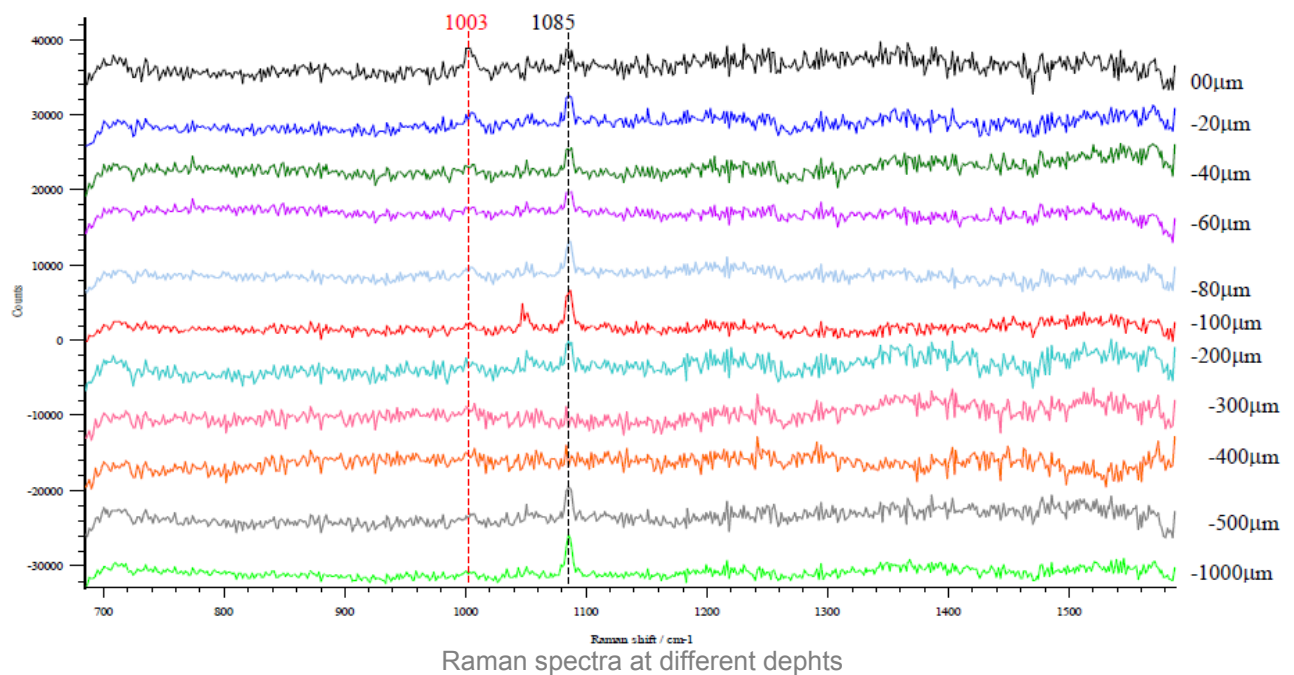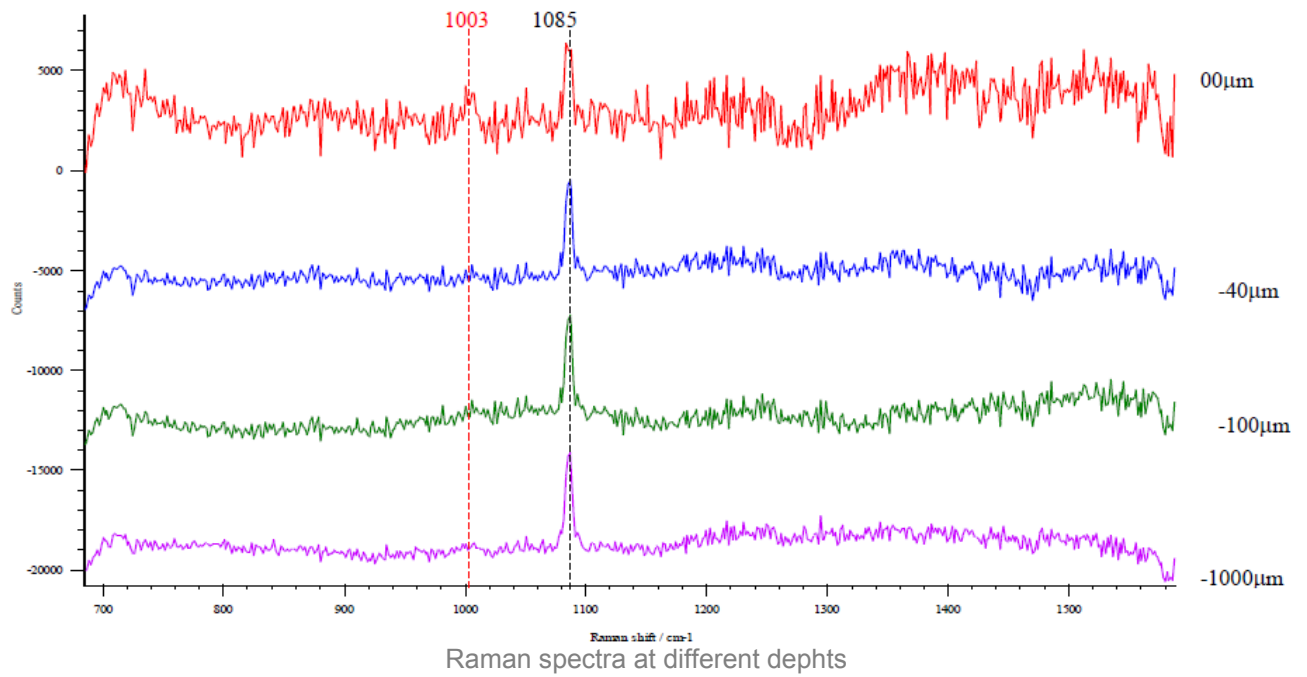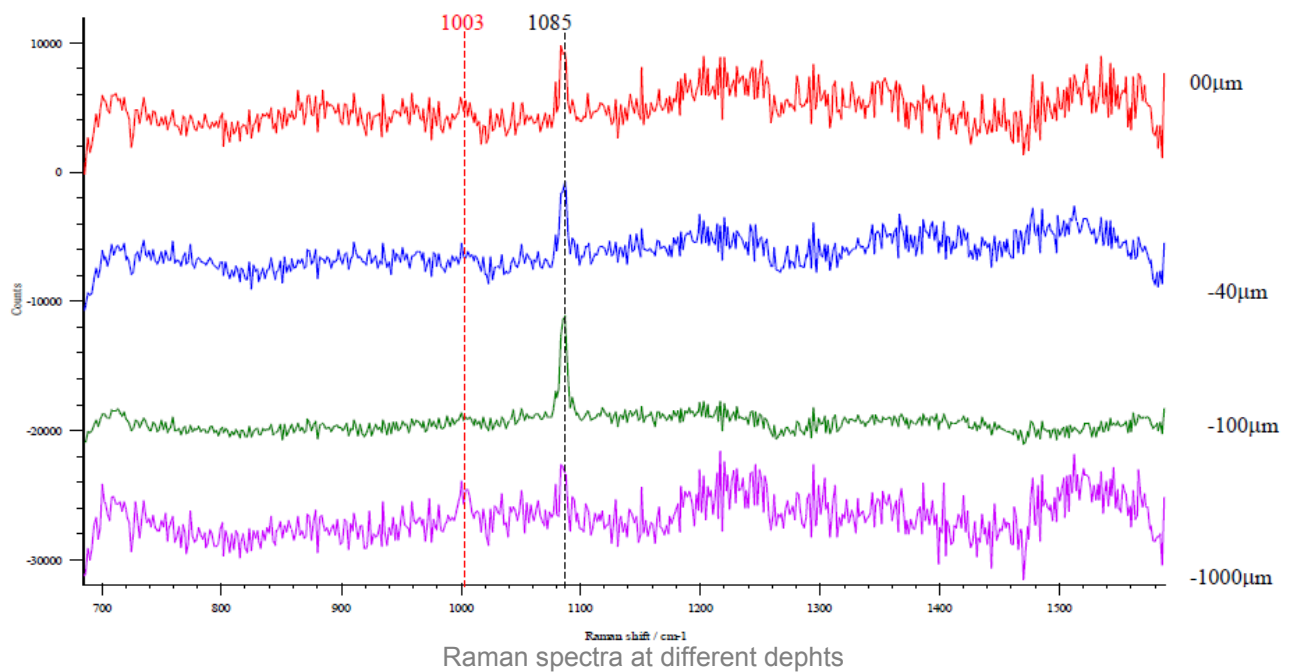
SEM-EDS analysis

Chemical analyses and maps reveal traces of gypsum (Ca, S) in the thickness of the layer and exclude the presence of phosphorus (P).
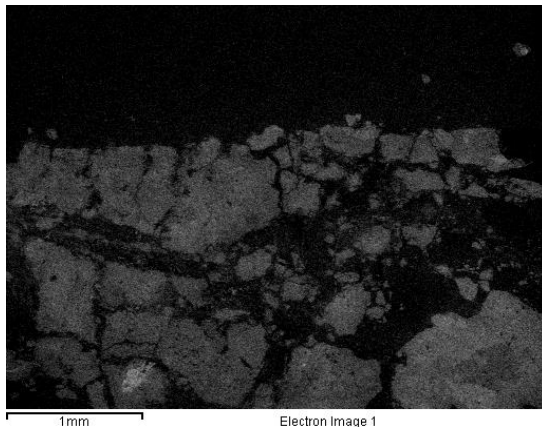
BSE image of the sample

Element	Weight%	Weight% Sigma	Atomic%
C K	50.36	0.17	61.68
O K	35.19	0.15	32.35
Na K	0.19	0.01	0.12
Mg K	0.54	0.01	0.32
Al K	0.36	0.01	0.20
Si K	2.71	0.02	1.42
S K	0.17	0.01	0.08
Cl K	0.11	0.01	0.05
K K	0.45	0.01	0.17
Ca K	9.68	0.04	3.55
Fe K	0.24	0.01	0.06
Totals	100.00		

concentrations of chemical elements
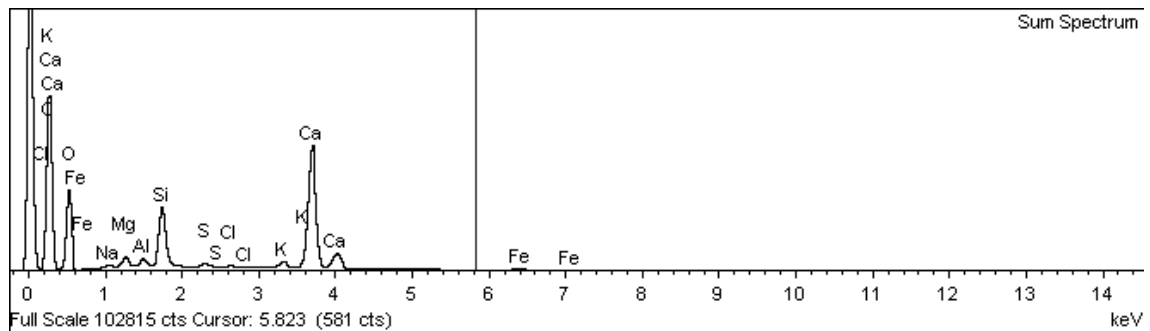
EDS spectrum
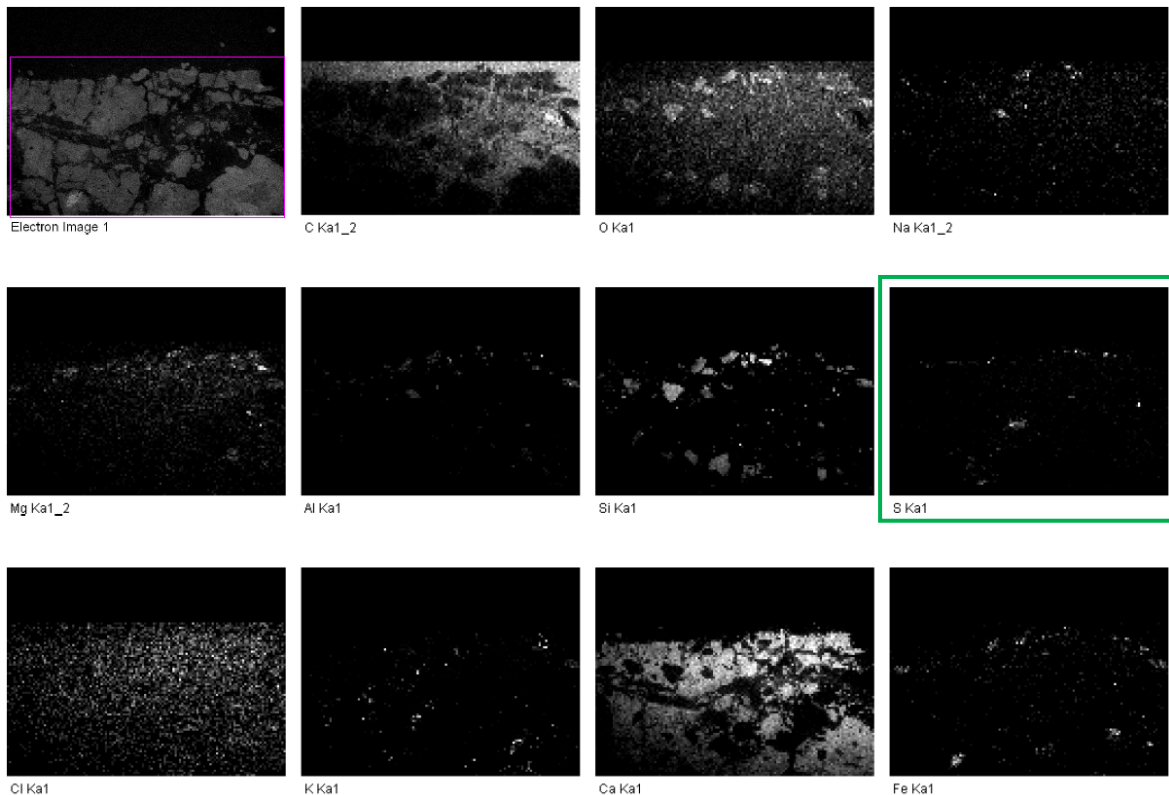
distribution maps of chemical elements

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

23

Code	Sample type	Sampling zone	Adopted analisys
Am-Ox	fragment of plaster treated with Ammonium Oxalate	west arm, southern wall	OM-RL, micro-Raman

AmOx sampling point

sample Am-Ox: cross-section photograph (white reflected light).

The sample belongs to the outermost layer of the plaster having a maximum thickness of 4 mm and a medium cohesion.

Micro-Raman analysis

Analyses were carried out along 5 different line-scans, with different steps, oriented orthogonally to the sample surface; the compounds identified are calcite (1085 cm^{-1}), gypsum (1000 cm^{-1}) and calcium oxalate (1477 cm^{-1}) in the form of weddellite ($CaC_2O_4*2H_2O$); the latter is present, if only with a weak signal, up to a maximum depth of 60-80 µm.

Line-scan n. 1

Raman spectra at different depths

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

24
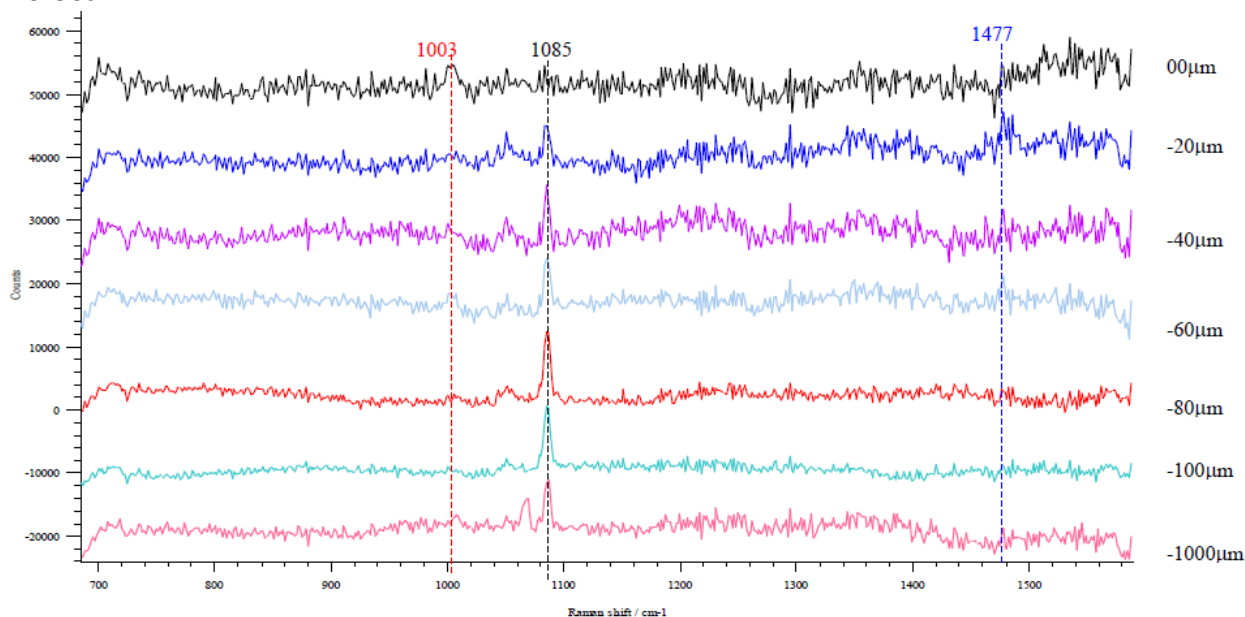
Line-scan n. 2

Raman spectra at different depths

Line-scan n. 3

Raman spectra at different depths

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

25

Line-scan n. 4

Raman spectra at different dephts

Line-scan n. 5

Raman spectra at different dephts

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

26
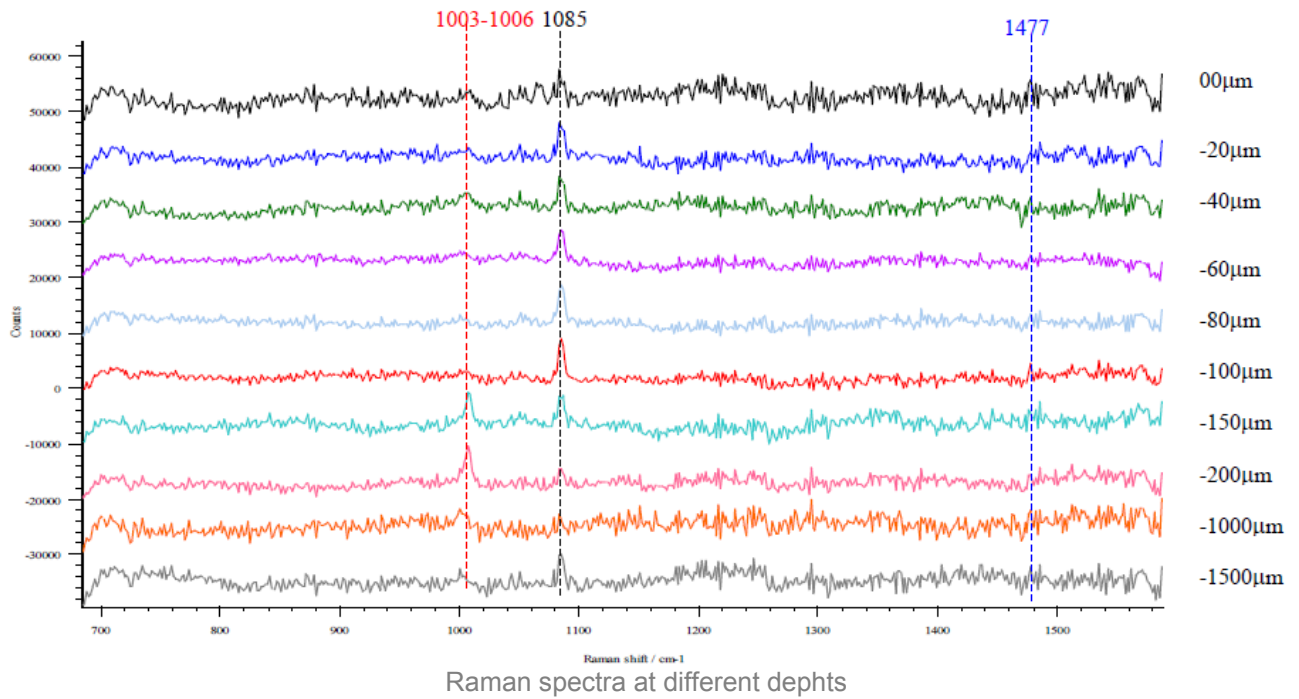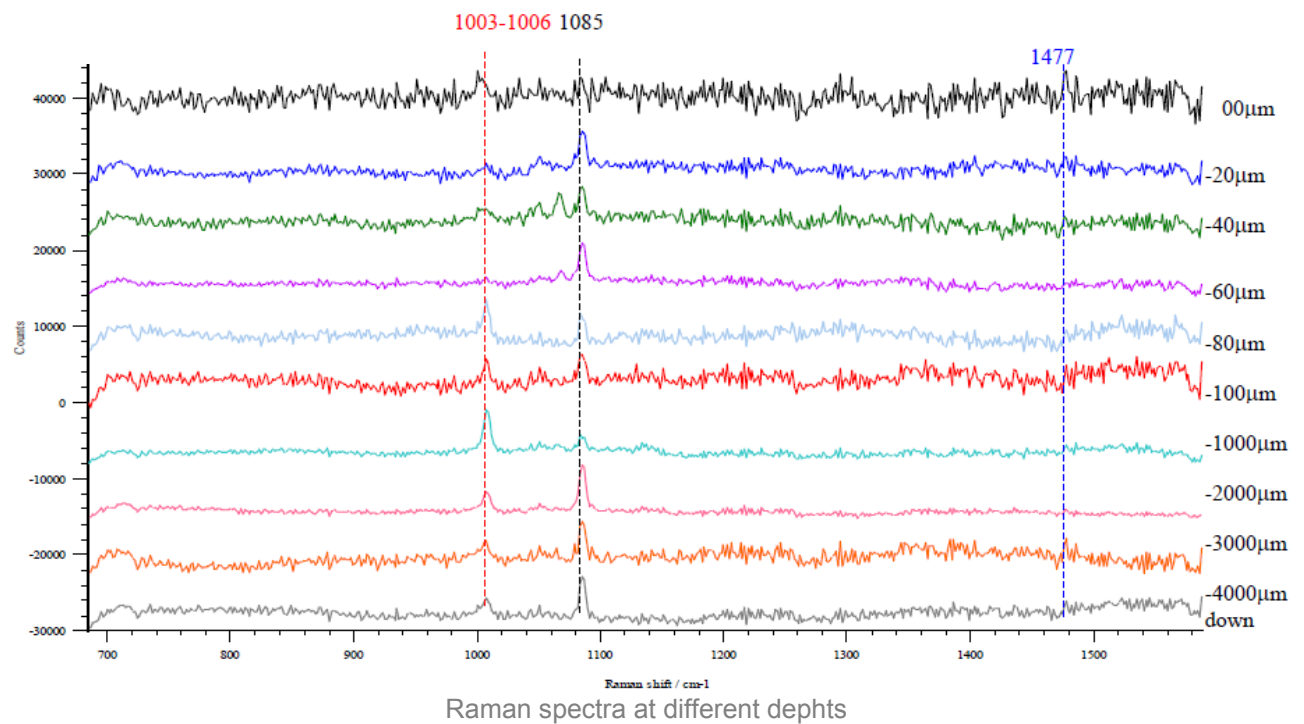
SEM-EDS analysis

Elemental chemical analyses and maps confirm the presence of gypsum (Ca, S) and the absence of phosphates (P).
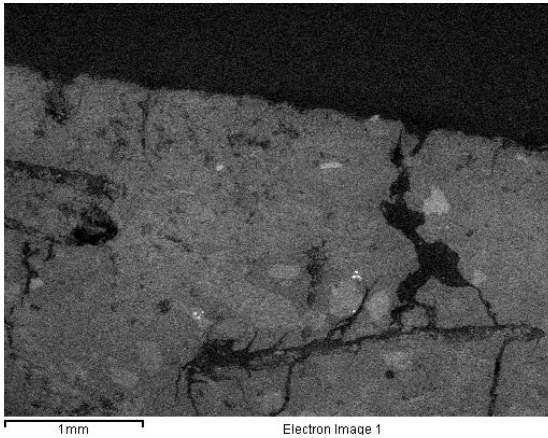
BSE image of the sample (area 1)

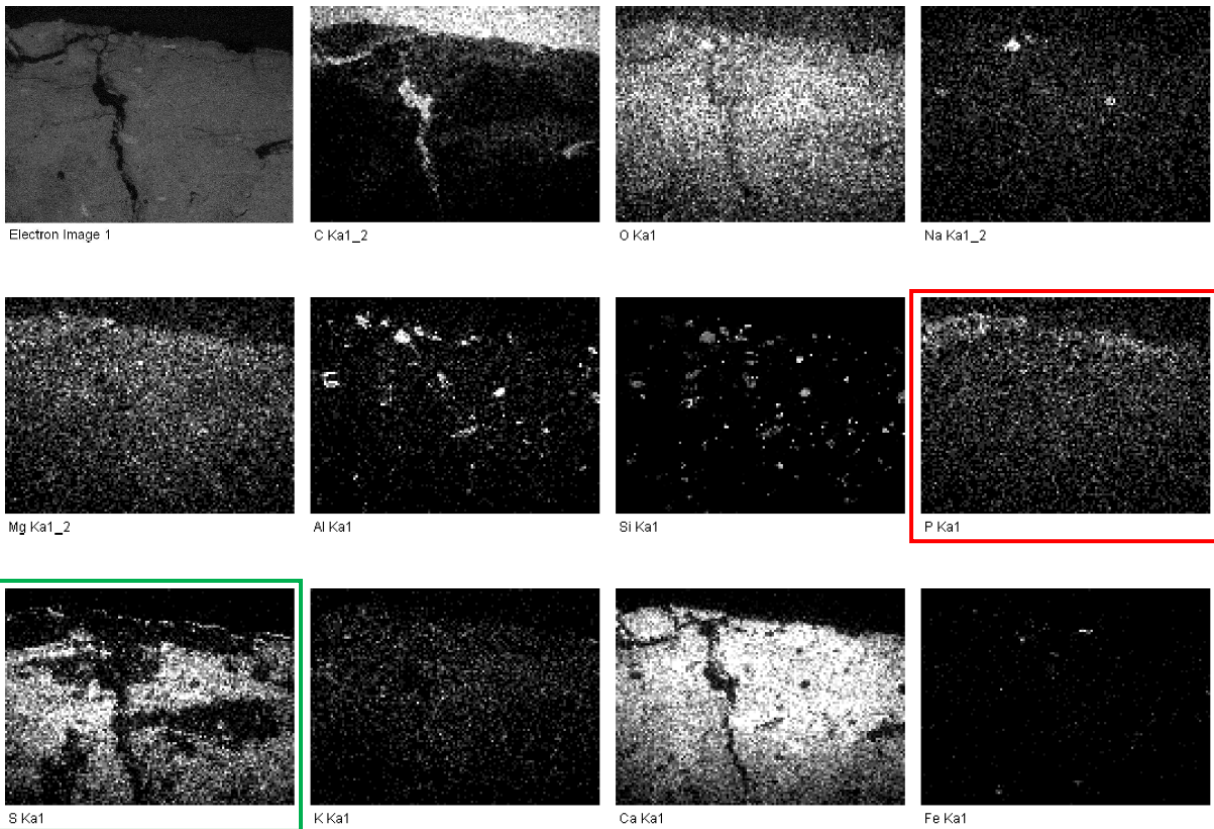| Element	Weight%	Weight% Sigma	Atomic%
C K	45.15	0.32	57.10
O K	37.16	0.27	35.28
Na K	0.51	0.02	0.34
Mg K	0.59	0.02	0.37
Al K	0.48	0.02	0.27
Si K	2.55	0.03	1.38
S K	1.60	0.02	0.76
Cl K	0.10	0.01	0.04
K K	0.43	0.02	0.17
Ca K	11.09	0.08	4.20
Fe K	0.34	0.03	0.09
Totals	100.00		

concentrations of chemical elements (area 1)
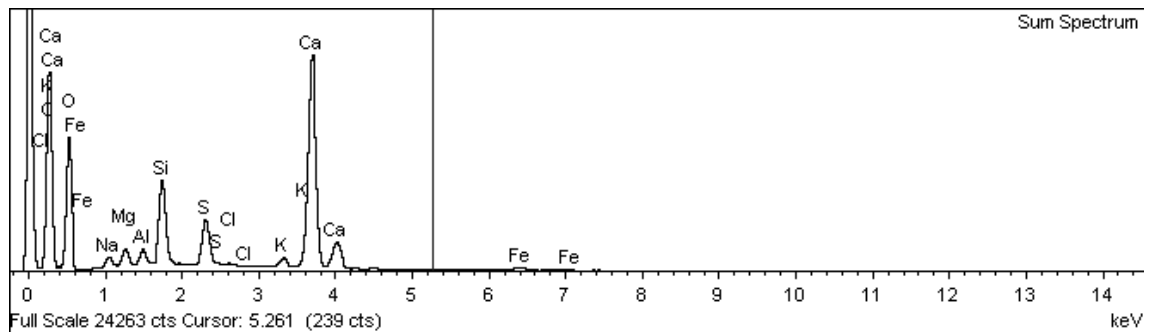
EDS spectrum (area 1)

distribution maps of chemical elements (area 1)

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

27
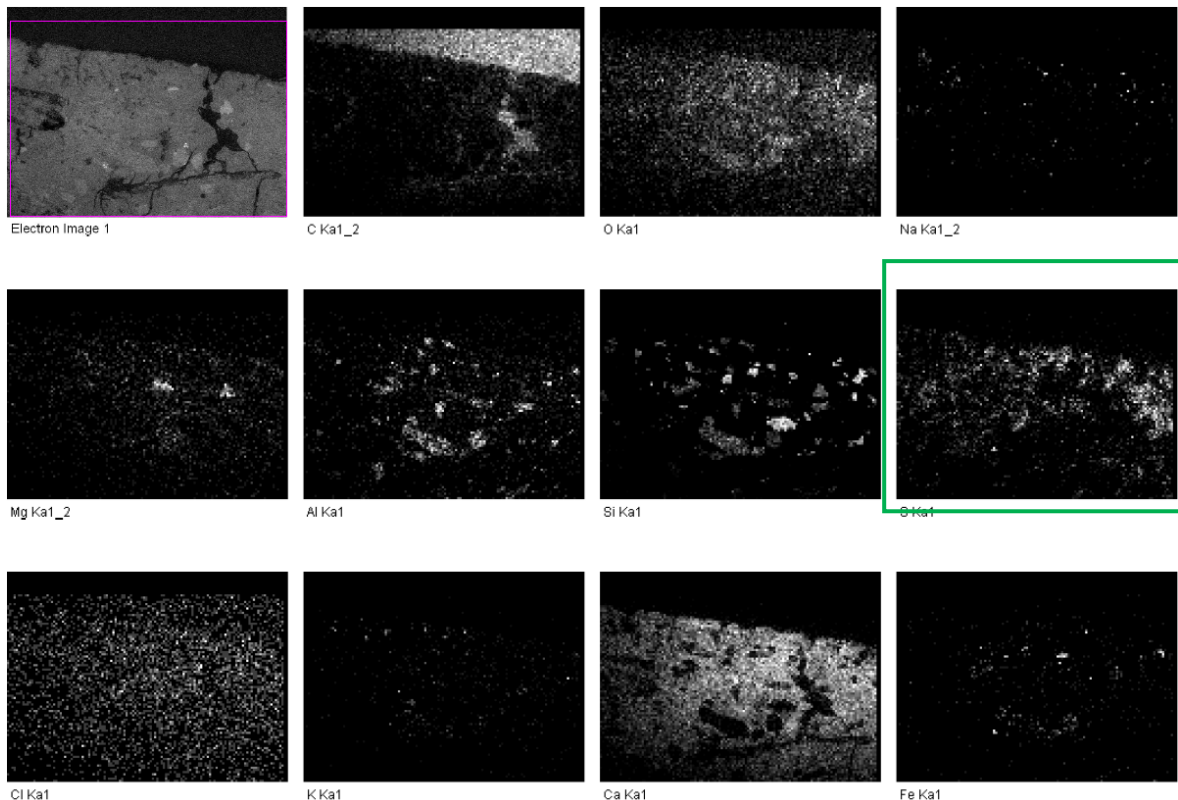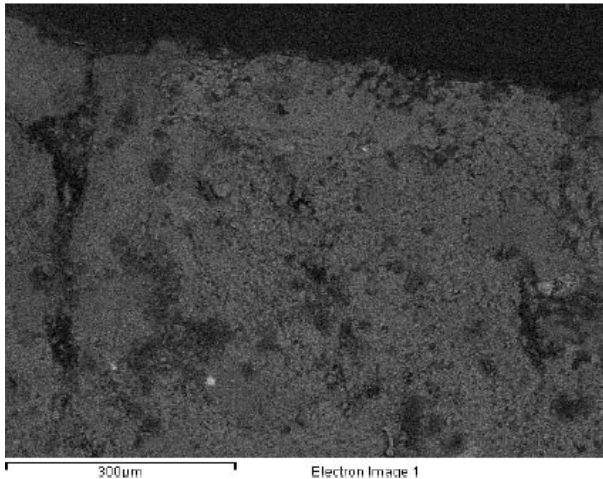
BSE image of the sample (area 2)

Element	Weight%	Weight% Sigma	Atomic%
C K	39.85	0.32	52.02
O K	39.84	0.26	39.05
Na K	0.43	0.02	0.29
Mg K	0.77	0.02	0.50
Al K	0.51	0.02	0.30
Si K	2.37	0.03	1.32
S K	1.95	0.03	0.96
Cl K	0.11	0.01	0.05
K K	0.61	0.02	0.24
Ca K	13.32	0.09	5.21
Fe K	0.23	0.02	0.06
Totals	100.00		

concentrations of chemical elements (area 2)
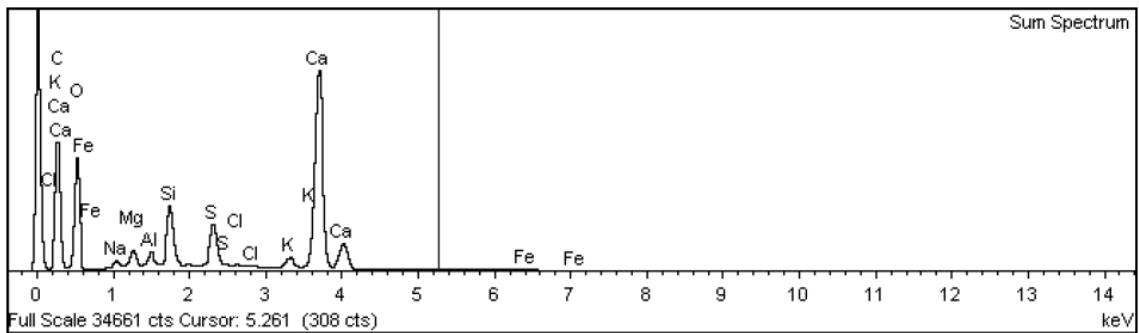
EDS spectrum (area 2)
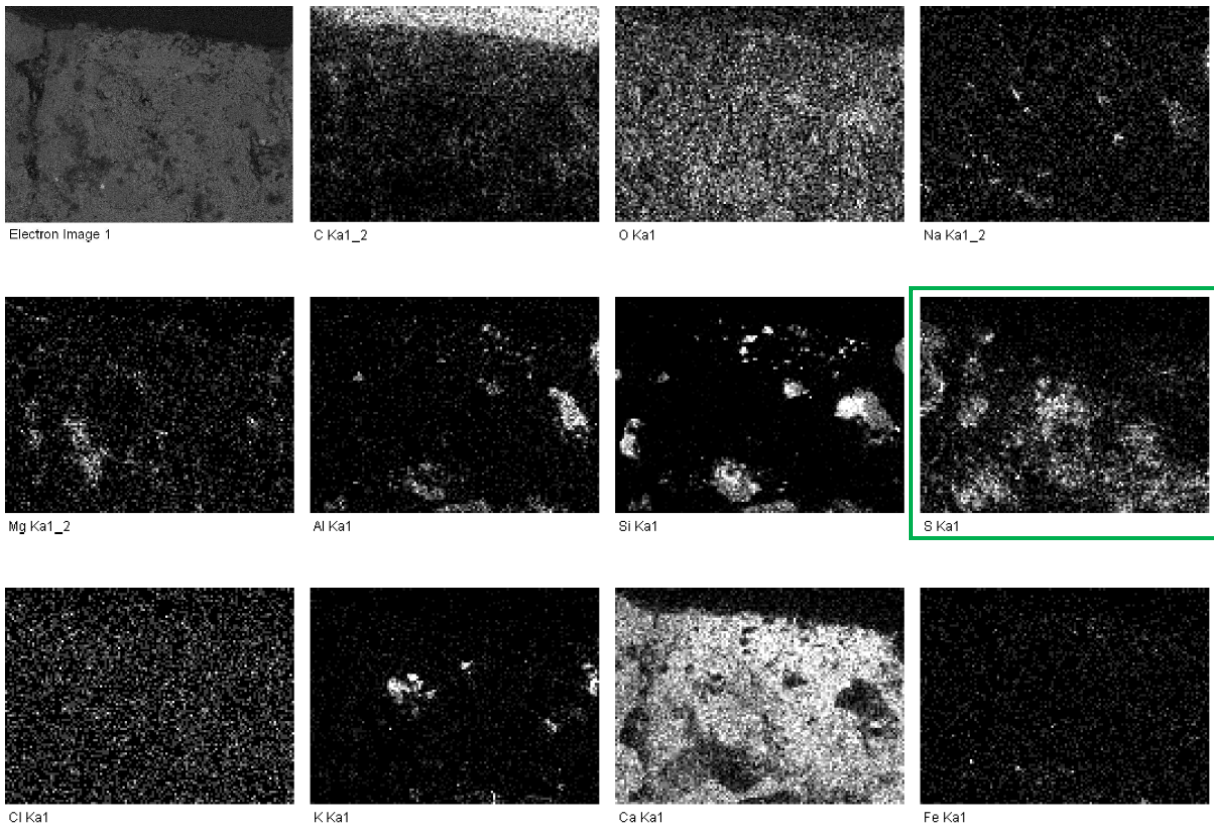
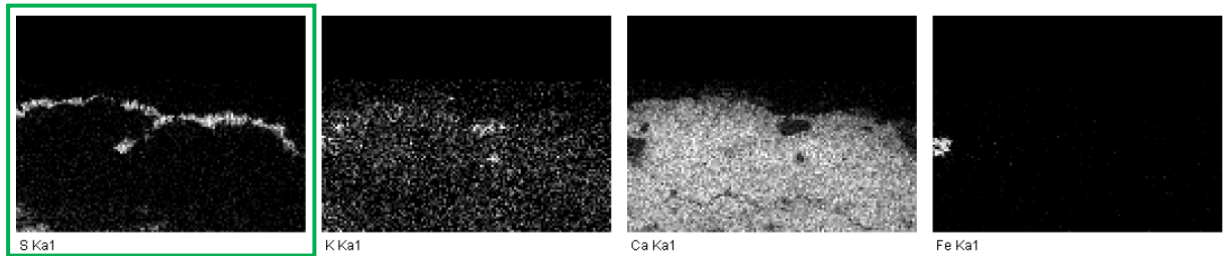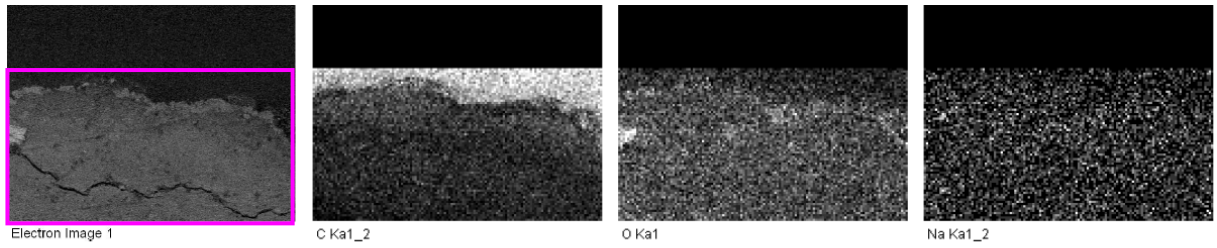distribution maps of chemical elements (area 2)

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

28

Code	Sample type	Sampling zone	Adopted analisys
Am-Ph	fragment of plaster treated with Di-Ammonium Phosphate (DAP)	west arm, southern wall	OM-RL, micro-Raman

Am-Ph sampling point

sample Am-Ph: cross-section photograph (white reflected light).

The sample belongs to the outermost layer of the plaster, having a maximum thickness of 3.7 mm and a medium cohesion.

Micro-Raman analysis

Analyses were carried out along 3 different line-scans, with different steps, oriented orthogonally to the surface of the sampl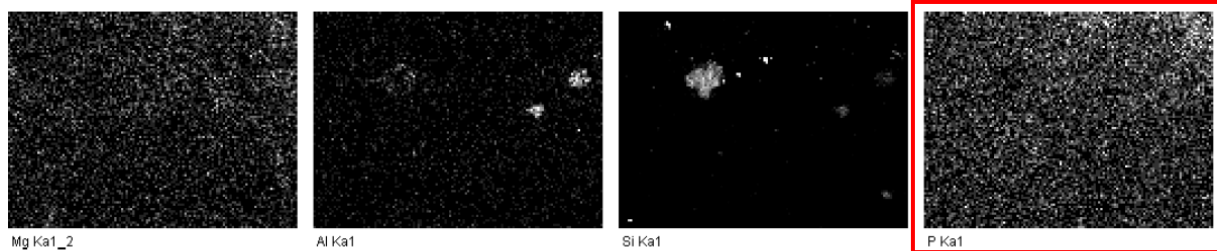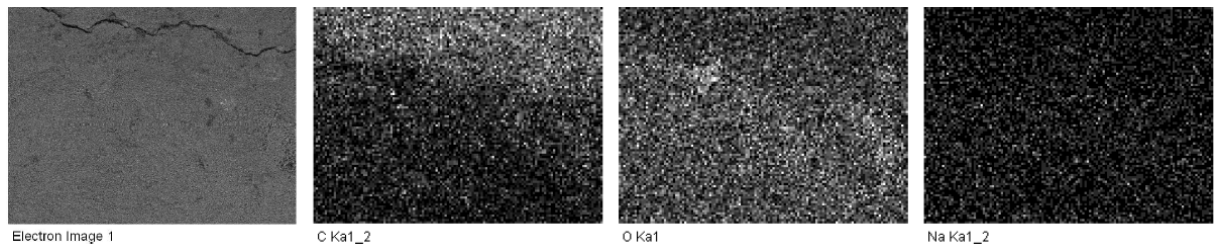e; in addition to the calcite (1085 cm^{-1}) and gypsum (1000 cm^{-1}) signals, a band at 1050 cm^{-1} was visible at all depths, which can probably be attributed to phosphates; however, their most intense signal located around 950 cm^{-1} is missing. The 1050 cm^{-1} medium intensity signal appears in the Raman spectra of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] and anhydrous calcium phosphate [$Ca(HPO_4)_2$] reported in the literature.

Line-scan n. 1

0-100 µm
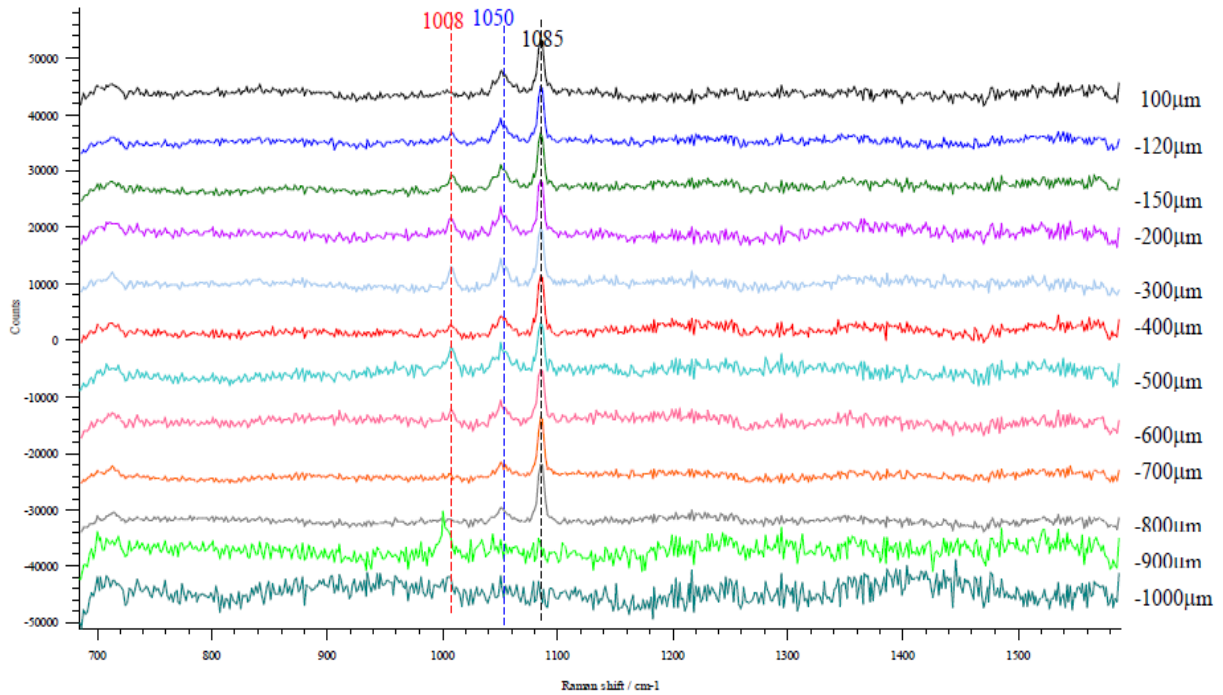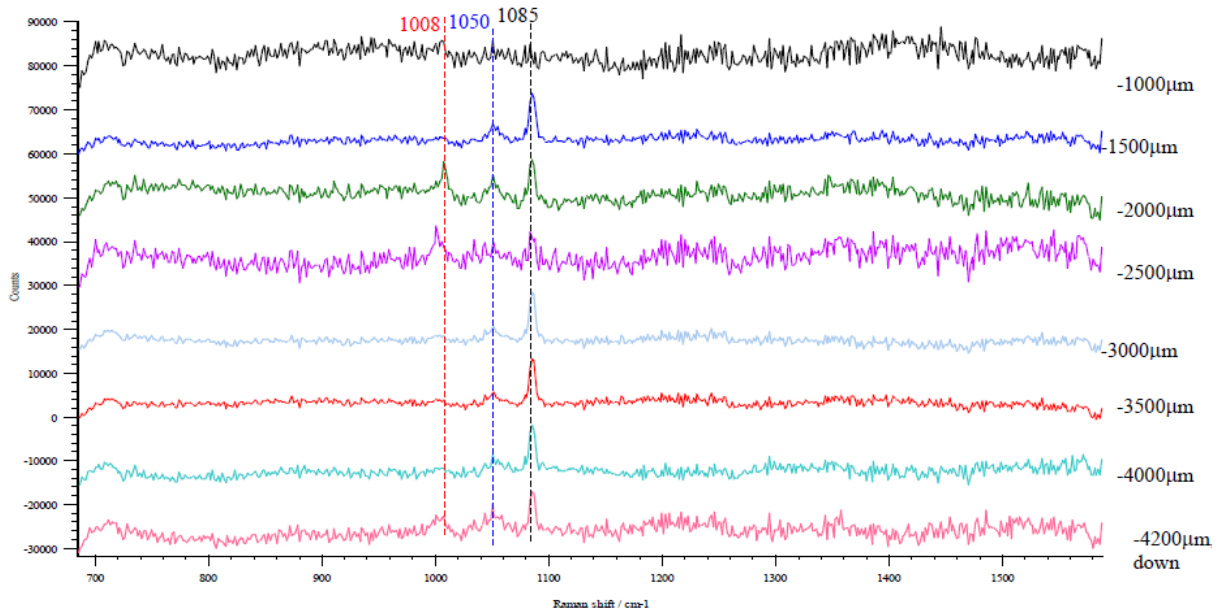
Raman spectra at different dephts

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

29

100-1000 µm

Raman spectra at different dephts

1000-4000 µm

Raman spectra at different dephts

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

30

Line-scan n. 2
0-100 µm

Raman spectra at different dephts

100-1000 µm

Raman spectra at different dephts

1000-3500 µm

Raman spectra at different dephts

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

31

Line-scan n. 3
0-100 µm

Raman spectra at different dephts

100-1000 µm

Raman spectra at different dephts

1000-3800 µm

Raman spectra at different dephts

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

32
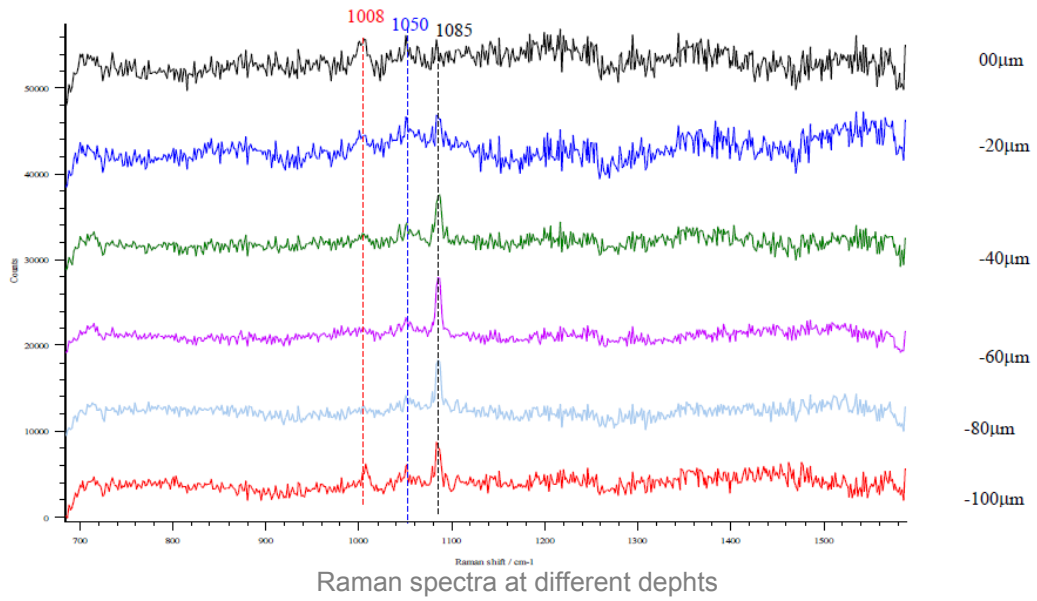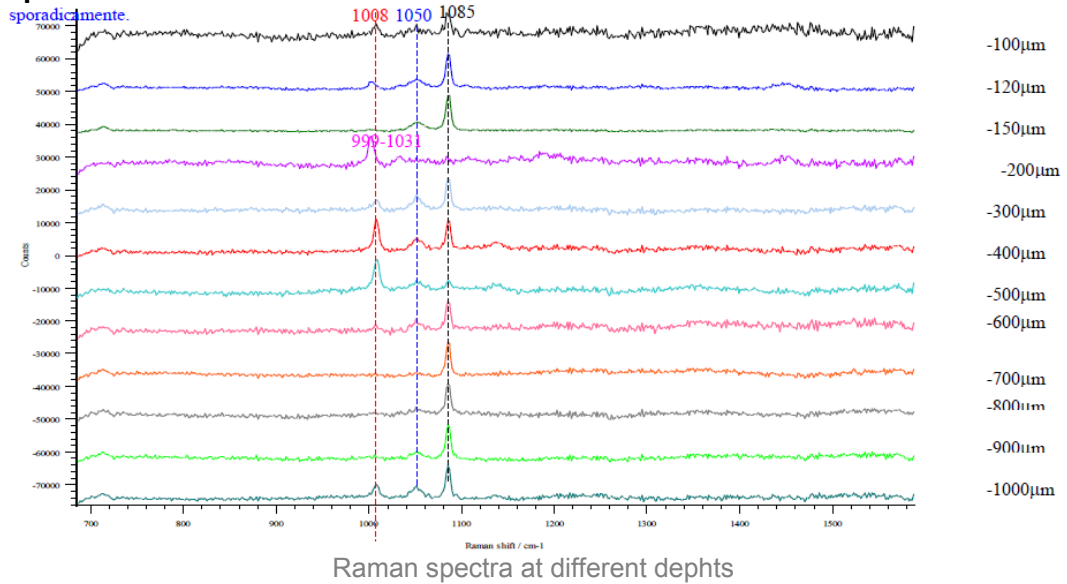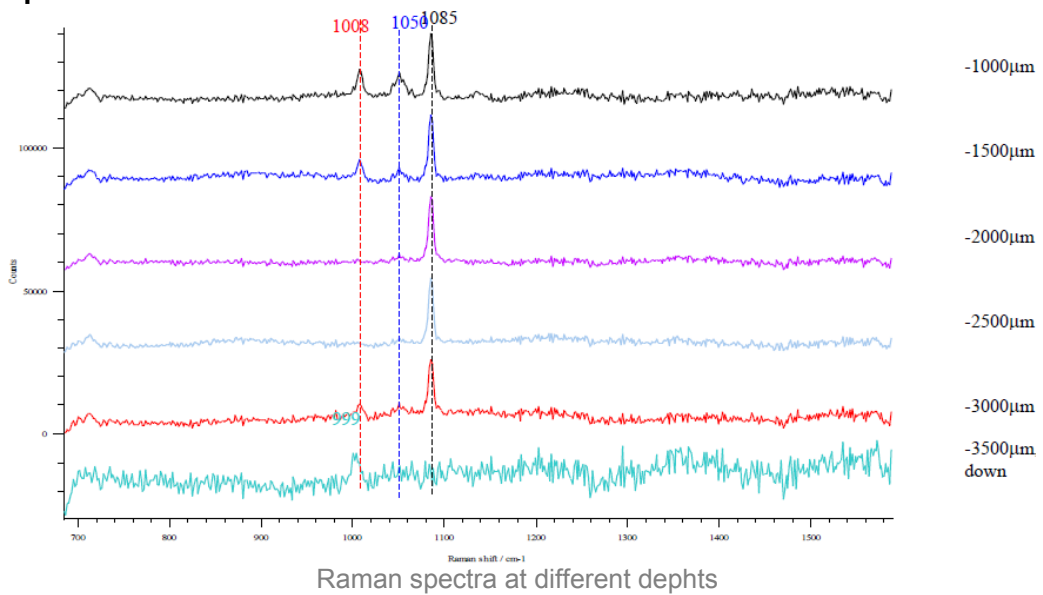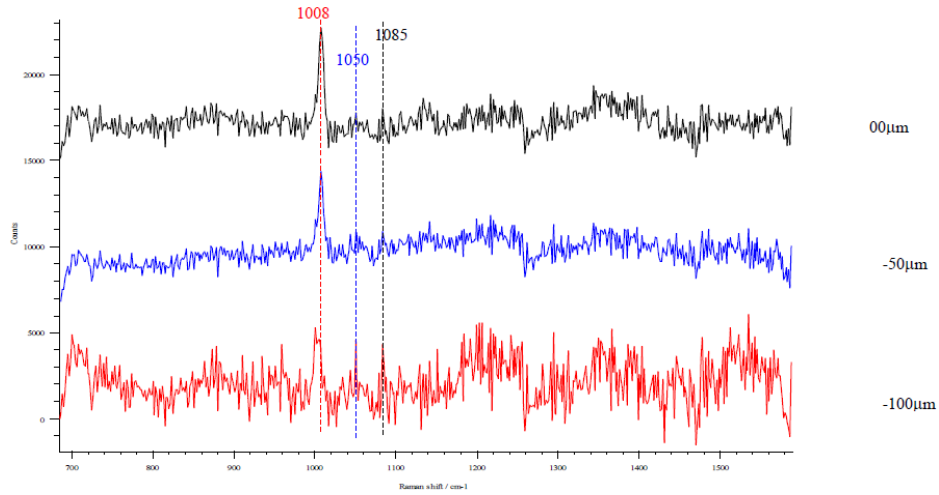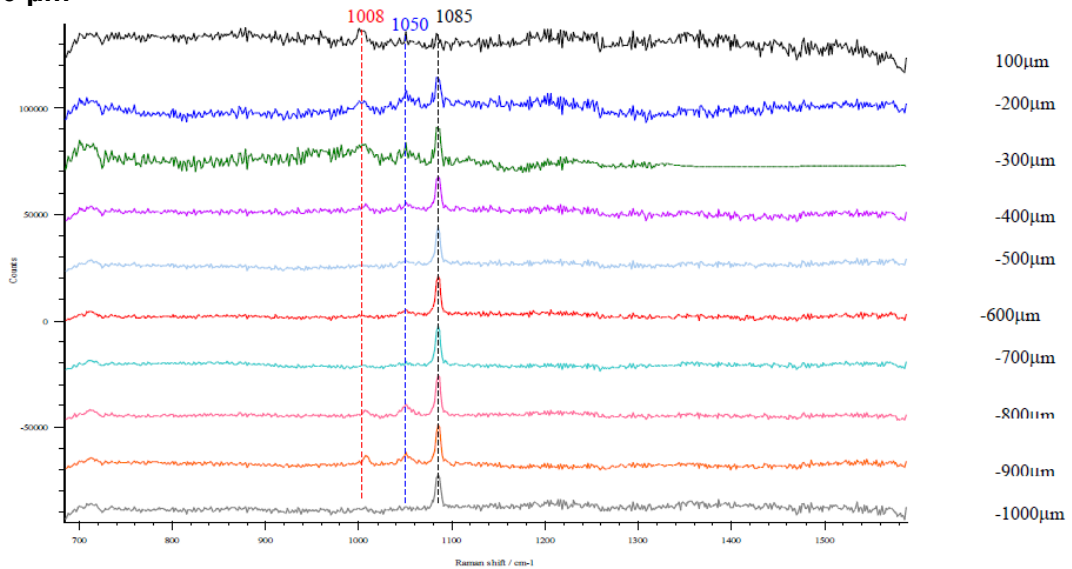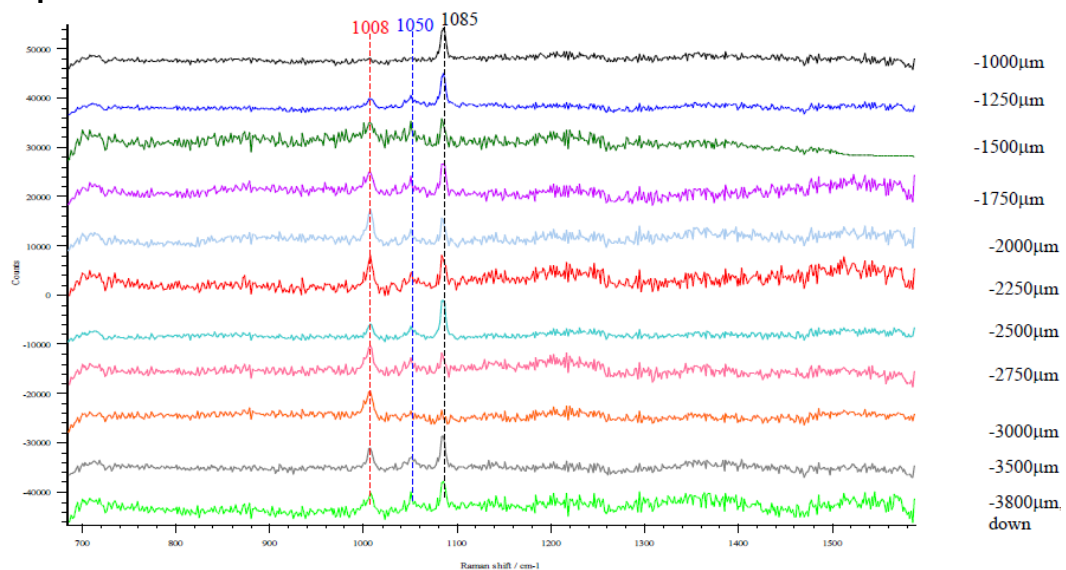
SEM-EDS analisys

In addition to gypsum, elemental chemical analyses reveal the presence of heterogeneously distributed phosphorus; in some areas of the sample, this element is concentrated on the surface while in others it appears to be distributed throughout the thickness of the sample and also associated with magnesium.
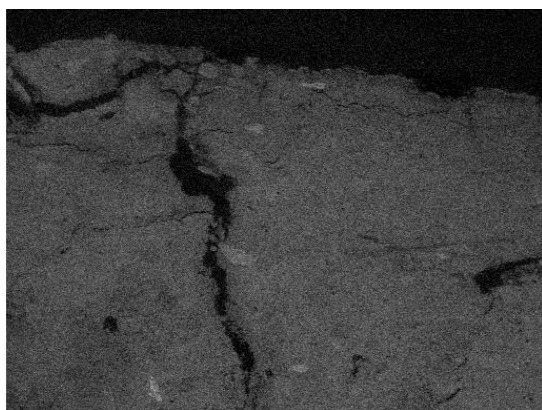
BSE image of the sample (area **1**, part **a**)

Element	Weight%	Weight% Sigma	Atomic%
C K	40.76	0.26	52.57
O K	40.65	0.22	39.36
Na K	0.33	0.02	0.22
Mg K	0.70	0.02	0.45
Al K	0.25	0.01	0.15
Si K	1.30	0.02	0.72
P K	0.14	0.01	0.07
S K	3.54	0.03	1.71
K K	0.58	0.01	0.23
Ca K	11.58	0.07	4.47
Fe K	0.16	0.02	0.04
Totals	100.00		

concentrations of chemical elements (area 1a)
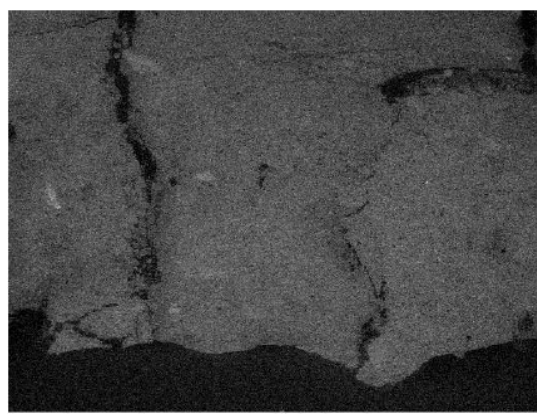
BSE image of the sample (area **1**, part **b**)

Element	Weight%	Weight% Sigma	Atomic%
C K	33.55	0.28	45.20
O K	44.29	0.23	44.80
Na K	0.27	0.02	0.19
Mg K	0.56	0.02	0.37
Al K	0.19	0.01	0.11
Si K	1.33	0.02	0.76
P K	0.03	0.01	0.01
S K	5.59	0.04	2.82
K K	0.60	0.01	0.25
Ca K	13.42	0.07	5.42
Fe K	0.17	0.02	0.05
Totals	100.00		

concentrations of chemical elements (area 1b)
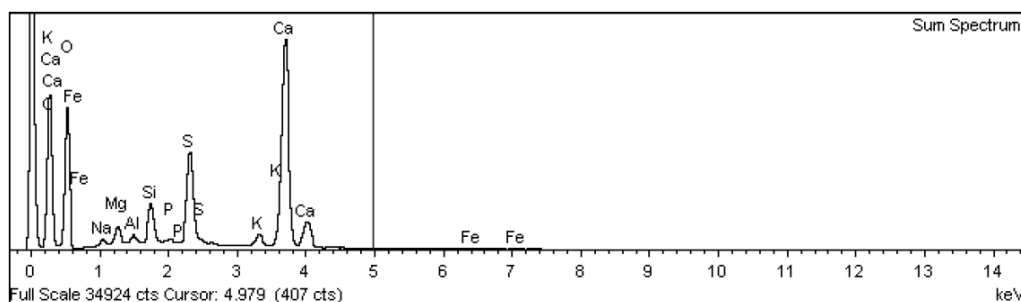
EDS spectrum (area **1**, part **a**)

EDS spectrum (area **1**, part **b**)

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione
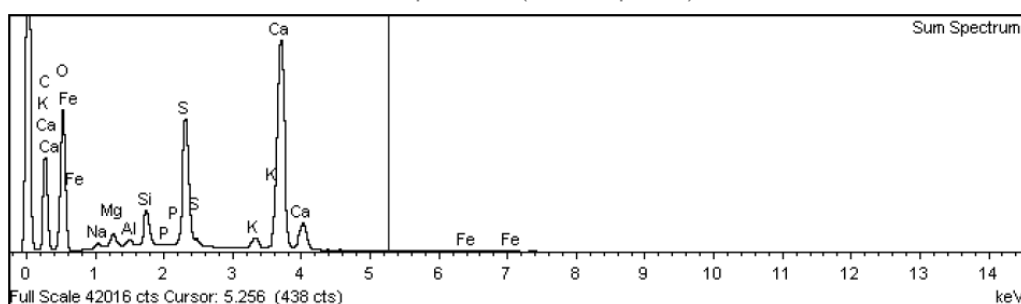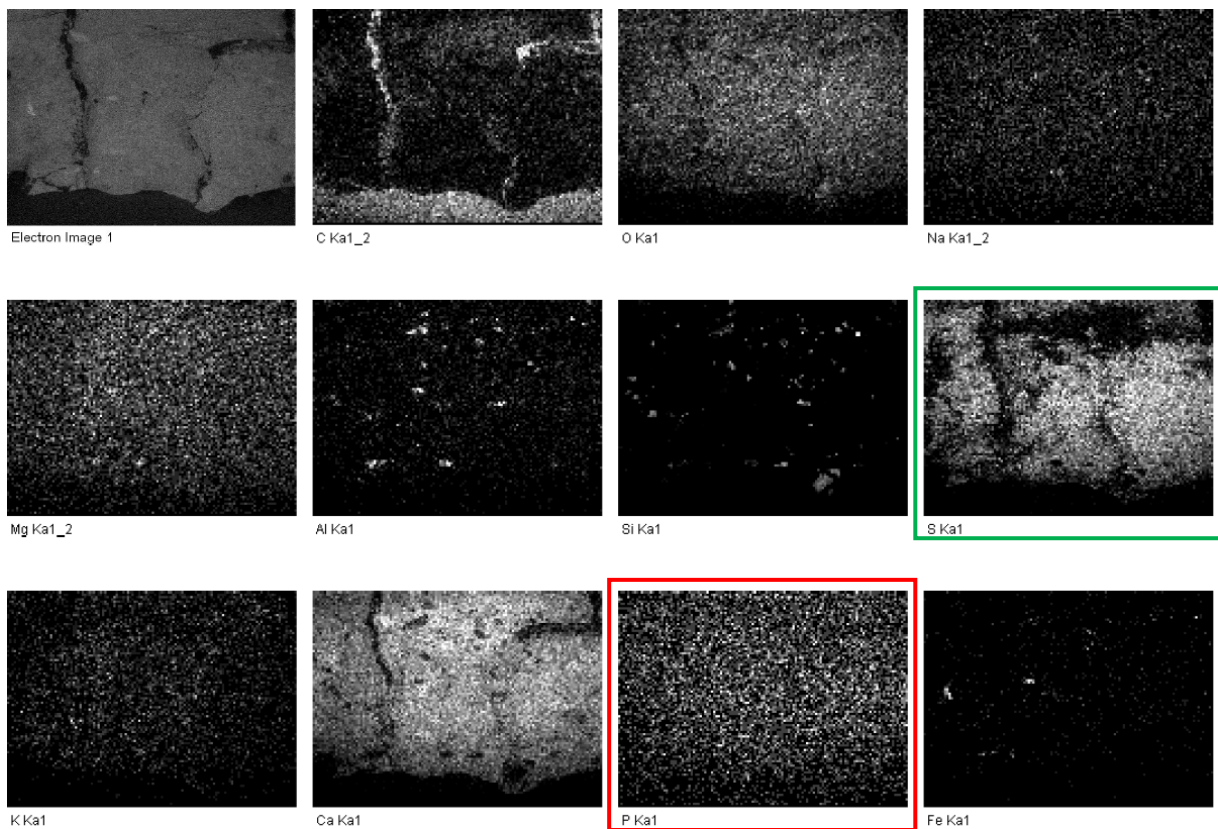
distribution maps of chemical elements (area **1**, part **a**)

distribution maps of chemical elements (area **1**, part **b**)

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

34
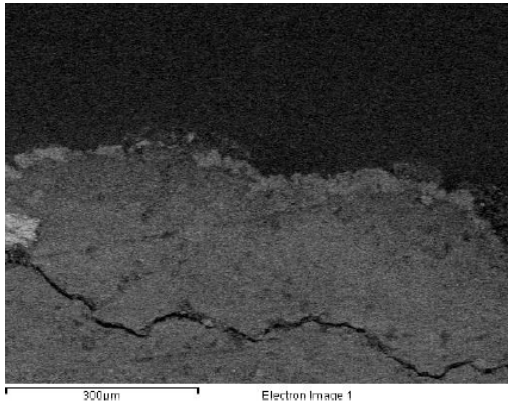
Element	Weight%	Weight% Sigma	Atomic%
C K	45.89	0.20	57.86
O K	37.03	0.18	35.06
Na K	0.16	0.02	0.11
Mg K	1.00	0.02	0.63
Al K	0.16	0.01	0.09
Si K	0.94	0.01	0.51
P K	0.56	0.01	0.27
S K	1.09	0.01	0.52
K K	0.46	0.01	0.18
Ca K	12.46	0.06	4.71
Fe K	0.23	0.02	0.06
Totals	100.00		

BSE image of the sample (area **2**, part **a**)   concentrations of chemical elements (area 2a)
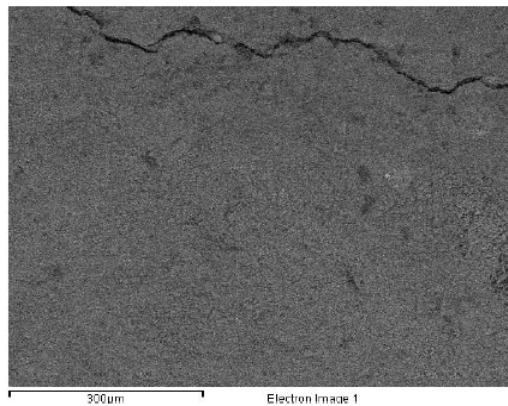
Element	Weight%	Weight% Sigma	Atomic%
C K	29.93	0.30	41.40
O K	45.51	0.24	47.27
Na K	0.39	0.02	0.28
Mg K	1.01	0.02	0.69
Al K	0.19	0.01	0.11
Si K	1.37	0.02	0.81
P K	0.25	0.02	0.14
S K	4.41	0.04	2.28
K K	0.74	0.02	0.31
Ca K	16.08	0.09	6.67
Fe K	0.13	0.02	0.04
Totals	100.00		

BSE image of the sample (area **2**, part **b**)   concentrations of chemical elements (area 2b)
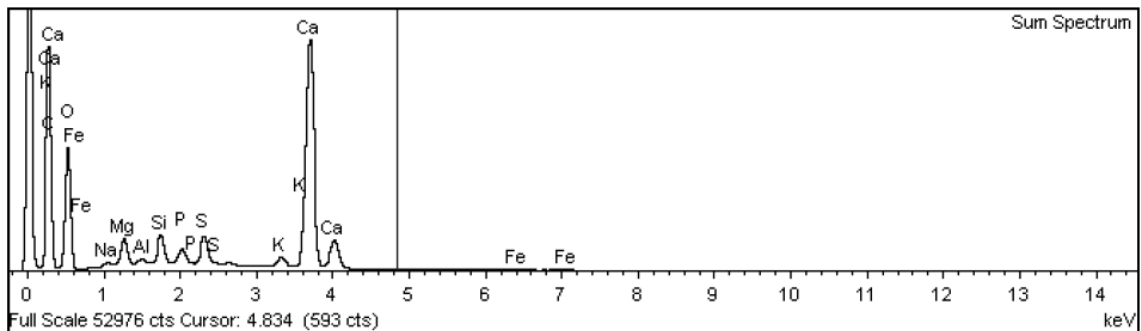
EDS spectrum of area **2**, part **a**

EDS spectrum of area **2**, part **b**

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione
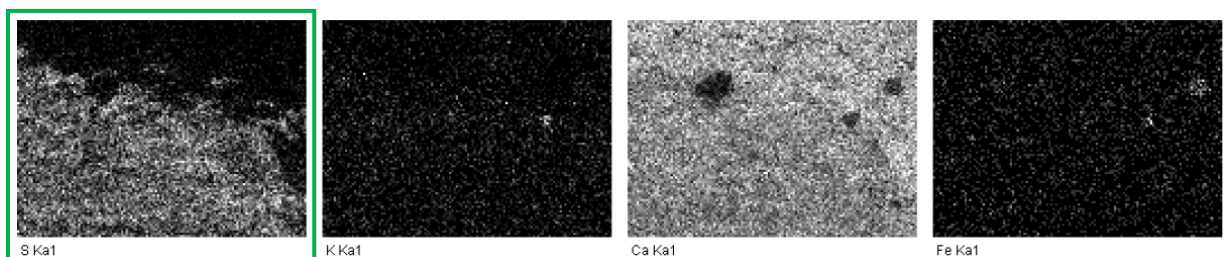
35

distribution maps of chemical elements (area 2a)

distribution maps of chemical elements (area 2b)

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

36

Code	Sample type	Sampling zone	Adopted analisys
A1	gray pictorial fragment	west arm, western side (uncleaned zone)	ST, OM-RL, HT

sample A1: sampling point.

Stereoscopic microscopy

1 mm
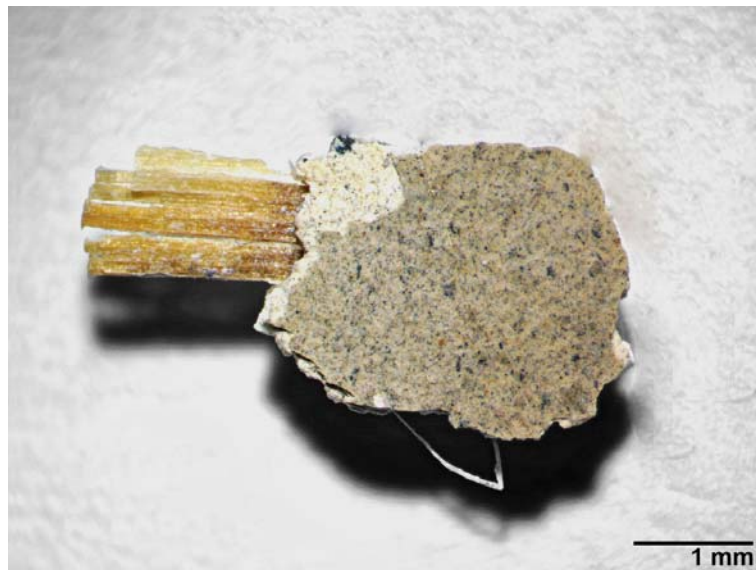
sample A1: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

37

Optical microscopy on cross section
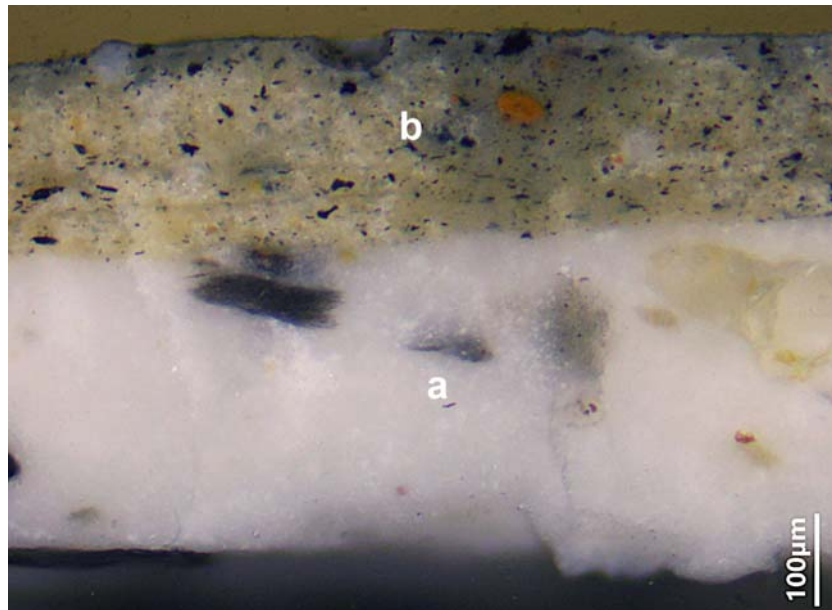
sample A1: cross-section photograph with indication of the layers (white reflected light).
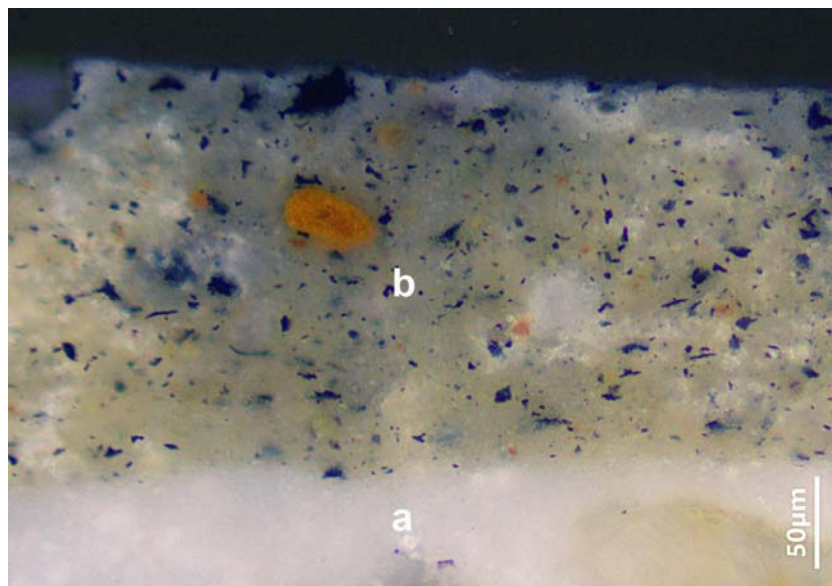
sample A1: detail (white reflected light).

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (µm)	description and composition
b	gray		200-230	lime based paint layer containing Carbon Black and scarce Yellow Ochre
a	white		-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

38

Code	Sample type	Sampling zone	Adopted analisys
A2	pale-yellow pictorial fragment with shiny appearance	west arm, northern side	ST, FT-IR

sample A2: sampling point.

Stereoscopic microscopy

1 mm
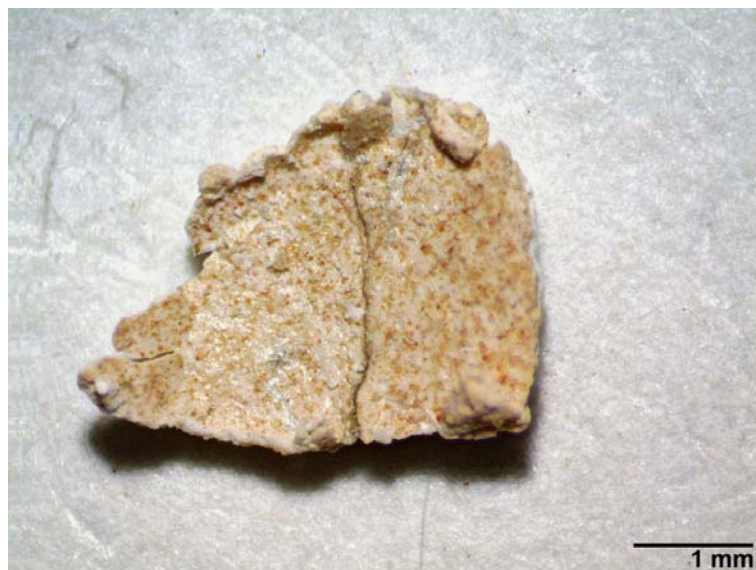
sample A2: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

39

FT-IR spectroscopy

layer	compounds	signals (cm^{-1})	estimated quantity
surface	organic compound (acrilic resin)	2984, 2952, 2930, 2853, 1728, 1258, 1234, 1172, 1158, 1098, 1024, 757	+++
	calcite	1793, 1400, 872, 711	++++
	Ca-oxalates	1628, 1322, 781, 516	+
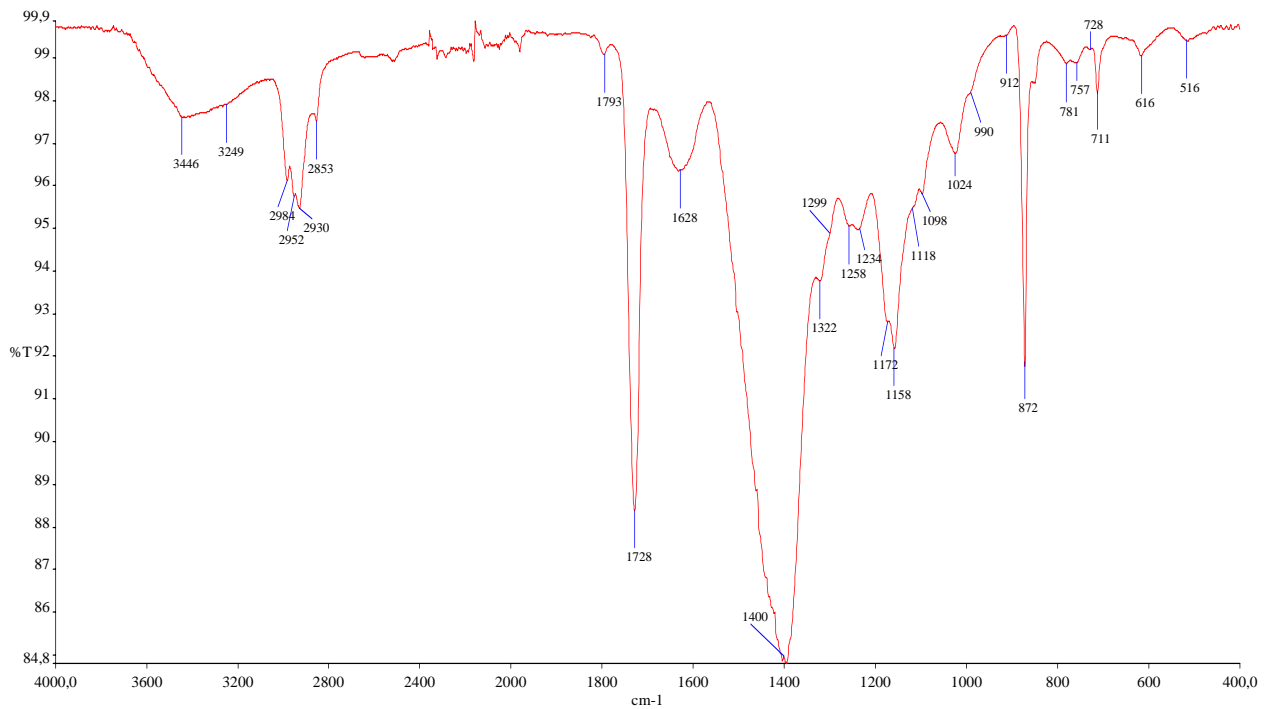
sample A2: FT-IR spectrum of the surface.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

40

Code	Sample type	Sampling zone	Adopted analisys
A3	gray pictorial fragment	west arm, western side (cleaned zone)	ST, OM-RL, HT

sample A3: sampling point.

Stereoscopic microscopy
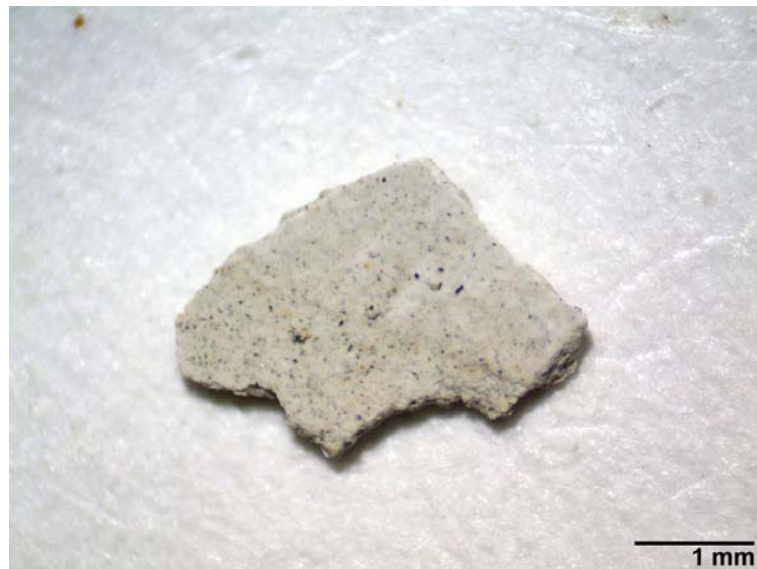
sample A3: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

41

Optical microscopy on cross section
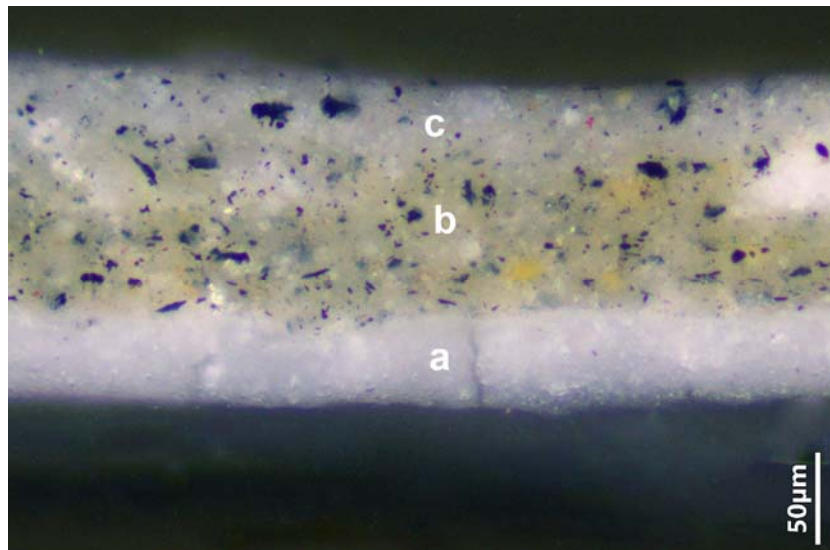
sample A3: cross-section photograph with indication of the layers (white reflected light).
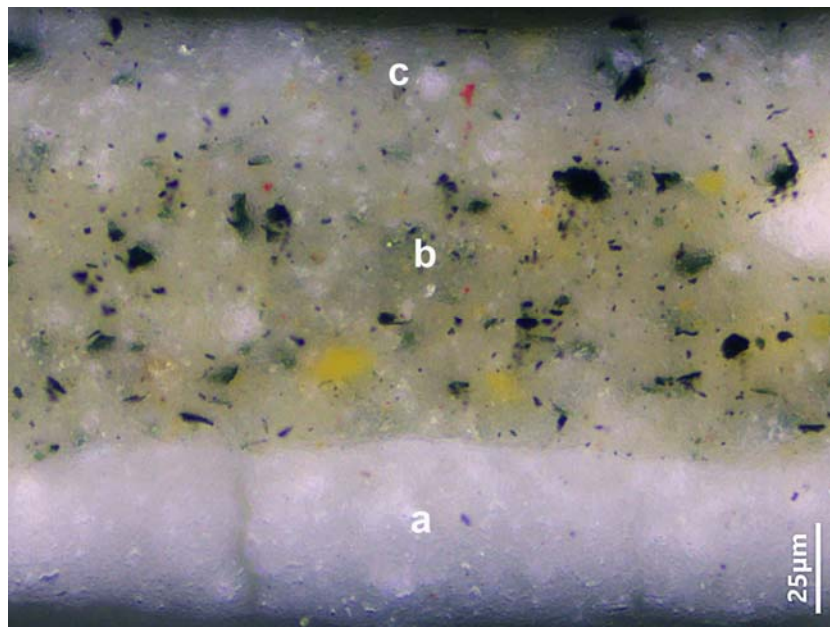
sample A3: detail (white reflected light).

<u>Description of the stratigraphic sequence:</u>

layer	color	UV fluo.	thickness (µm)	description and composition
c	gray		~25	thin lime based paint layer pigmented by scarce Carbon Black and traces of Yellow Ochre
b	yellowish gray		90-100	paint layer containing Carbon Black and Yellow Ochre
a	white		-	plaster

<u>Results of the histochemical tests</u>: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

42

Code	Sample type	Sampling zone	Adopted analisys
A4	red pictorial fragment with shiny appearance	west arm, northern side (uncleaned zone)	ST, FT-IR

sample A4: sampling point.

Stereoscopic microscopy
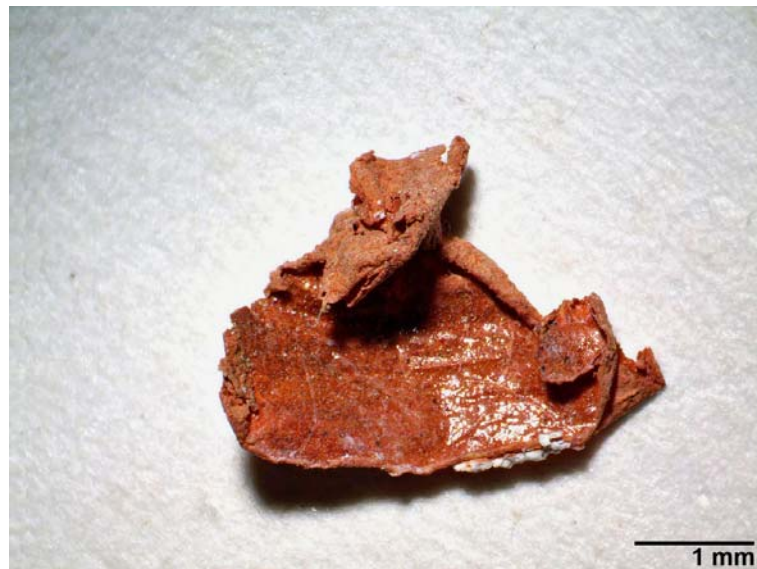
sample A4: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

43

FT-IR spectroscopy

layer	compounds	signals (cm^{-1})	estimated quantity
surface	organic compound (acrilic resin)	2981, 2950, 1726, 1256, 1234, 1175, 1155, 1097, 1026, 758	++++
	calcite	2513, 1795, 1437, 874, 710	++++
	natural earths (ochres)	3694, 3651, 3620, 1026, 1006, 940, 913, 536, 466, 431	+++
	Ca-oxalates	3486, 3435, 3335, 3263, 3061, 1622, 1316, 778, 667, 516	++
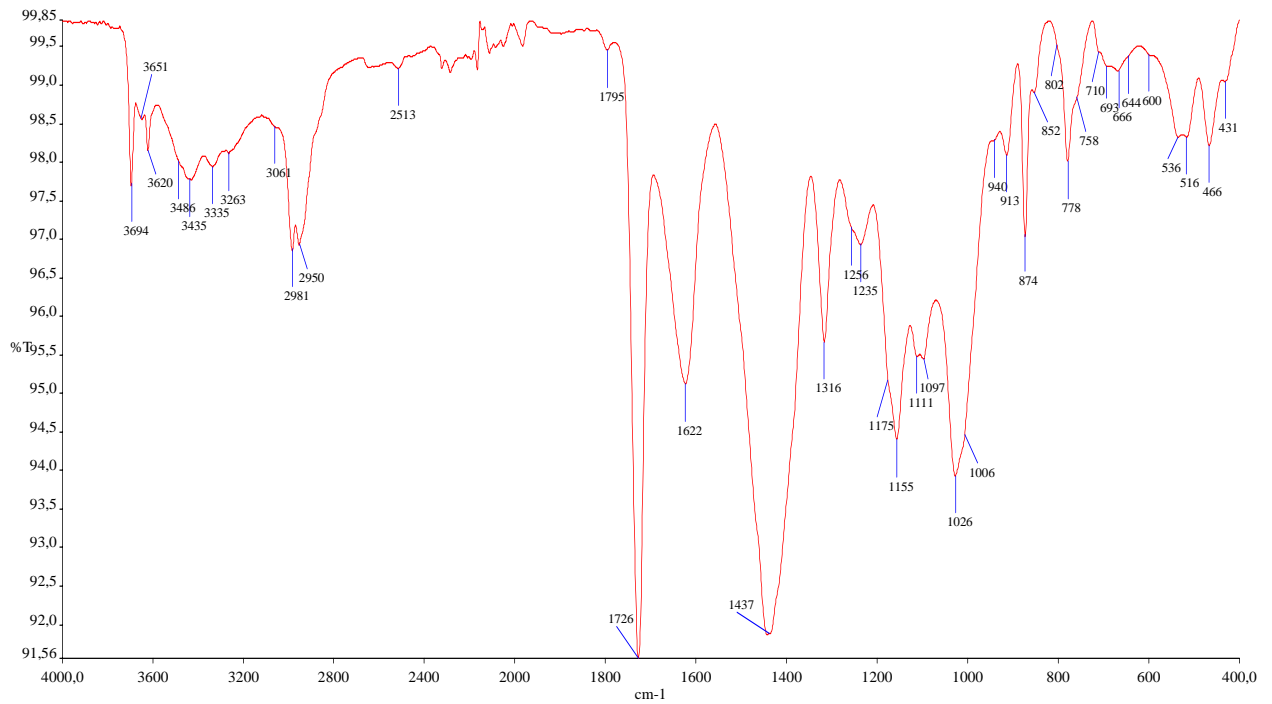
sample A4: FT-IR spectrum of the surface.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

44

| Code	Sample type	Sampling zone	Adopted analisys
A5	red pictorial fragment	west arm, northern side (cleaned zone)	ST, FT-IR

sample A5: sampling point.

Stereoscopic microscopy

1 mm
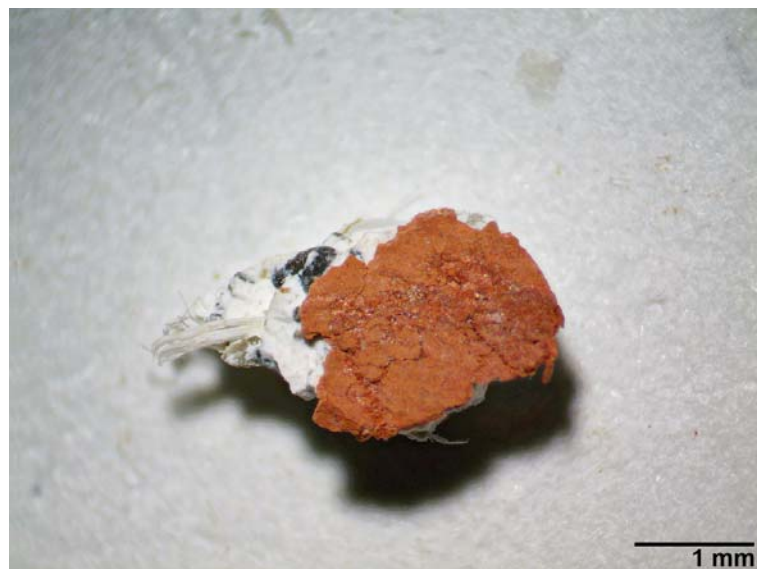
sample A5: photograph under the stereomicroscope.

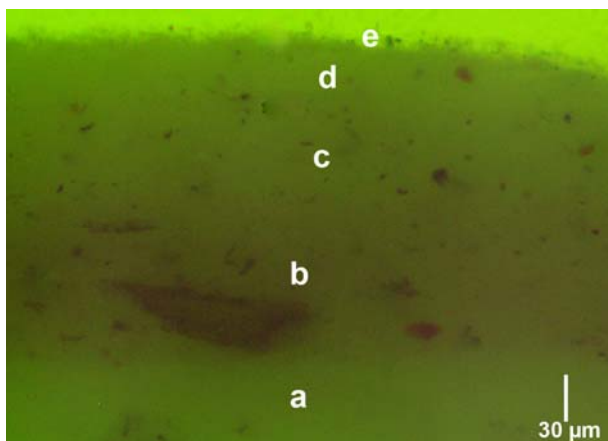Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

45

FT-IR spectroscopy

layer	compounds	signals (cm^{-1})	estimated quantity
surface	organic compound (acrilic resin)	2984, 2952, 1730	+
	calcite	1796, 1430, 874, 710	++++
	natural earths (ochres)	3694, 3649, 3620, 1026, 1004, 936, 912, 532, 465, 428	++++
	Ca-oxalates	3477, 3420, 3332, 3252, 3055, 1619, 1318, 778, 667, 519	++++
	quartz	1162, 1084, 798, 778, 693, 512	++
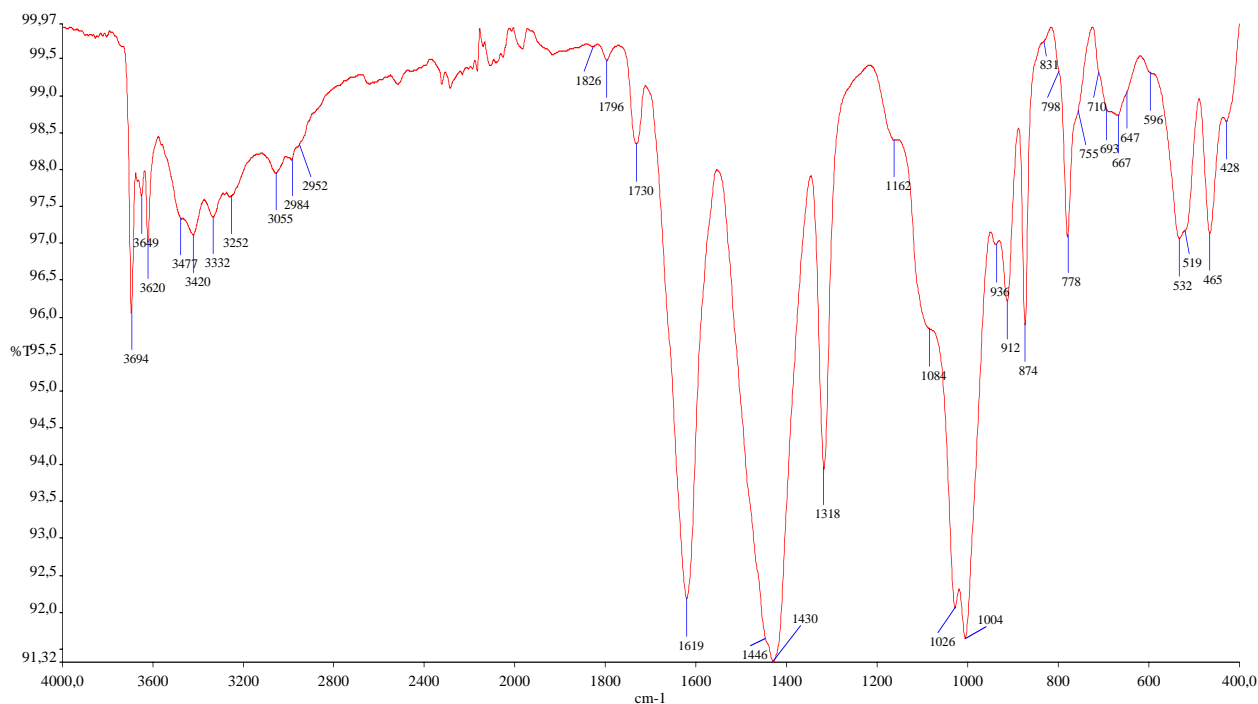
sample A5: FT-IR spectrum of the surface.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

46

Code	Sample type	Sampling zone	Adopted analisys
31	blue pictorial fragment	west arm, western side, background	ST, XRF, OM-RL, HT

sample 31: sampling point.

Stereoscopic microscopy

0.5 mm

sample 31: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

47

XRF measurements

layer	Chemical Elements				possible compounds
	main	**secondary**	**minority**	**in traces**	
blue	Ca	-	K Cr Fe Co	Al Si S Zn	calcite, cobalt pigment containing Cr and Zn
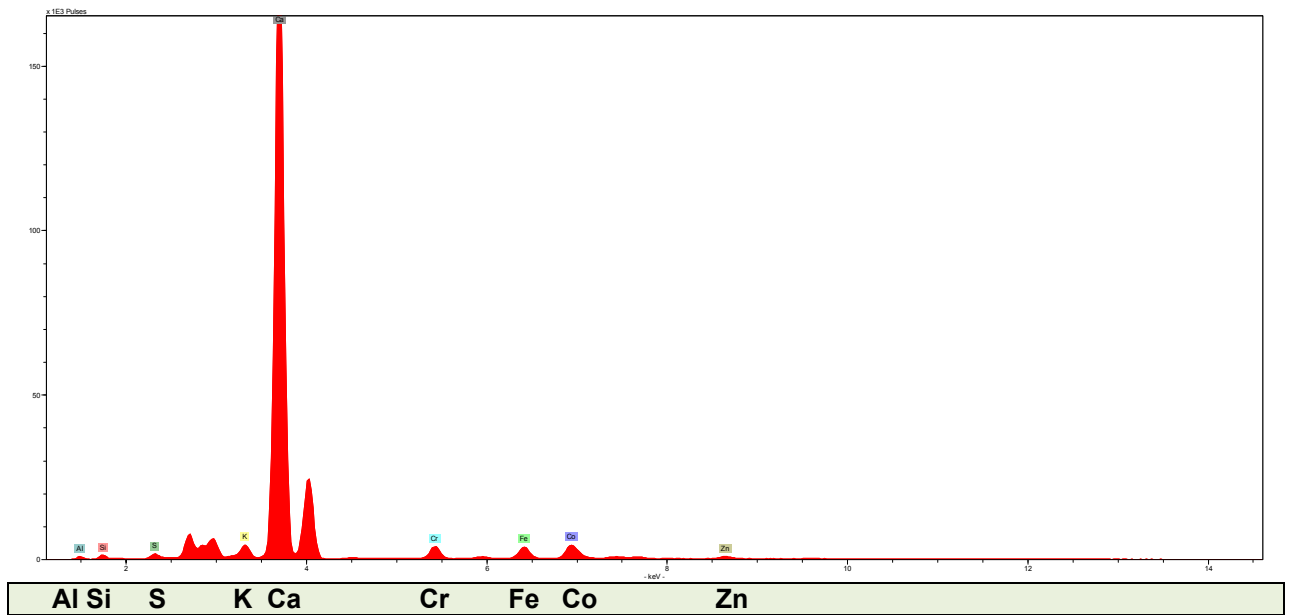
sample 31: 15 kV XRF spectrum of the blue layer.

Optical microscopy on cross section
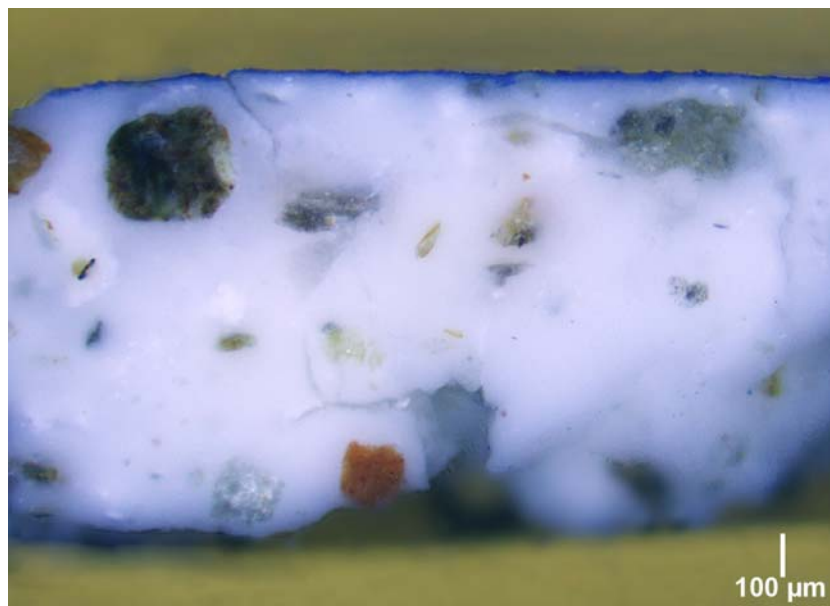
sample 31: cross-section photograph (white reflected light).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

48
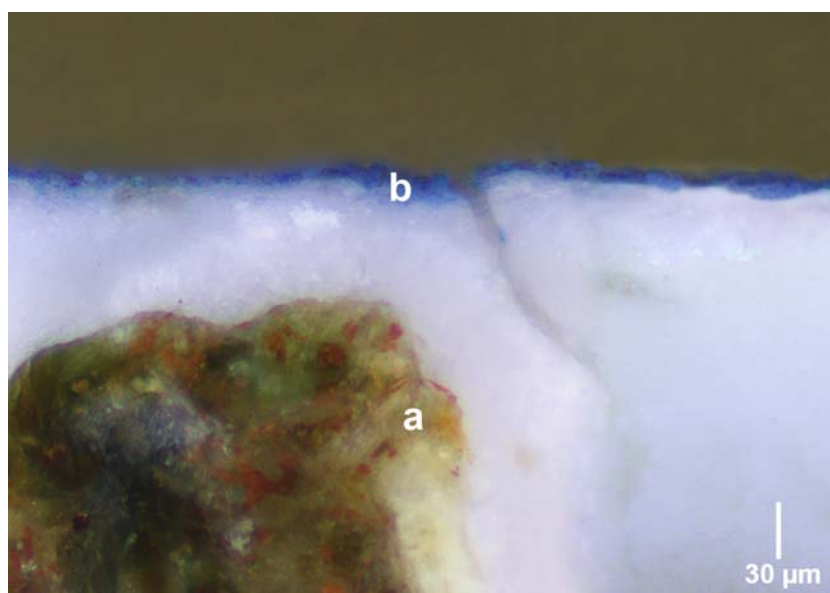
sample 31: detail with indication of the layers (white reflected light).
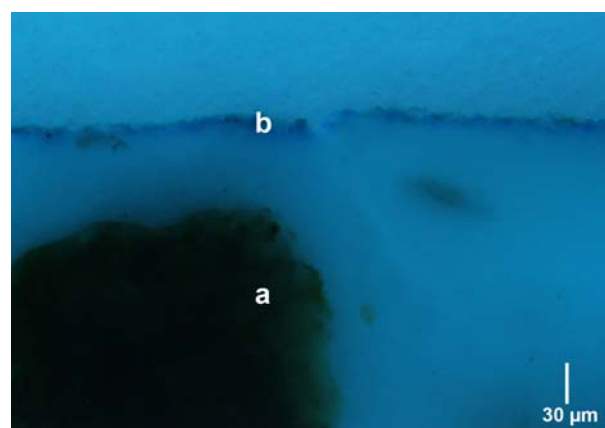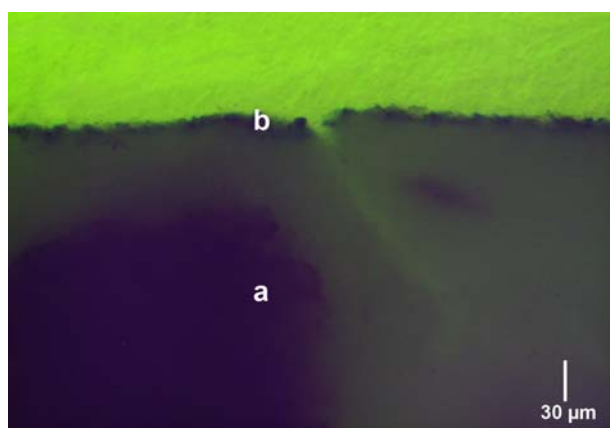
sample 31: detail (reflected light, on the left SWB filter, on the right UV filter).

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (µm)	description and composition
b	blue		10-12	paint layer of a blue modern pigment (probably Cobalt Blue with modified chemical composition)
a	white		-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

49

Code	Sample type	Sampling zone	Adopted analisys
32	electric blue pictorial fragment	west arm, western side, background	ST, XRF, OM-RL, HT, FT-IR
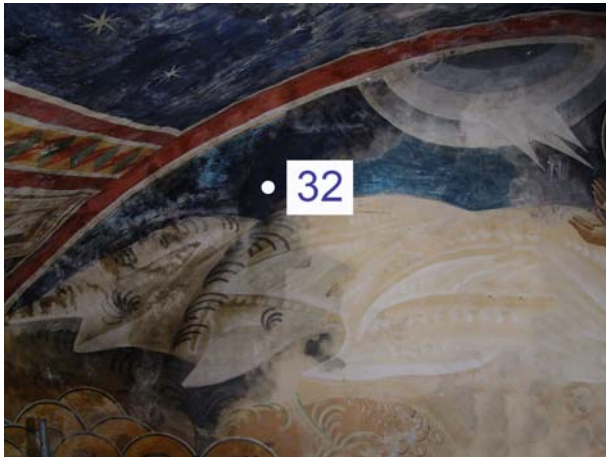
sample 32: sampling point.

Stereoscopic microscopy

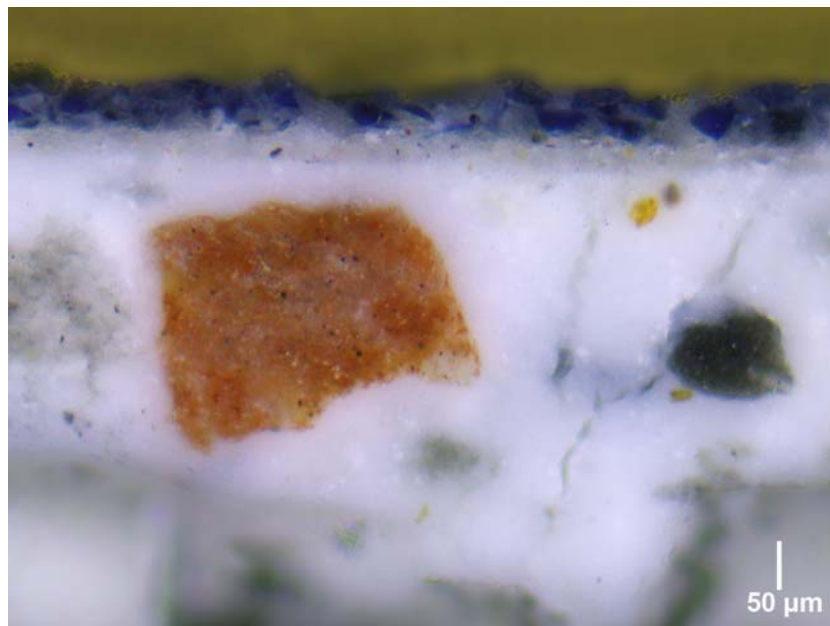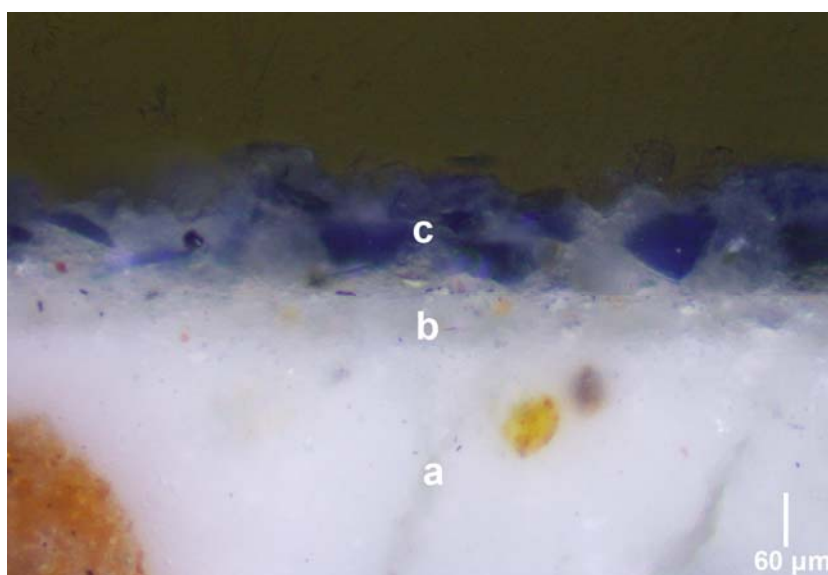sample 32: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

50

XRF measurements

layer	Chemical Elements				possible compounds
	main	secondary	minority	in traces	
blue	Ca		Si S Fe Co	K Ti Mn Ni Cu As	calcite, Smalt
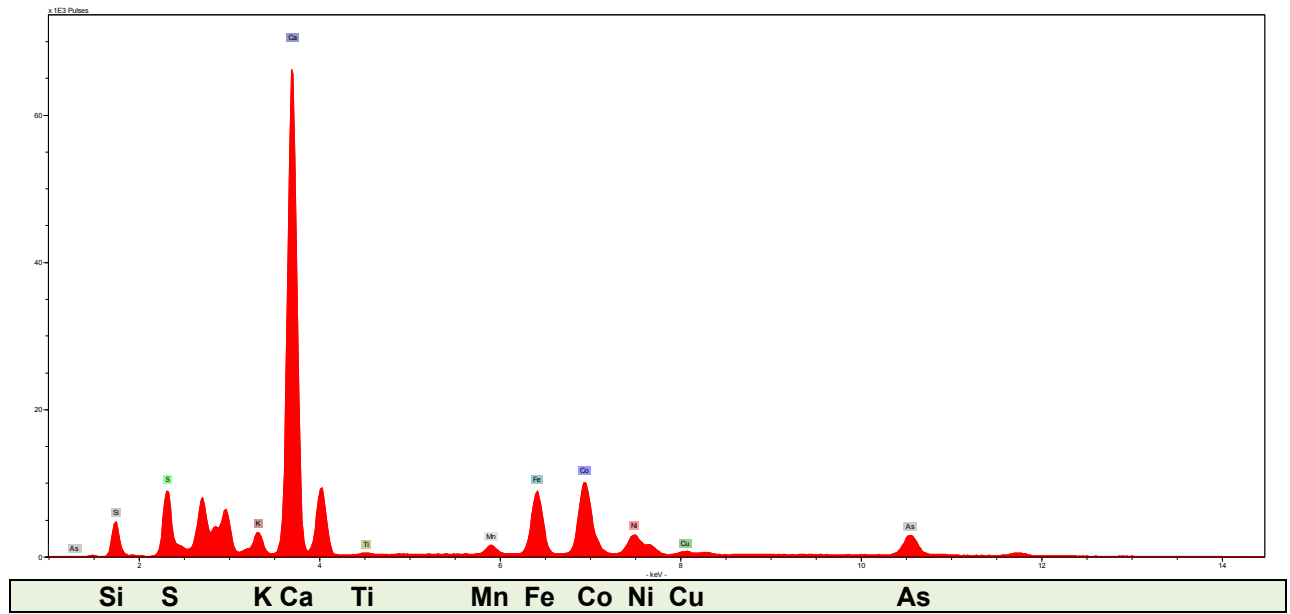
sample 32: 15 kV XRF spectrum of the blue layer.

Optical microscopy on cross section
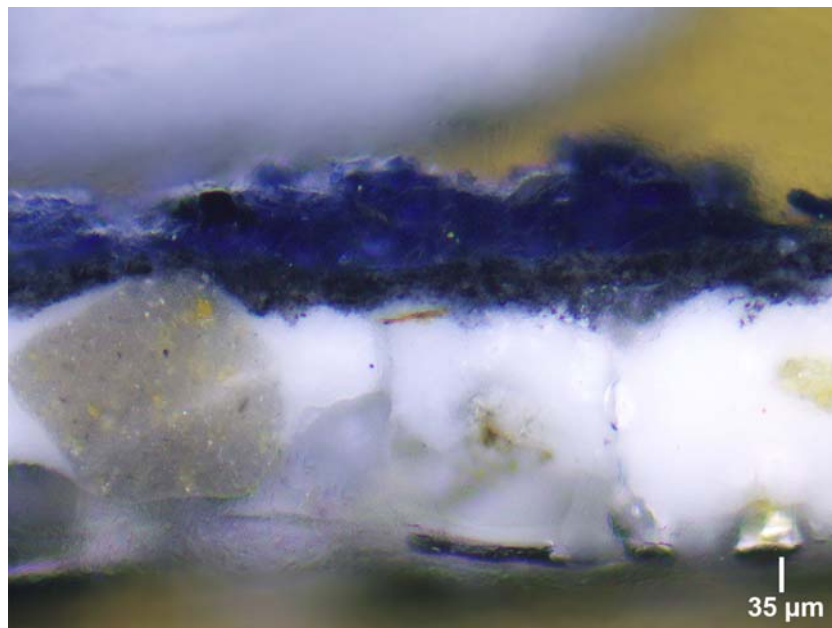
sample 32: cross-section photograph (white reflected light).

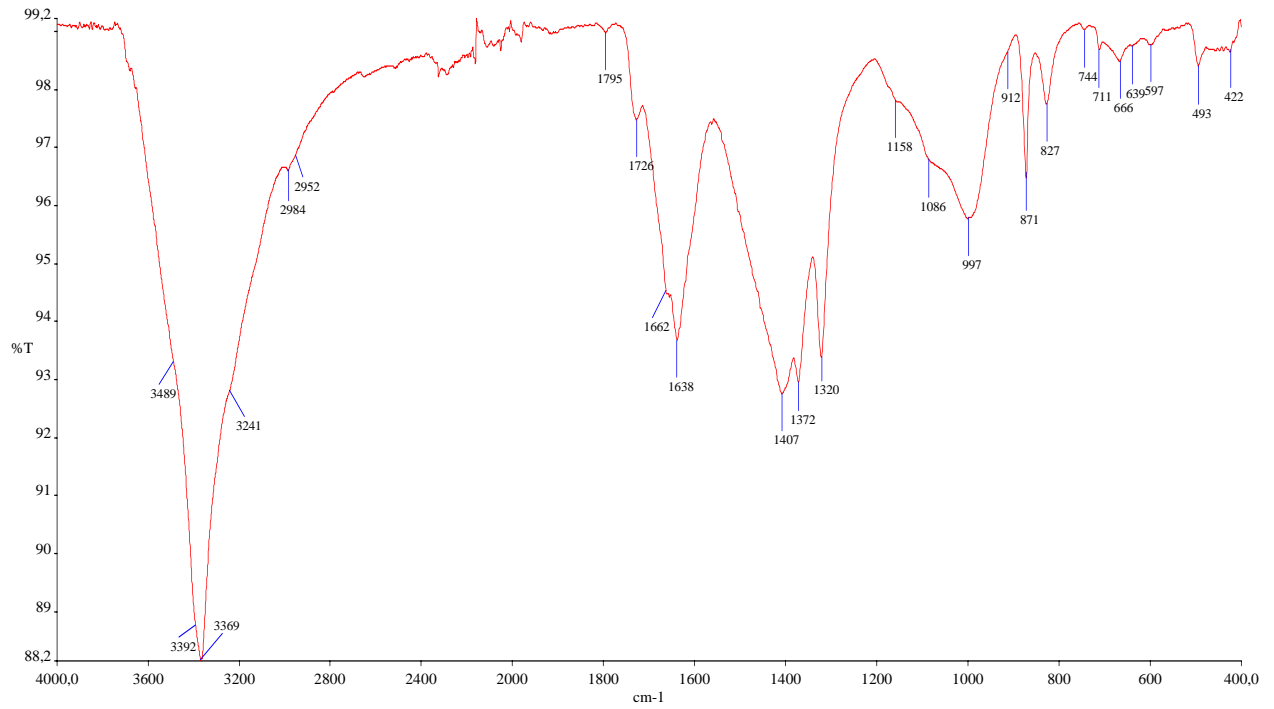Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

51
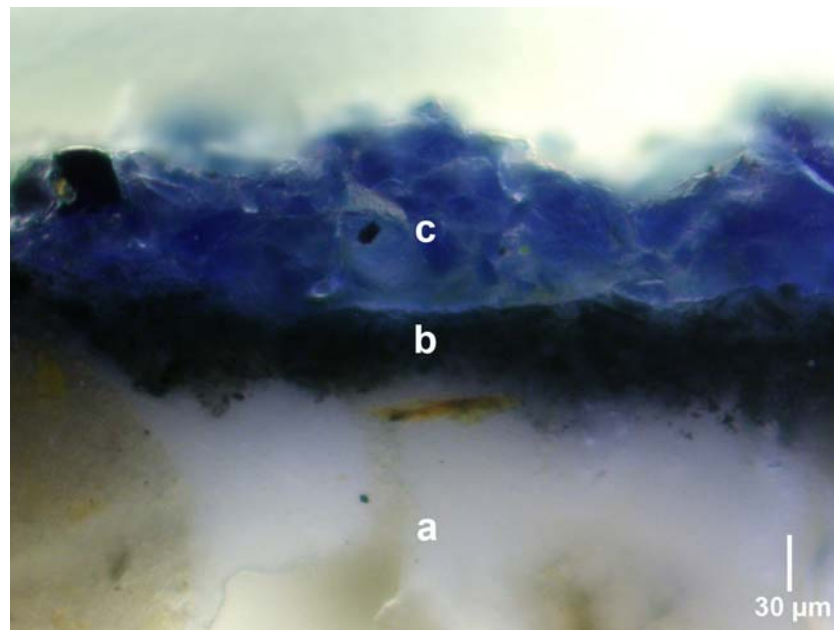
sample 32: detail with indication of the layers (white reflected light).
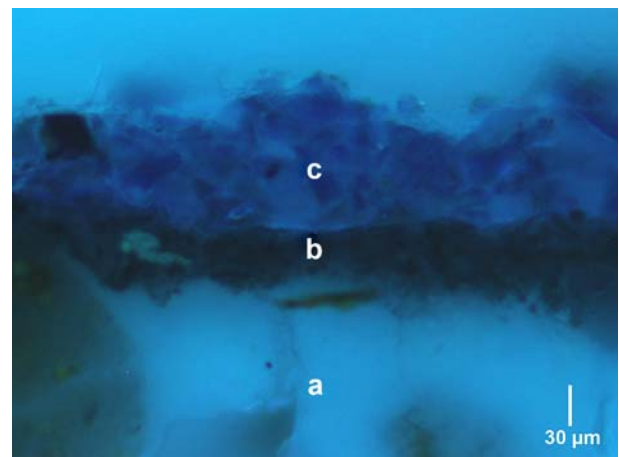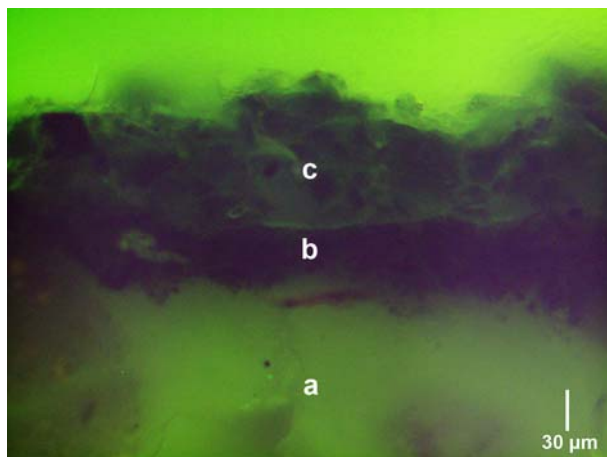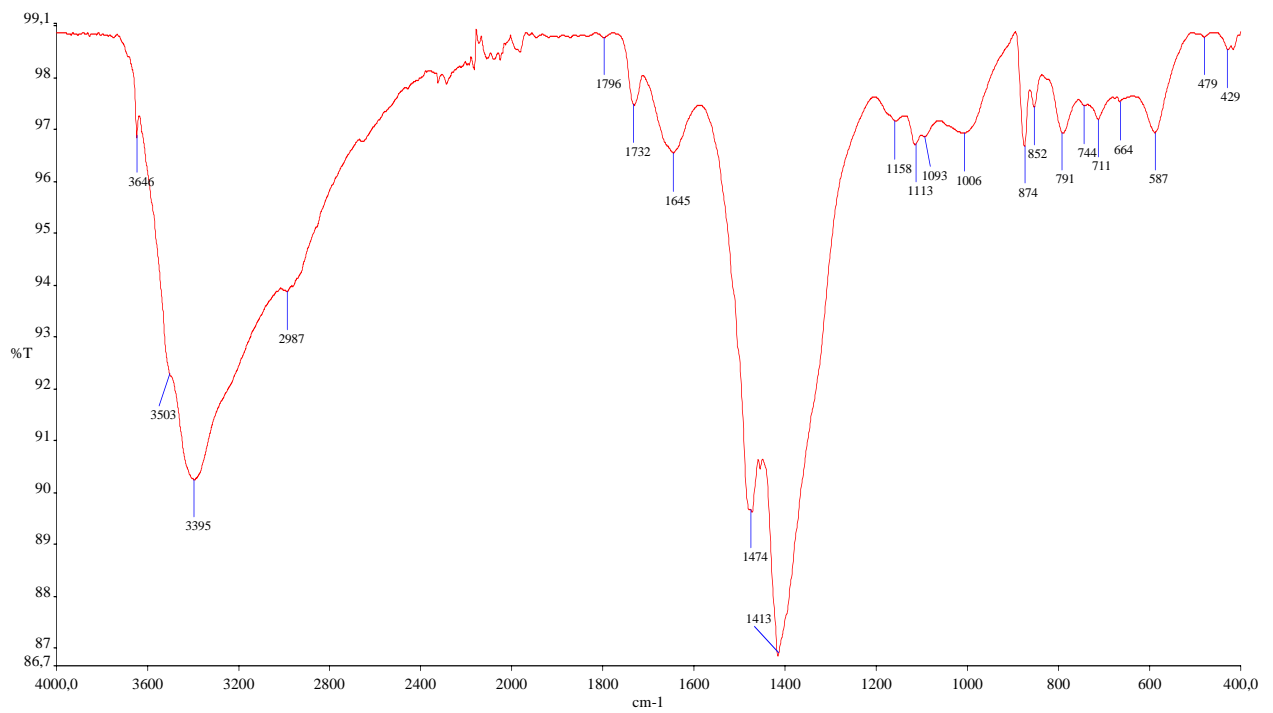

sample 32: detail (reflected light, on the left SWB filter, on the right UV filter).

FT-IR spectroscopy

layer	compounds	signals (cm⁻¹)	estimated quantity
c	Smalt	1013, 780, 455	++++
	calcite	1447	+
	Ca-oxalates	1641, 1323, 780	++
	Mg-oxalates	3392, 1373	traces
	organic compound	1730	traces

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

52
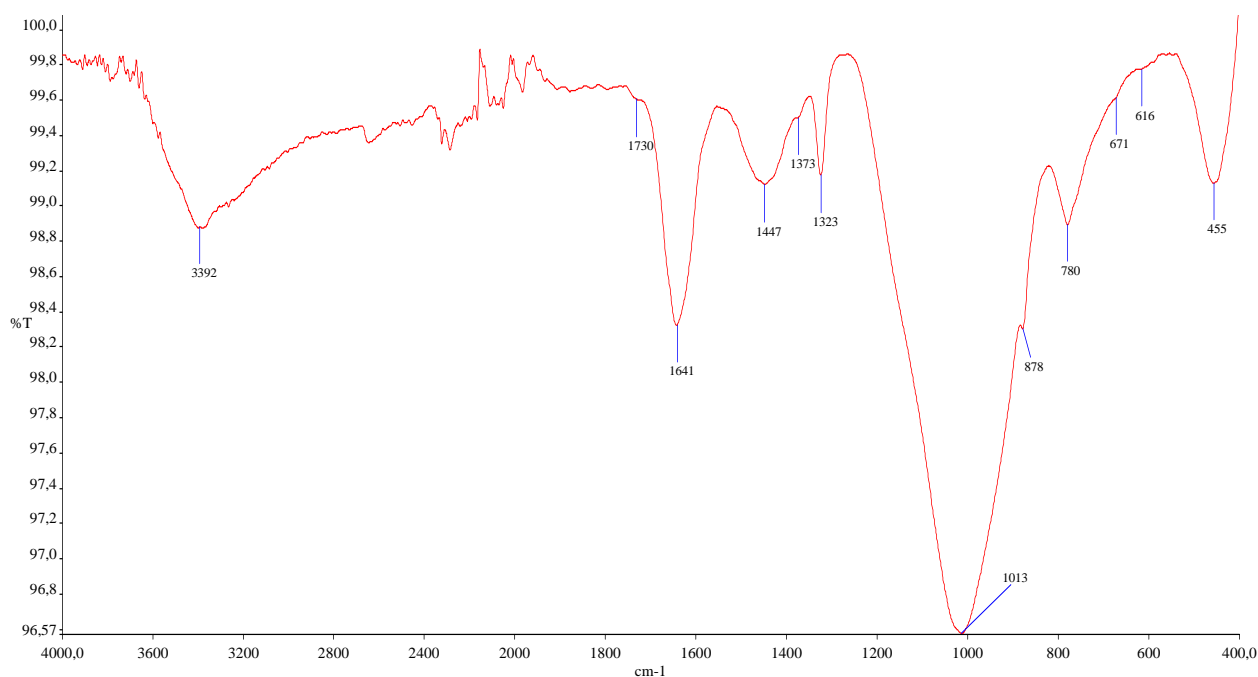
sample 32: FT-IR spectrum of the layer (**c**).

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (µm)	description and composition
c	blue		20-120	paint layer containing Smalt and oxalates; a scarce quantity of calcite and traces of an organic compound were also recognized
b	black		20-50	lime-based paint layer of Carbon Black
a	white		-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

53

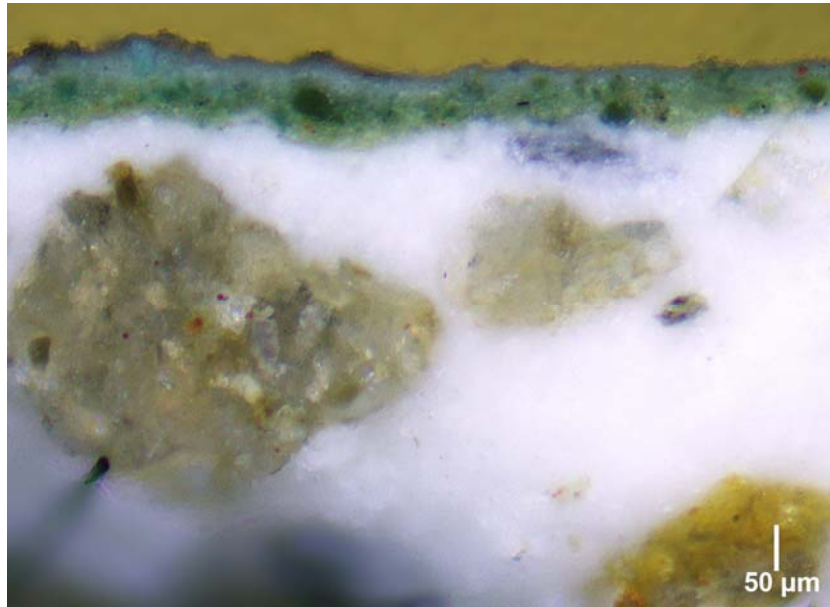| Code	Sample type	Sampling zone	Adopted analisys
33	gray pictorial fragment	west arm, western side	ST, OM-RL, HT

sample 33: sampling point.

Stereoscopic microscopy

sample 33: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione
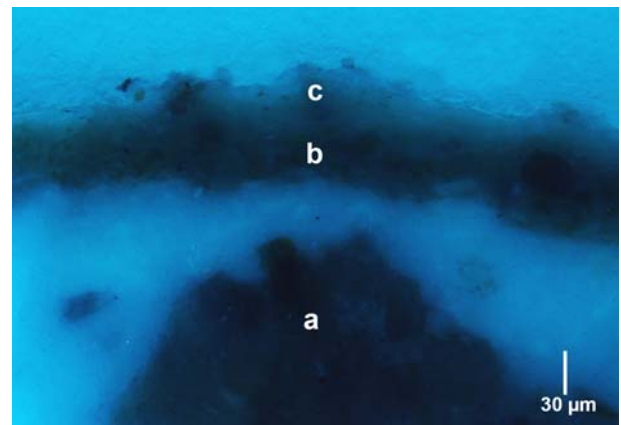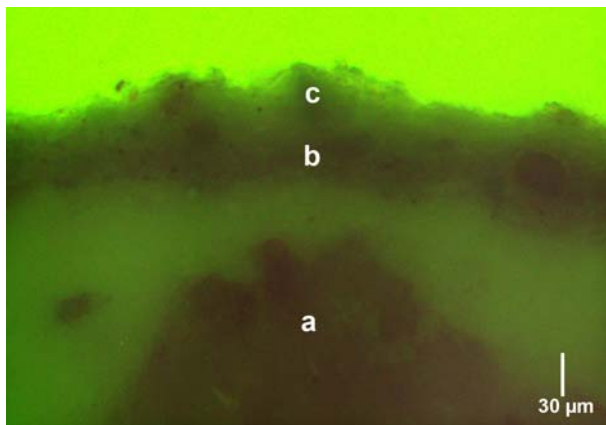
54

Optical microscopy on cross section
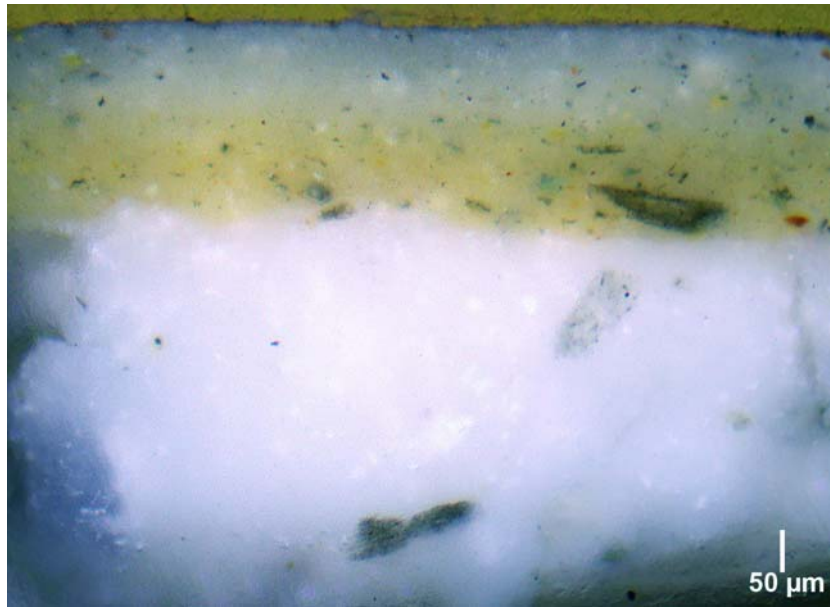
sample 33: cross-section photograph (white reflected light).
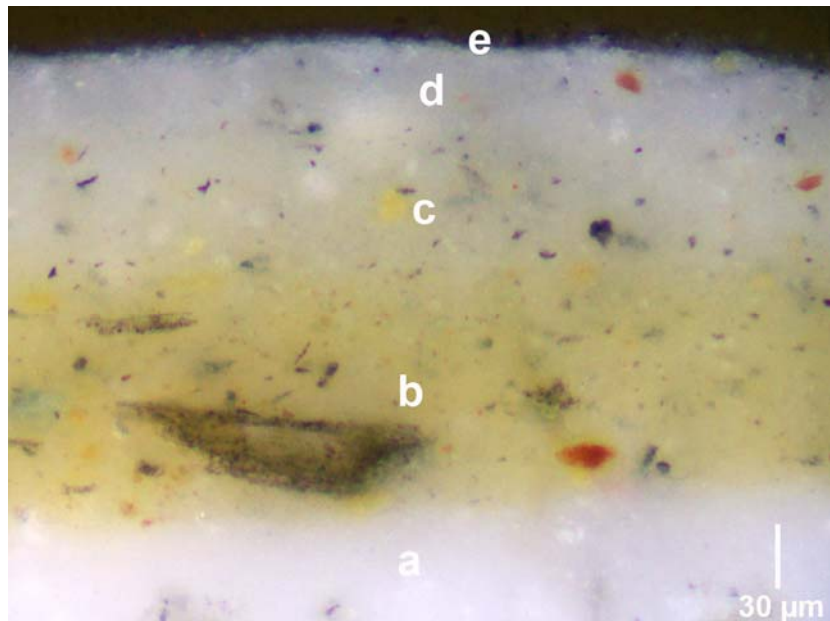
sample 33: detail with indication of the layers (white reflected light).
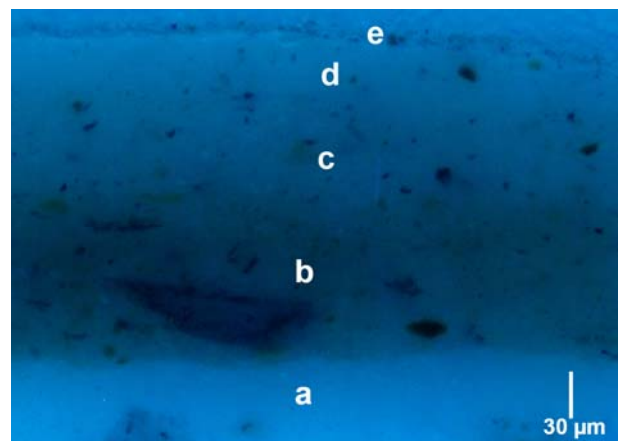
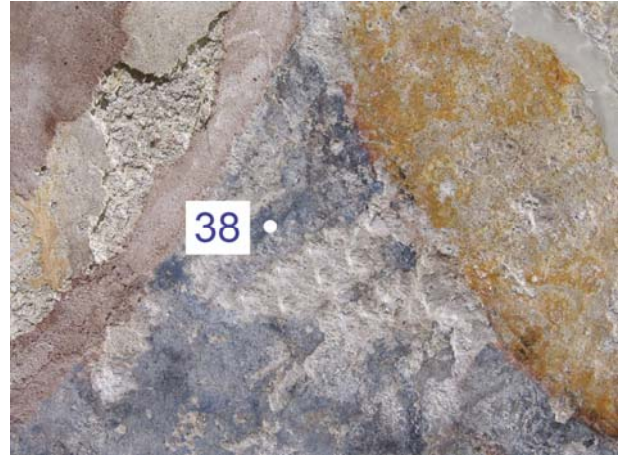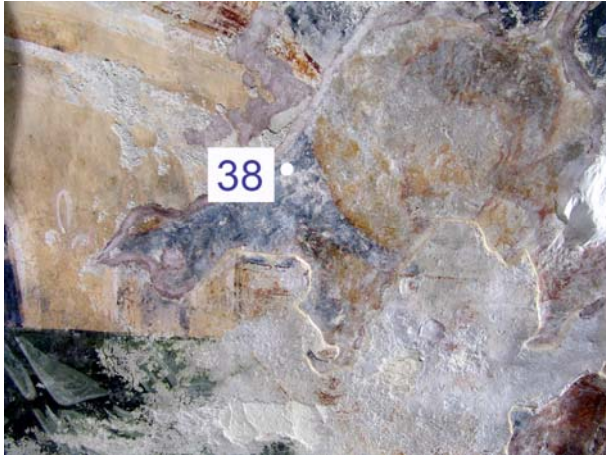sample 33: detail (reflected light, on the left SWB filter, on the right UV filter).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

55

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (µm)	description and composition
e	black		-	depositional carbon particles
d	pale-grey		~30	lime-based thin layer containing scarce Carbon Black
c	pale-grey		75-100	lime-based paint layer slightly pigmented by Carbon Black and Yellow Ochre
b	pale yellow		70-100	lime-based paint layer containing Yellow Ochre, Carbon Black and few particles of Red Ochre
a	white		-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

56

Code	Sample type	Sampling zone	Adopted analisys
34	salt efflorescences	west arm, western side	FT-IR
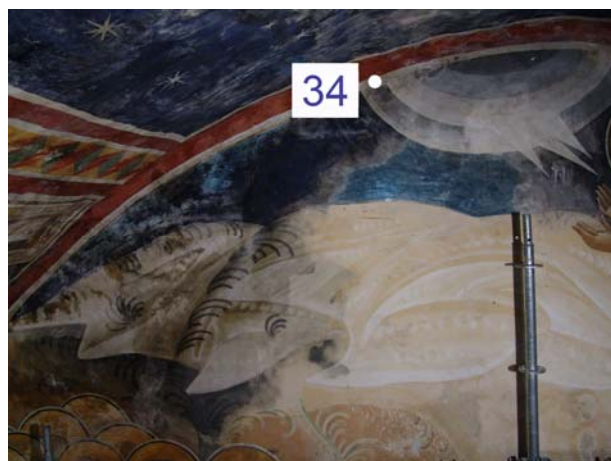
sample 34: sampling point.

FT-IR spectroscopy

layer	compounds	signals (cm^{-1})	estimated quantity
-	potassium nitrate (KNO$_3$)	1762, 1367, 824	

sample 34: FT-IR spectrum.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

57
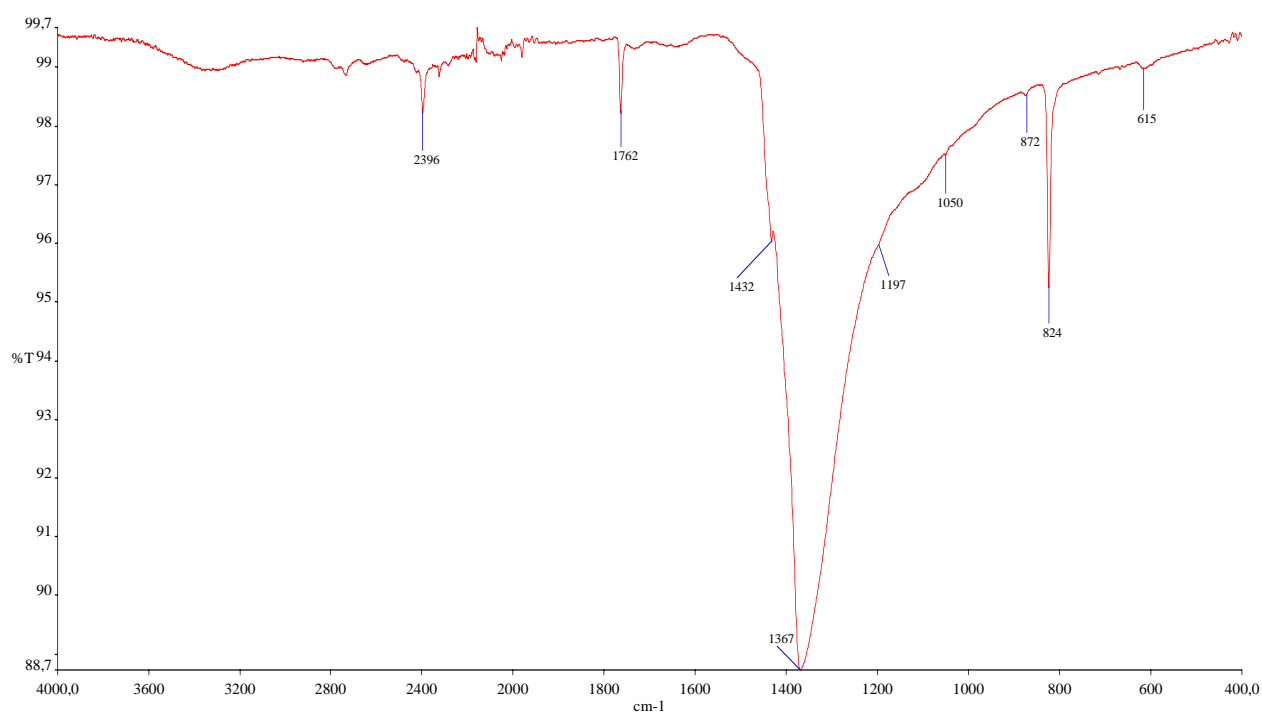
Code	Sample type	Sampling zone	Adopted analisys
35	blue pictorial fragment	west arm, southern side, left register, Saint's cloak	ST, XRF, OM-RL, HT, FT-IR
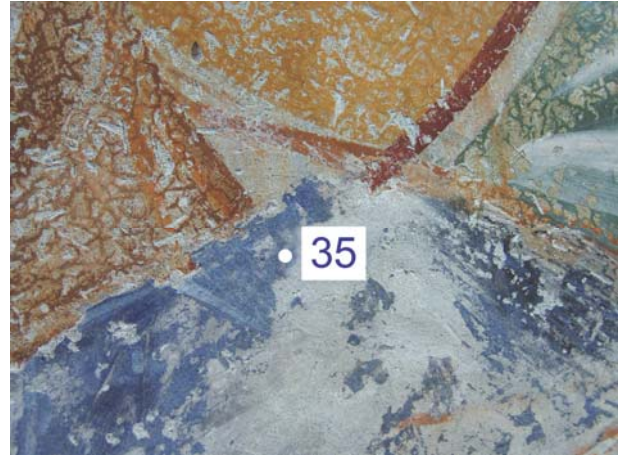
sample 35: sampling point.

Stereoscopic microscopy
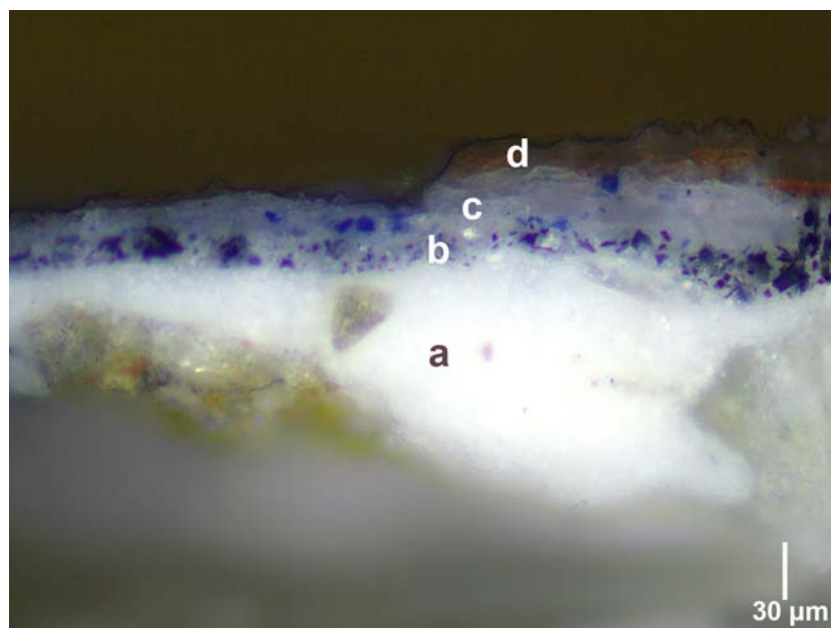

1 mm

sample 35: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

58

XRF measurements

| layer	Chemical Elements				possible compounds
	main	**secondary**	**minority**	**in traces**	
blue	Ca	Co	Si S K Fe Ni	Mg Al Mn Cu As	calcite, Smalt

sample 35: 15 kV XRF spectrum of the blue layer.
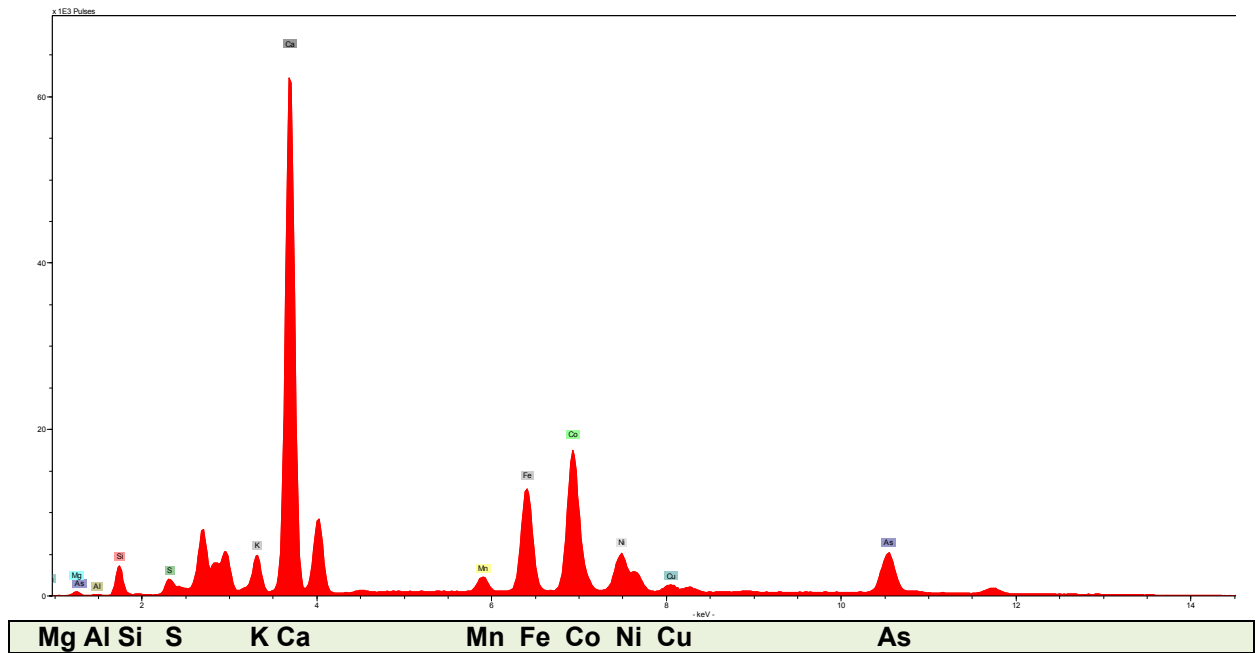
Optical microscopy on cross section

sample 35: cross-section photograph (white reflected light).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione
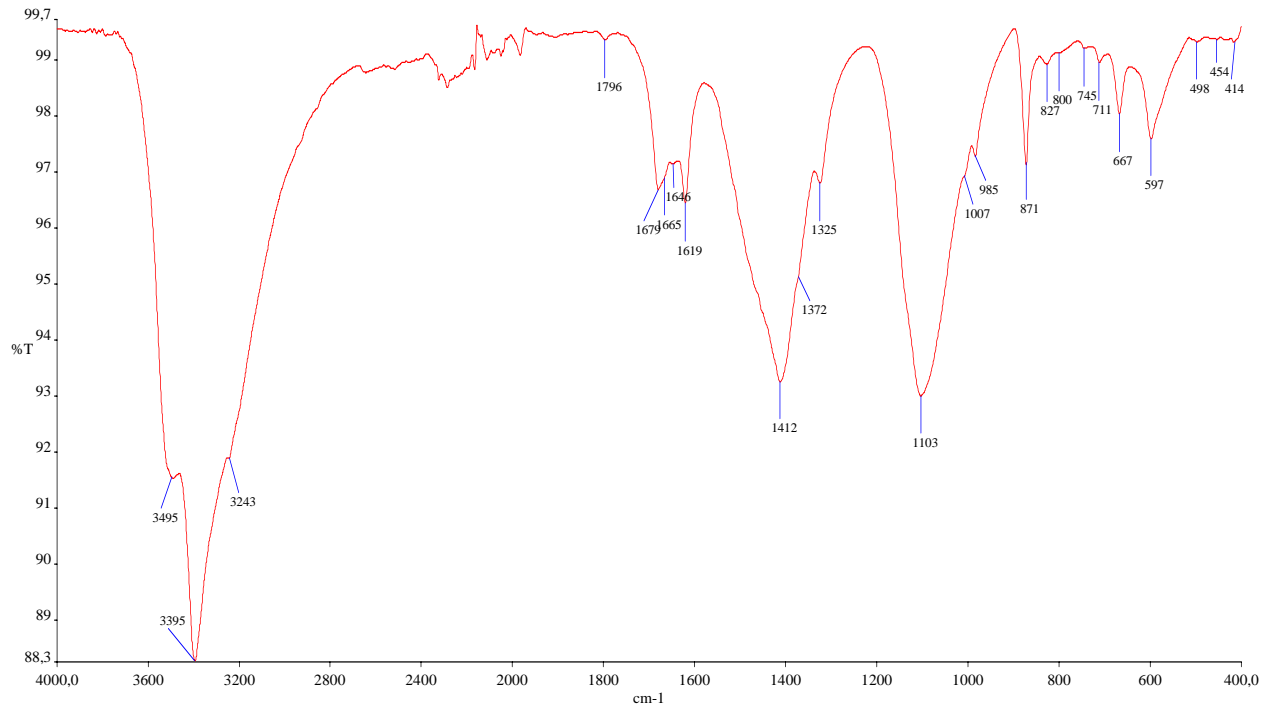
59

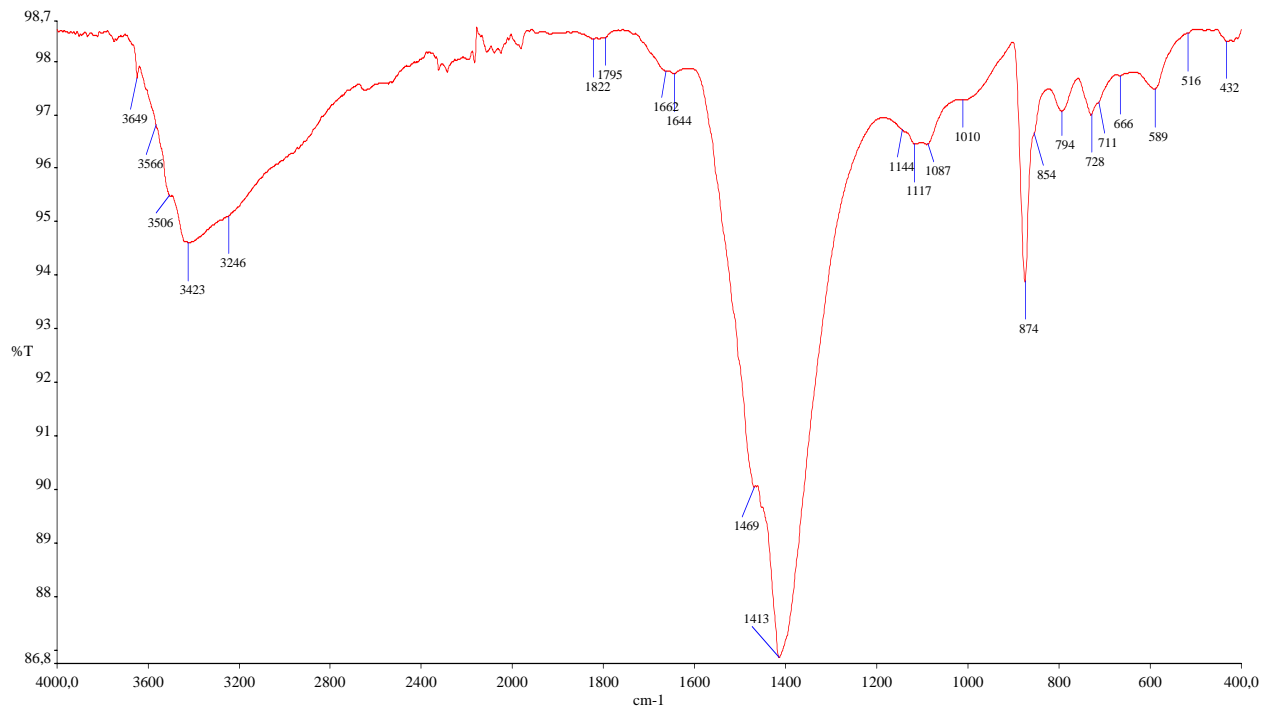sample 35: detail with indication of the layers (white reflected light).
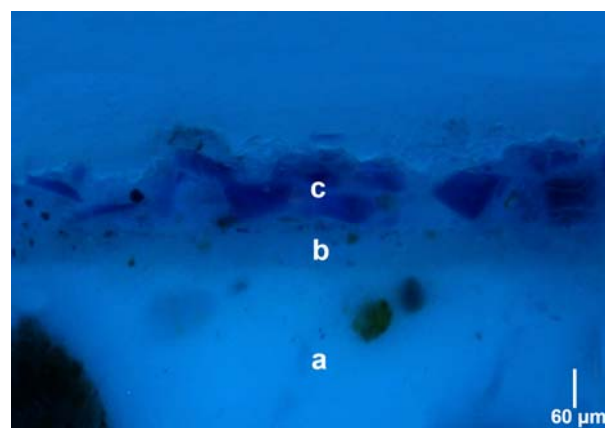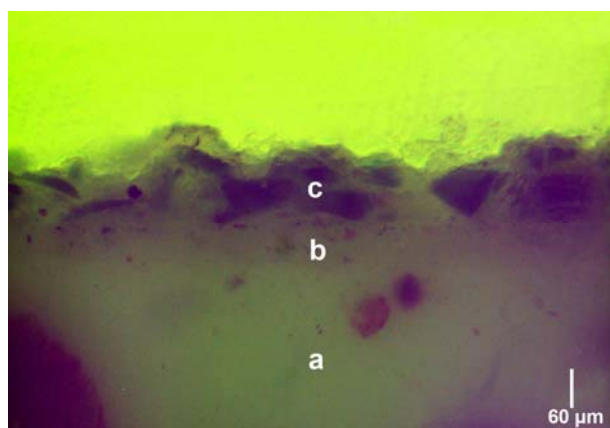
sample 35: detail (reflected light, on the left SWB filter, on the right UV filter).

FT-IR spectroscopy

layer	compounds	signals (cm⁻¹)	estimated quantity
c	calcite	1795, 1407, 871, 711	+++
	Ca-oxalates	1638, 1320	+++
	Mg-oxalates	3392, 3369, 1662, 1372, 1320, 827	+++
	Smalt	1086, 997, 455	++
	organic compound	2984, 2952, 1726	+
b	calcite	1796, 1413, 874, 711	++++
	hydromagnesite	3646, 3503, 3395, 1645, 1474, 852, 791	+++
	organic compound	2987, 1732, 1158	+

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

60

sample 35: FT-IR spectrum of the layer (**c**).

sample 35: FT-IR spectrum of the layer (**b**).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

61

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (µm)	description and composition
c	blue	-	55-85	lime-based paint layer containing Smalt, oxalates and traces of a lipidic compound
b	grey	-	35-40	lime-based paint layer pigmented by Carbon Black and scarce Yellow Ochre; it also contains hydromagnesite and a lipidic compound
a	white	-	-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

62

Code	Sample type	Sampling zone	Adopted analisys
36	green pictorial fragment	west arm, southern side, left register	ST, OM-RL, HT

sample 36: sampling point.

Stereoscopic microscopy

1 mm

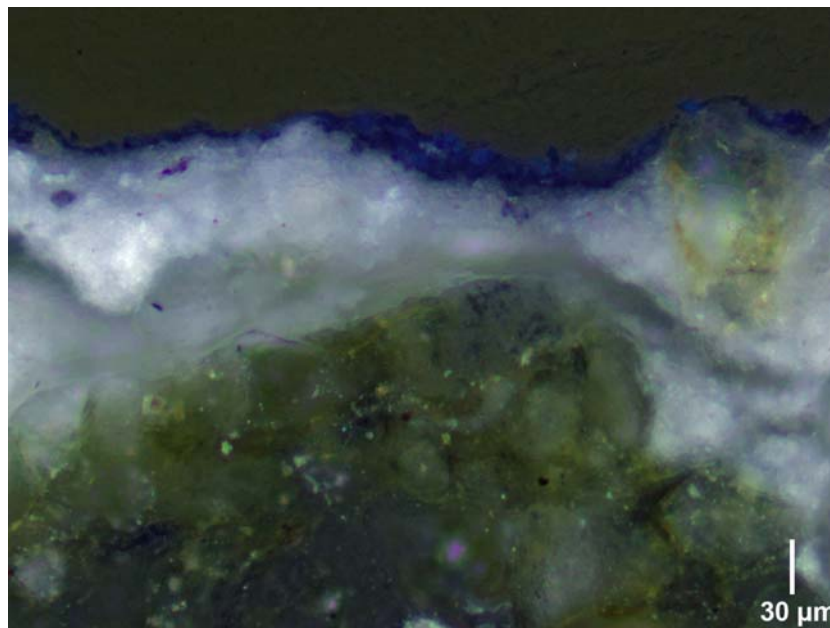sample 36: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione
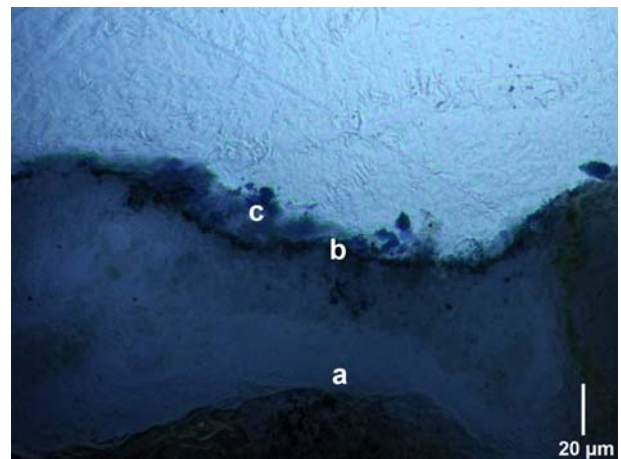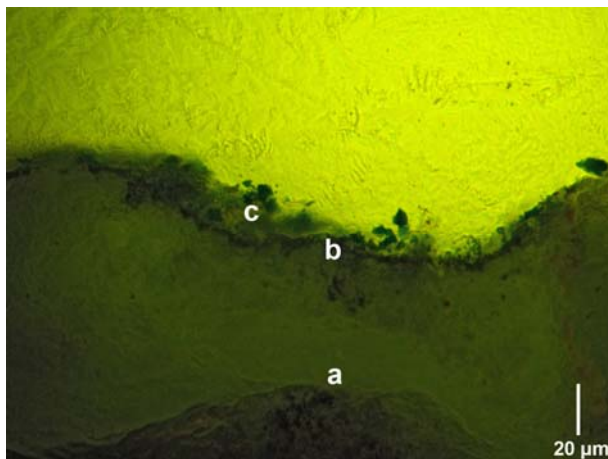
63

sample 36: cross-section photograph (white reflected light).
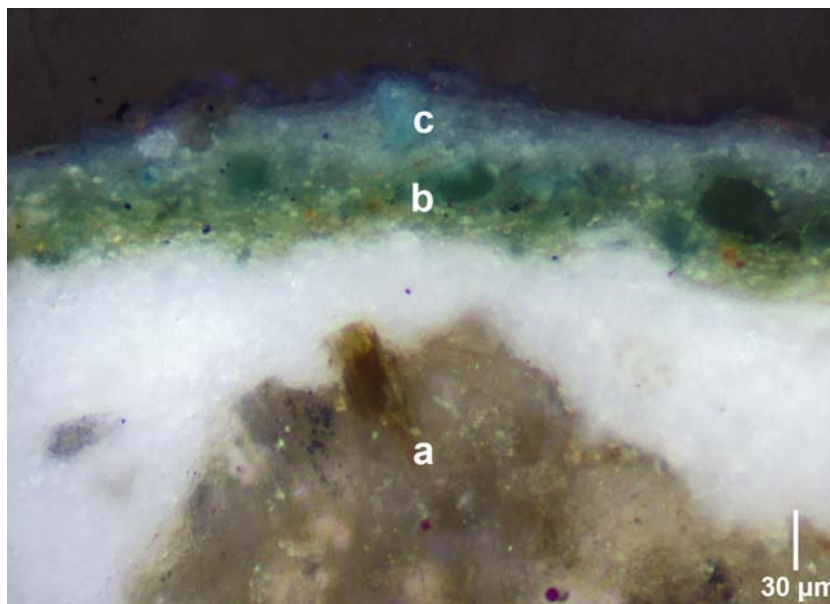
sample 36: detail with indication of the layers (white reflected light).

sample 36: detail (reflected light, on the left SWB filter, on the right UV filter).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

64

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (μm)	description and composition
c	pale green		20-25	lime-based paint layer containing Green Earth
b	dark green		45-71	lime-based paint layer pigmented by Green Earth; few particles of Yellow Ochre and Carbon Black are also present
a	white		-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

65

Code	Sample type	Sampling zone	Adopted analisys
38	blue pictorial fragment	west arm, northern side, right register	ST, XRF, OM-RL, HT FT-IR

sample 38: sampling point.

Stereoscopic microscopy

0.5 mm
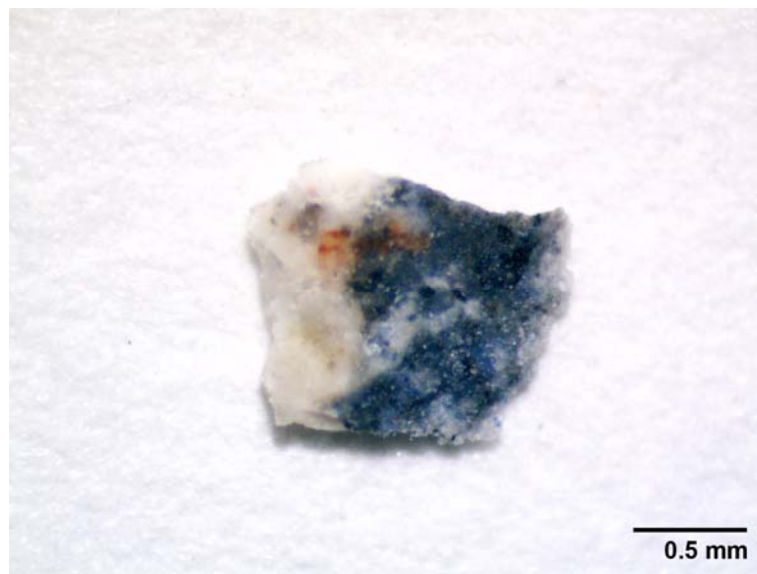
sample 38: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

66

XRF measurements

layer	Chemical Elements				possible compounds
	main	**secondary**	**minority**	**in traces**	
blue	Ca	S	Fe	Al Si K Ni Pb	calcite, gypsum, ochre

Al Si S   K Ca   Fe   Ni   Pb
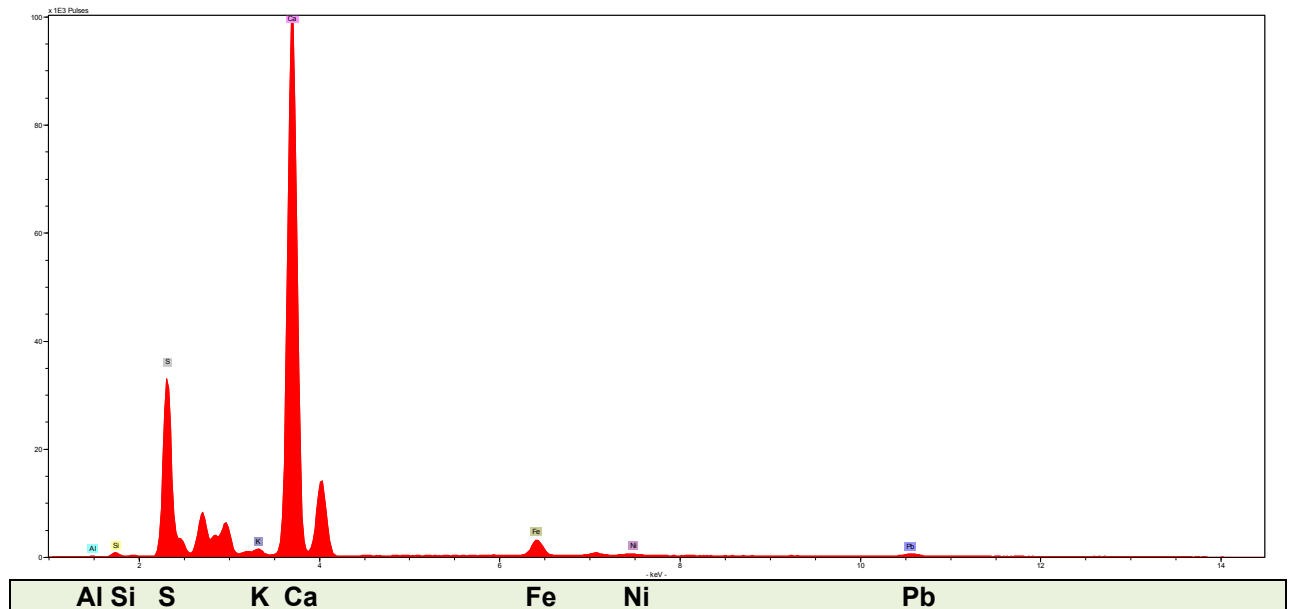
sample 38: 15 kV XRF spectrum of the blue layer.

Optical microscopy on cross section

sample 38: cross-section photograph (white reflected light).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

67
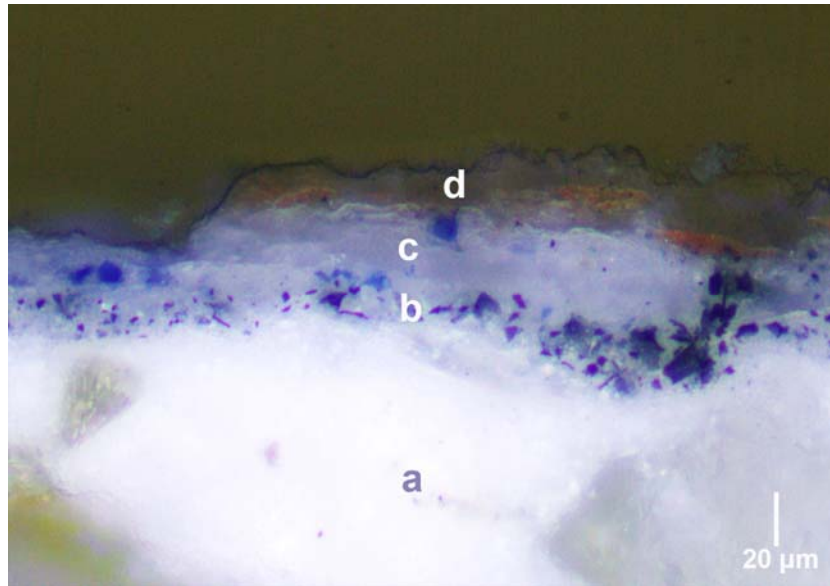
sample 38: detail with indication of the layers (white reflected light).
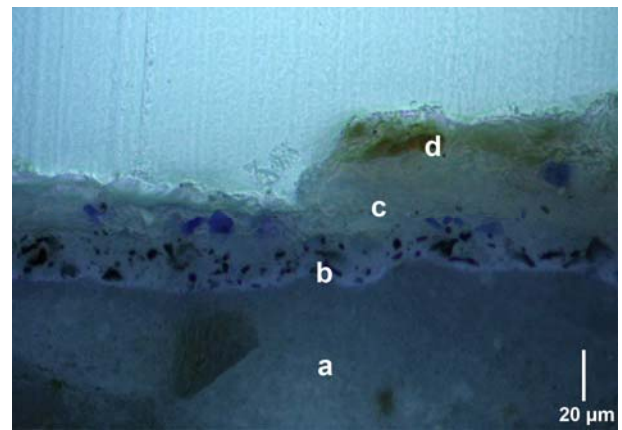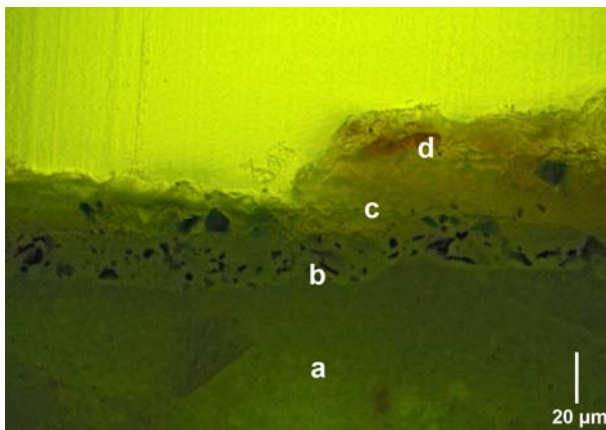
sample 38: detail (reflected light, on the left SWB filter, on the right UV filter).

FT-IR spectroscopy

layer	compounds	signals (cm^{-1})	estimated quantity
d	calcite	1796, 1412, 871, 711	+++
	gypsum	3495, 3243, 1679, 1619, 1103, 1007, 667, 597, 454	+++
	Mg-oxalates	3395, 1665, 1372, 1325, 827	++
	Ca-oxalates	1646, 1325	+
	sulphates?	985	+
b	hydromagnesite	3649, 3506, 3423, 1644, 1469, 1413, 1117, 854, 794, 589, 432	+++
	calcite	1795, 1413, 874, 711	++++
	dolomite	1822, 728	+

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

68

sample 38: FT-IR spectrum of the layer (**d**).

sample 38: FT-IR spectrum of the layer (**b**).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

69

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (µm)	description and composition
d	pink		0-30	residue of a patina composed by calcite, gypsum, oxalates and traces of Red Ochre finely grained
c	blue		15-30	deteriorated paint layer of Natural Ultramarine Blue (lapis lazuli)
b	black		12-20	irregular lime-based paint layer of Carbon Black also containing hidromagnesite and dolomite
a	white		-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

70

Code	Sample type	Sampling zone	Adopted analisys
39	blue pictorial fragment	western arm, vault, background of the cross	ST, XRF, OM-RL, HT
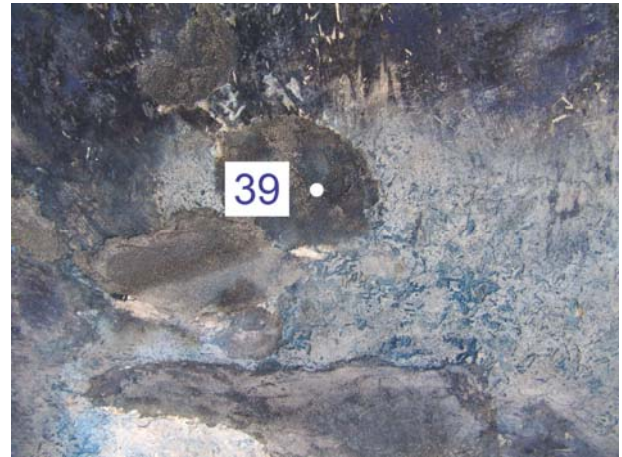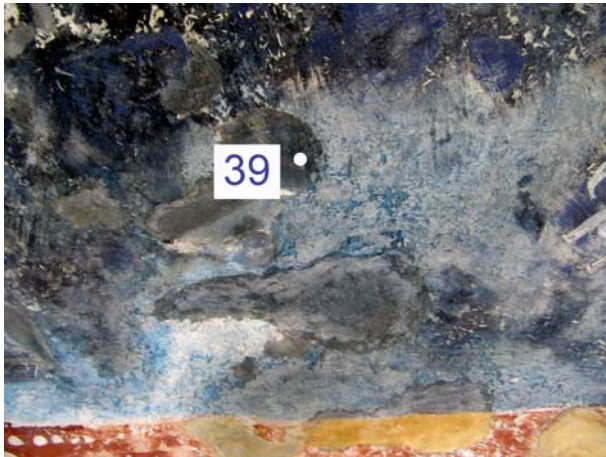
sample 39: sampling point.

Stereoscopic microscopy
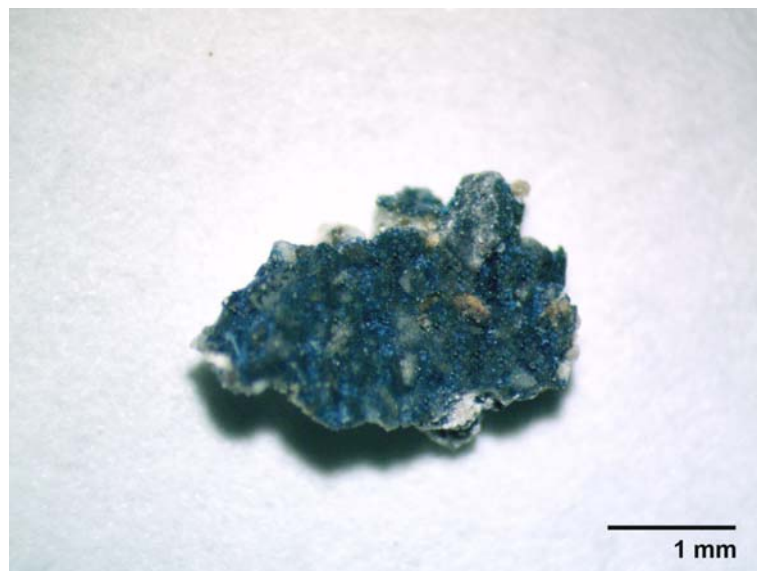
sample 39: photograph under the stereomicroscope.

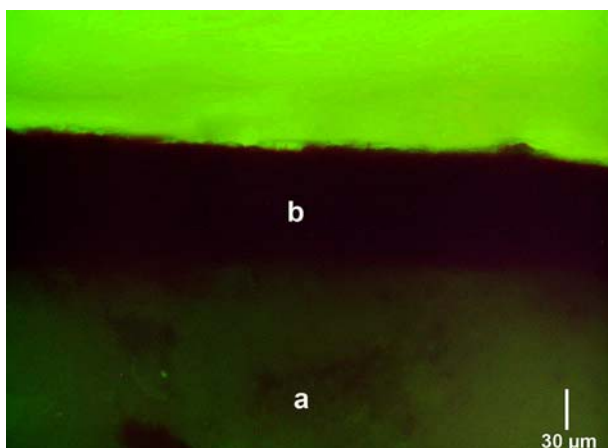Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

71

XRF measurements

layer	Chemical Elements				possible compounds
	main	**secondary**	**minority**	**in traces**	
blue	Ca	Fe	K Cr Co	Mg Al Si S Ti Ni Zn	calcite, cobalt pigment containing also Cr and Zn
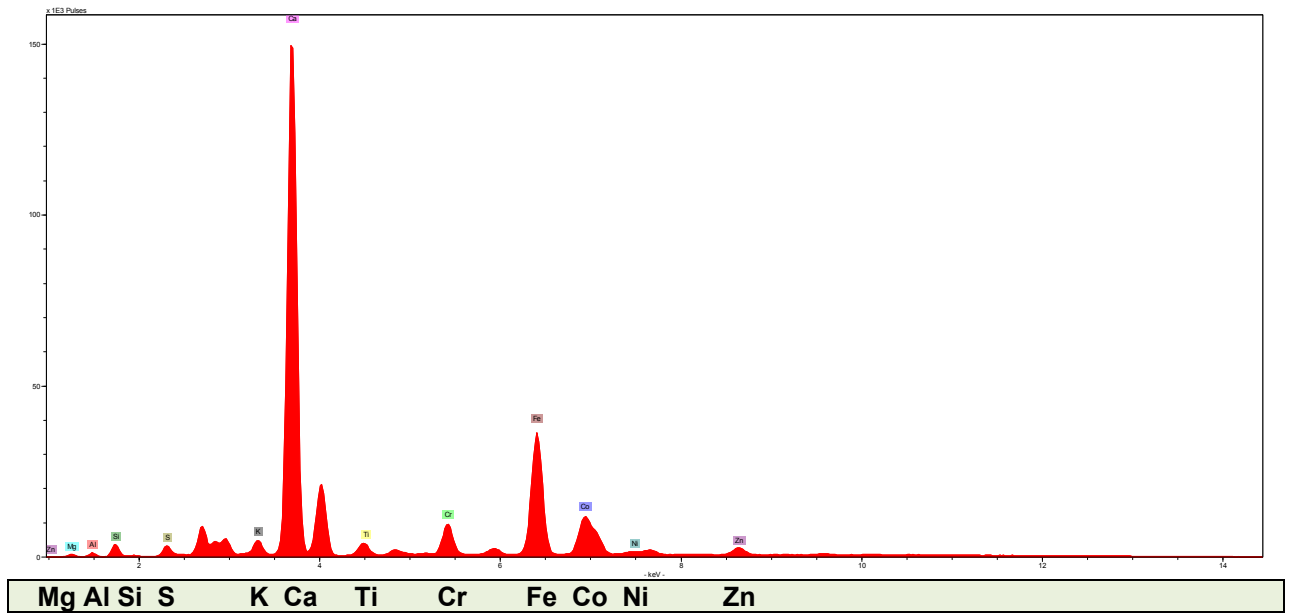
sample 39: 15 kV XRF spectrum of the blue layer.

Optical microscopy on cross section

sample 39: cross-section photograph (white reflected light).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

72
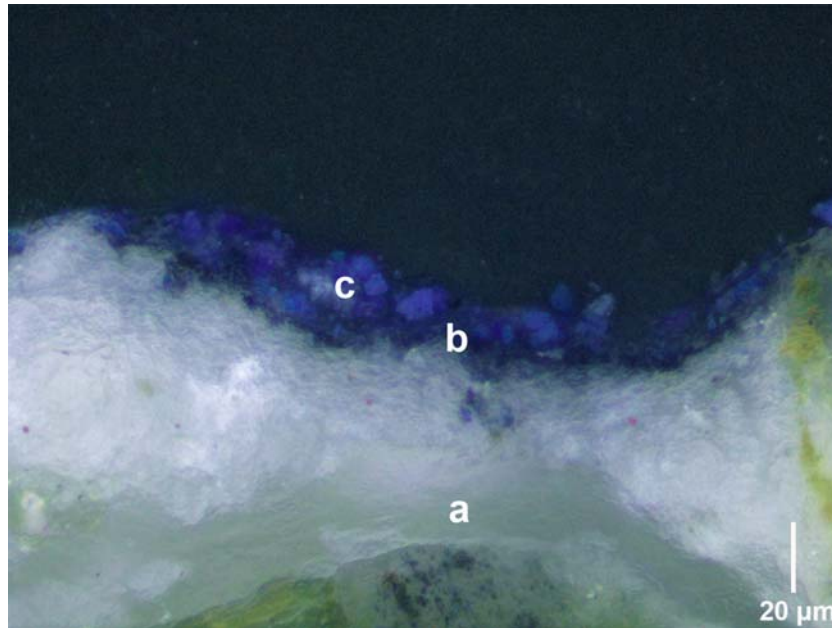
sample 39: detail with indication of the layers (white reflected light).

sample 39: detail (reflected light, on the left SWB filter, on the right UV filter).

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (µm)	description and composition
c	blue	-	0-15	paint layer of a blue modern pigment (probably Cobalt Blue with modified chemical composition)
b	black	-	0-10	thin layer of a very fine-grained black pigment
a	white	-	-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

73

Code	Sample type	Sampling zone	Adopted analisys
40	fibres	west arm, northern side, right register	OM-TL
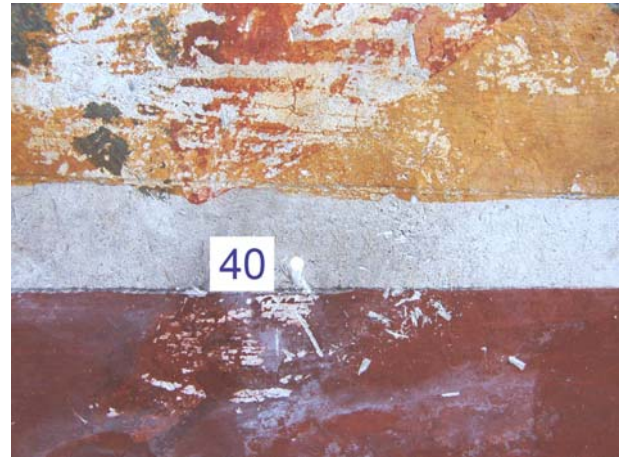
sample 40: sampling point.

Optical microscopy with transmitted light

The sample consists of two types of fibres: <u>wool</u> and probable <u>hemp</u>.

Under the microscope <u>wool fibre</u> is surrounded by a cuticle of flattened cells that look like overlapping scales. In addition, the intact fibre has a root with a larger diameter at its base.

<u>Hemp fibre</u> is cylindrical with some irregularities in form of transversal joints and longitudinal fractures; it looks like similar to flax's one, both in dimensions and general appearance, but joints are usually less abundant.
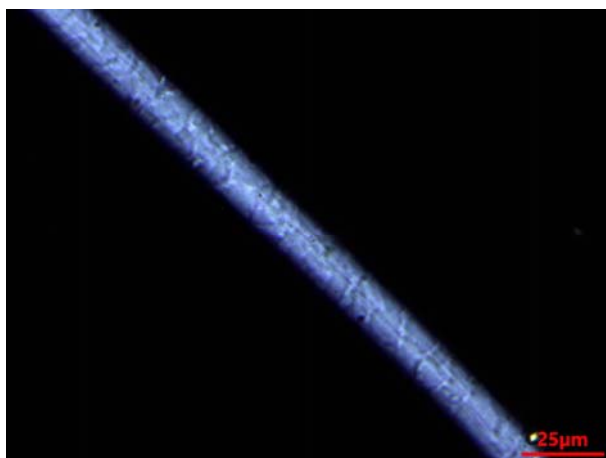
sample 40: wool fibre - microphotographs of the central zone
(transmitted light, X polars on the left, // polars on the right).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

74

sample 40: wool fibre - microphotographs of root (on the left) and termination (on the right)
(transmitted light, // polars).
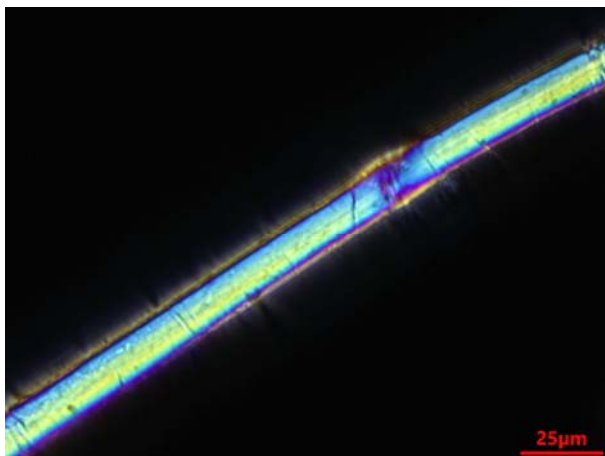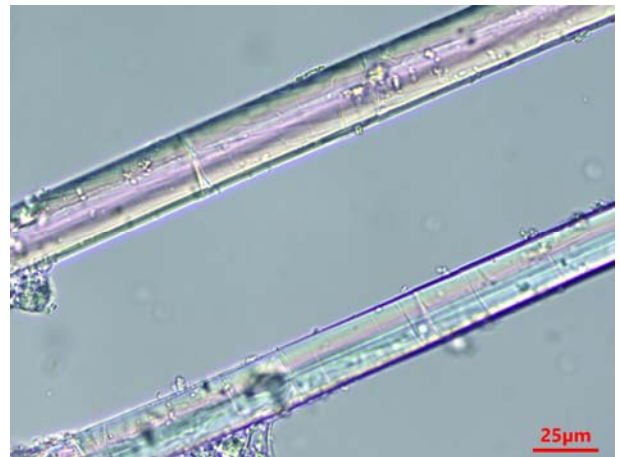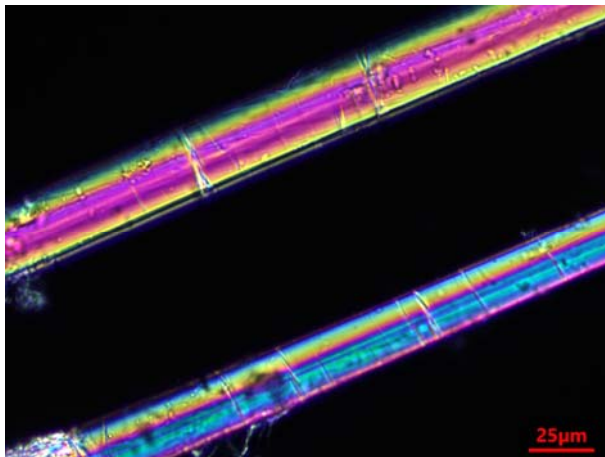
sample 40 – possible hemp fibre: microphotographs
(transmitted light, X polars on the left, // polars on the right).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

75

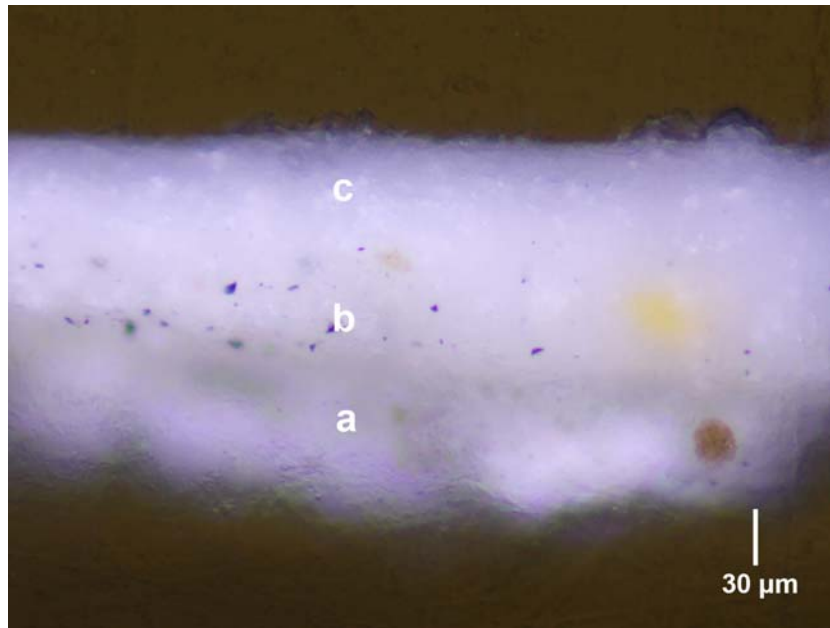| Code	Sample type	Sampling zone	Adopted analisys
41	red pictorial fragment with shiny appearance	west arm, northern side, right register	ST, OM-RL, HT FT-IR
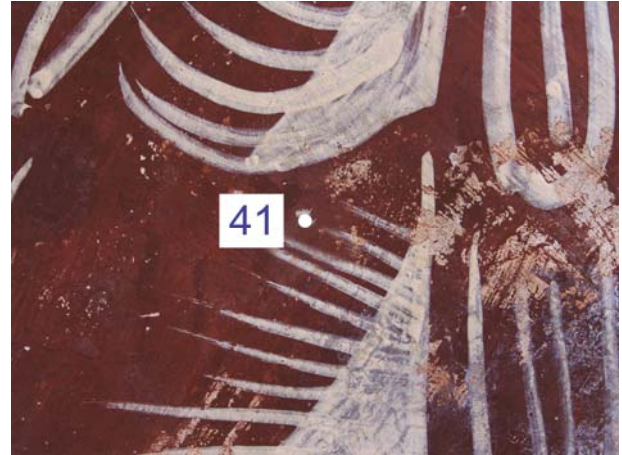
sample 41: sampling point.

Stereoscopic microscopy


0.5 mm
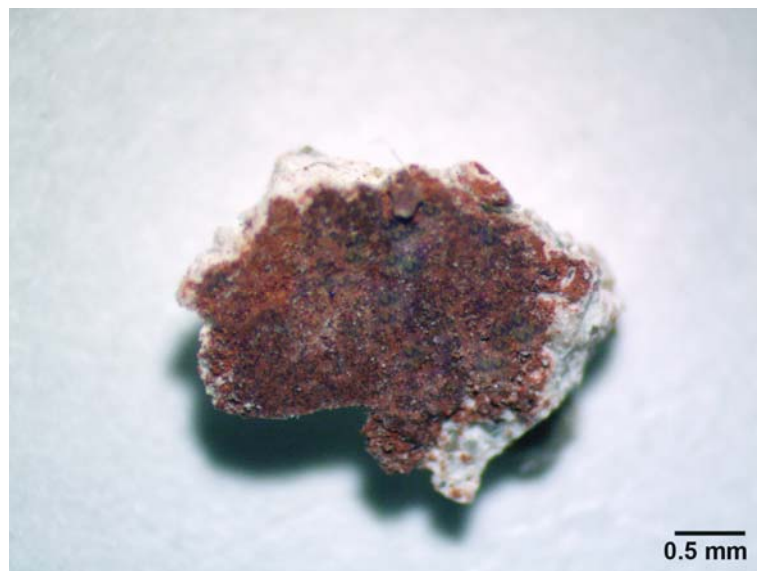
sample 41: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

76

Optical microscopy on cross section
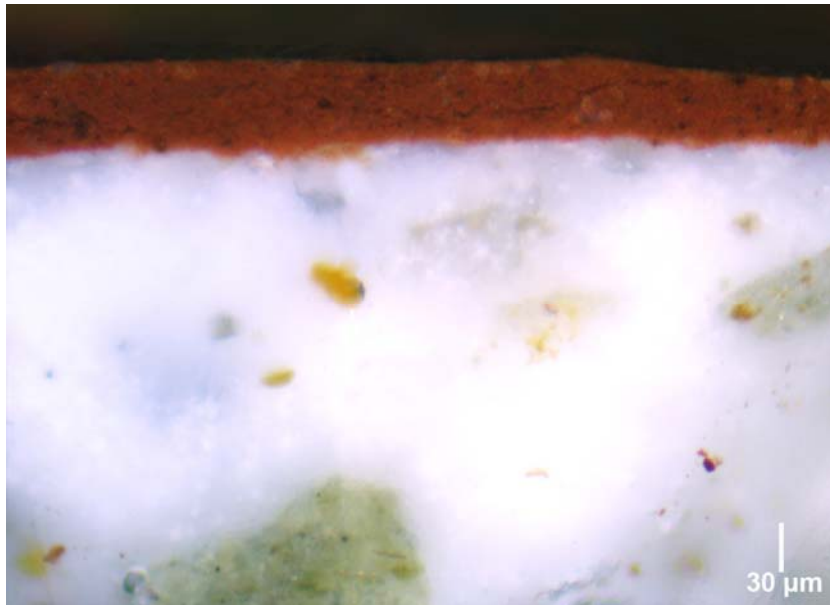
sample 41: cross-section photograph (white reflected light).
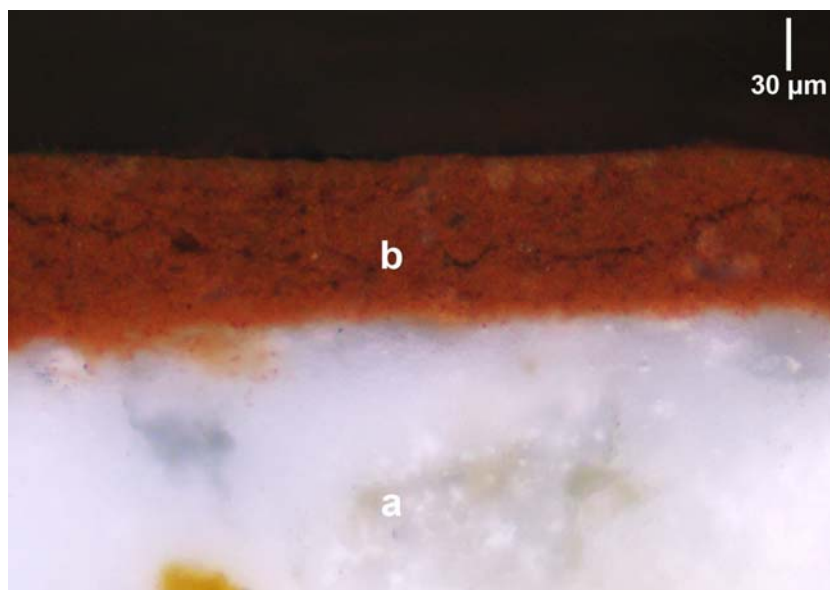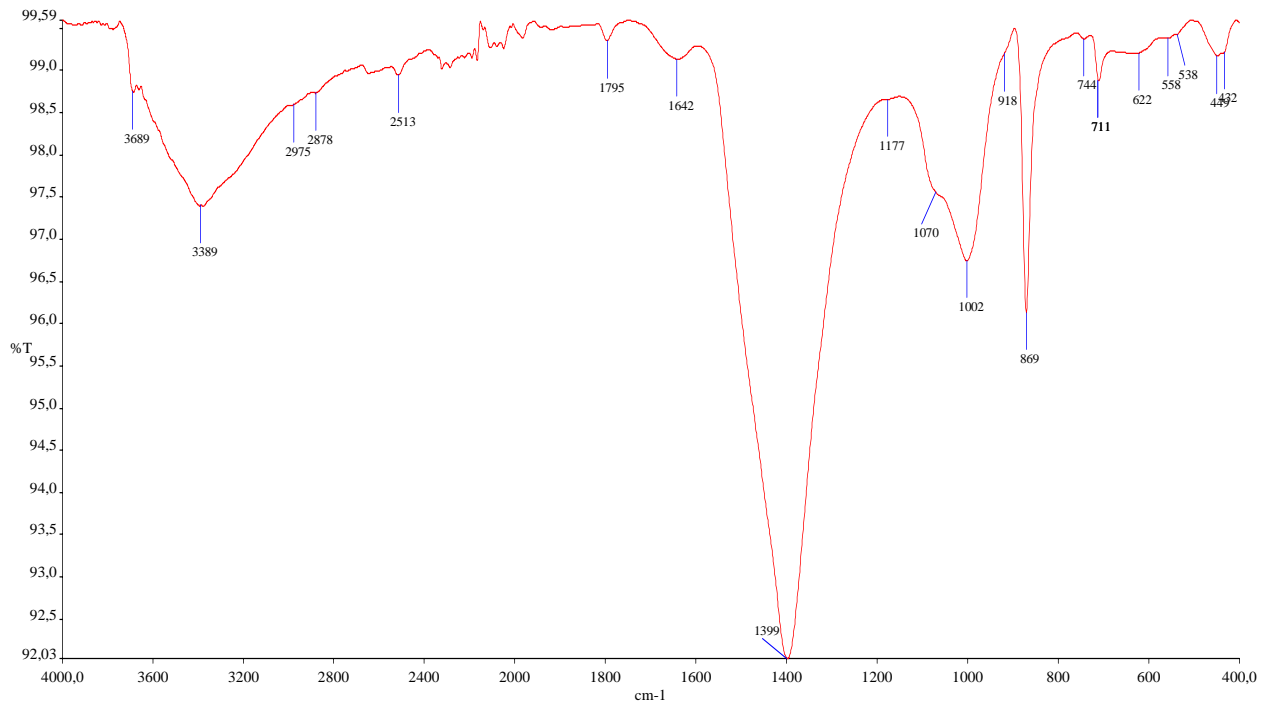

sample 41: detail with indication of the layers (white reflected light).
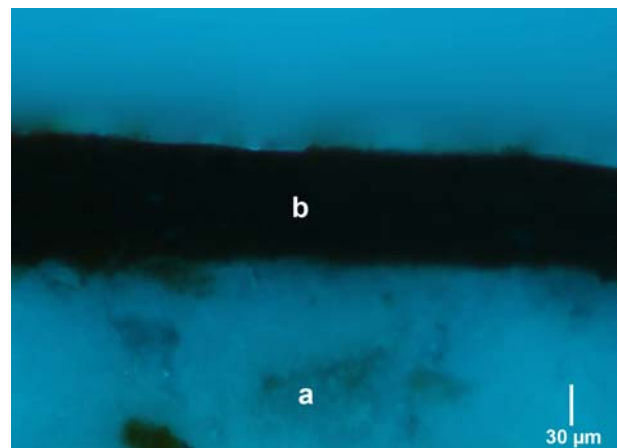
sample 41: detail (reflected light, on the left SWB filter, on the right UV filter).

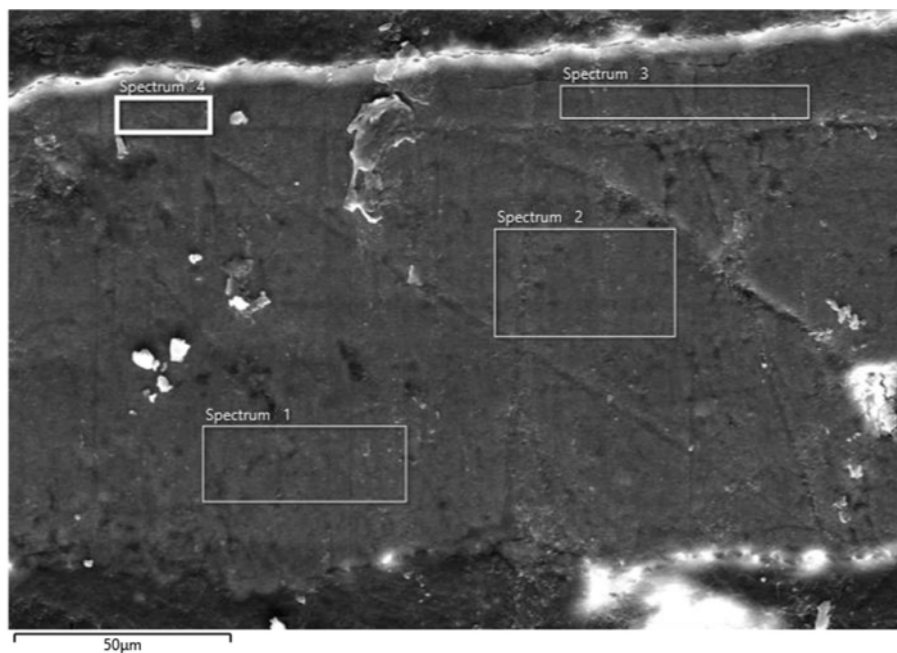Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

77

FT-IR spectroscopy

layer	compounds	signals (cm^{-1})	estimated quantity
b	calcite	1795, 1412, 874, 713	++++
	Mg-oxalates	3392, 3372, 1659, 1375, 1318, 828	+++
	Ca-oxalates	1634, 1318, 780	+
	gypsum	3495, 3243, 1621, 1140, 1103, 1004, 667, 597, 468	+++
	natural earths (ochres)	3694, 3640, 1034	++
	organic compound ?	1735	traces
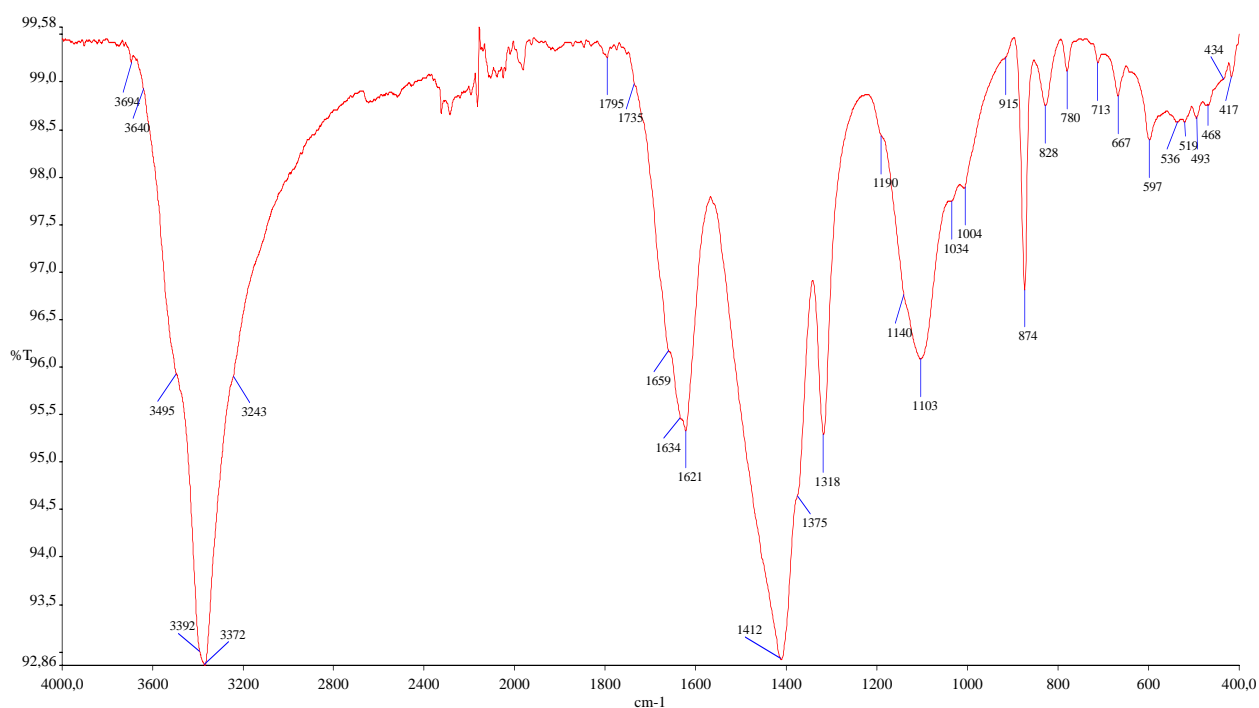
sample 41: FT-IR spectrum of the layer (**b**).

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (µm)	description and composition
b	red		75-100	lime-based paint layer with longitudinal fissures, pigmented by fine-grained Red Ochre; gypsum, oxalates and possible traces of an organic compound are also present
a	white		-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

78

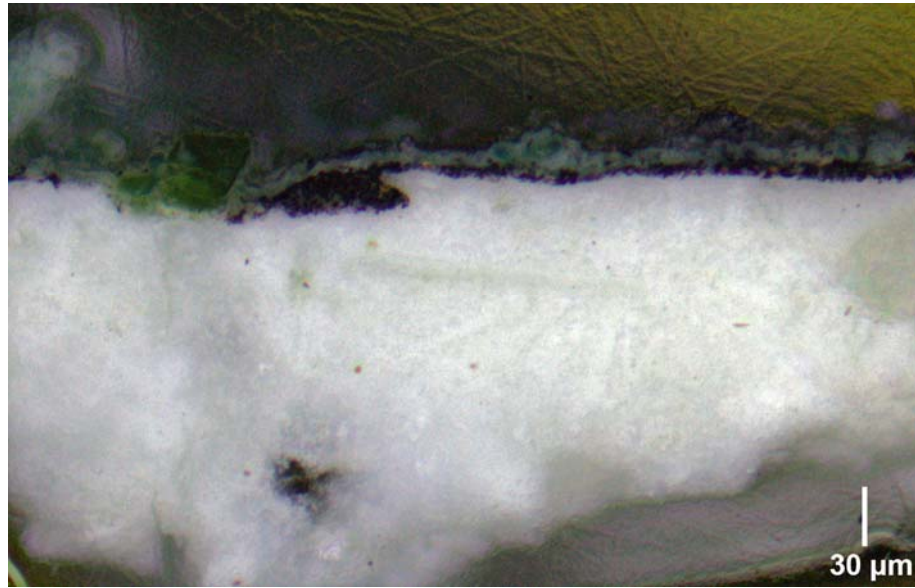| Code	Sample type	Sampling zone	Adopted analisys
42	white pictorial fragment	west arm, northern side, left register	ST, OM-RL, HT

sample 42: sampling point.

Stereoscopic microscopy

0.5 mm
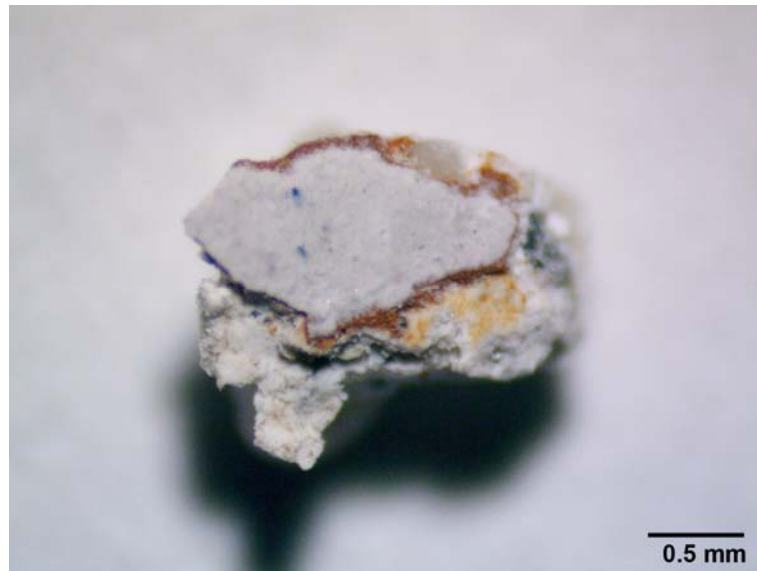
sample 42: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione
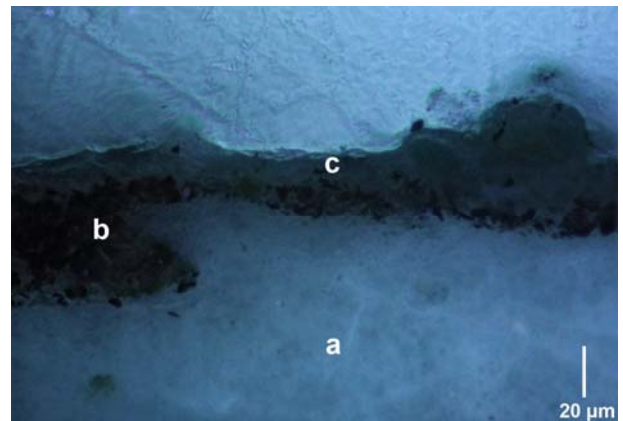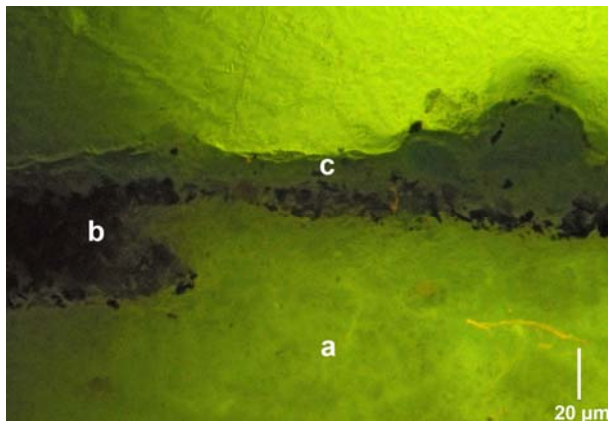
79

Optical microscopy on cross section
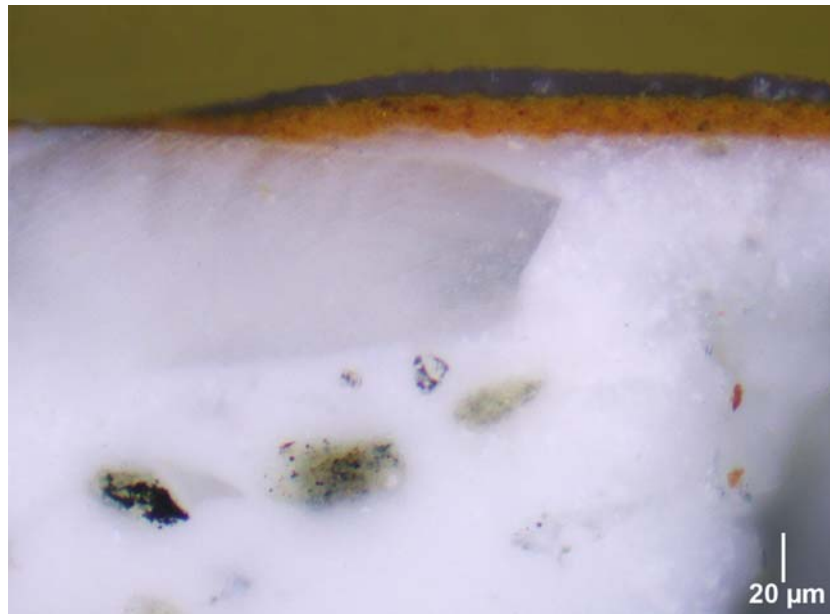
sample 42: cross-section photograph (white reflected light).
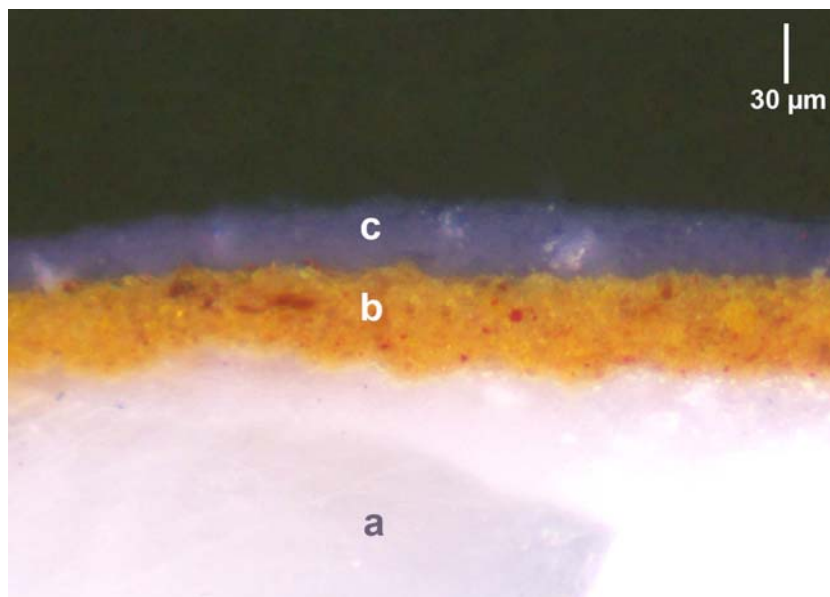
sample 42: detail with indication of the layers (white reflected light).
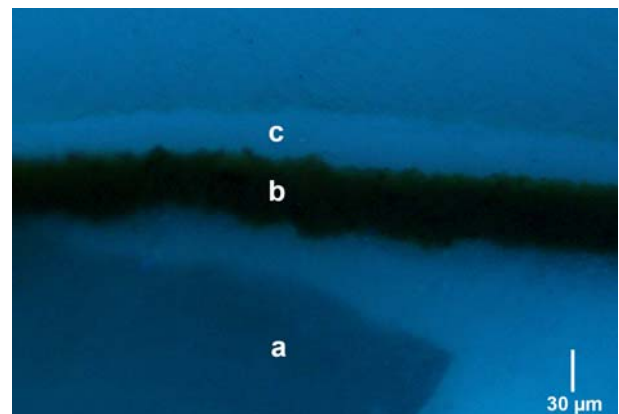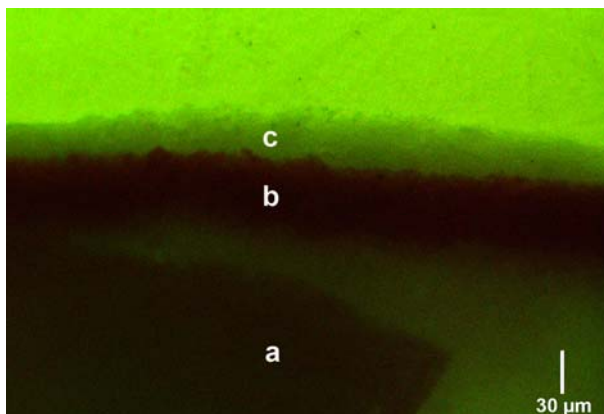
sample 42: detail (reflected light, on the left SWB filter, on the right UV filter).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

80

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (µm)	description and composition
c	grey		~20	lime-based paint layer
b	yellow		10-30	lime-based paint layer containing Yellow Ochre and scarce Red Ochre
a	white		-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

81

Code	Sample type	Sampling zone	Adopted analisys
43	grey pictorial fragment layer with shiny appearance	west arm, southern side, left register	ST, OM-RL, HT, FT-IR, SEM-EDS
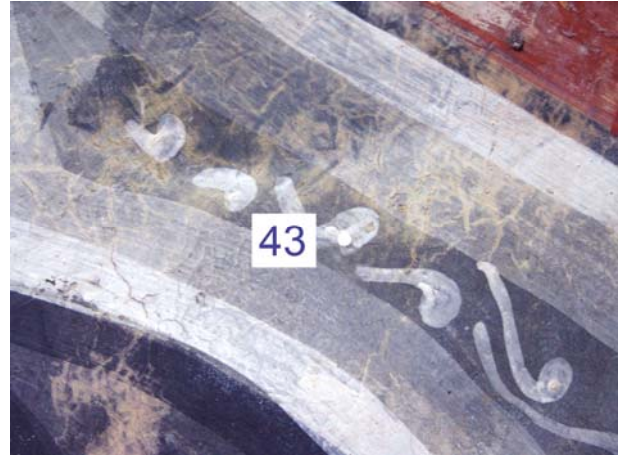
sample 43: sampling point.

Stereoscopic microscopy

0.5 mm
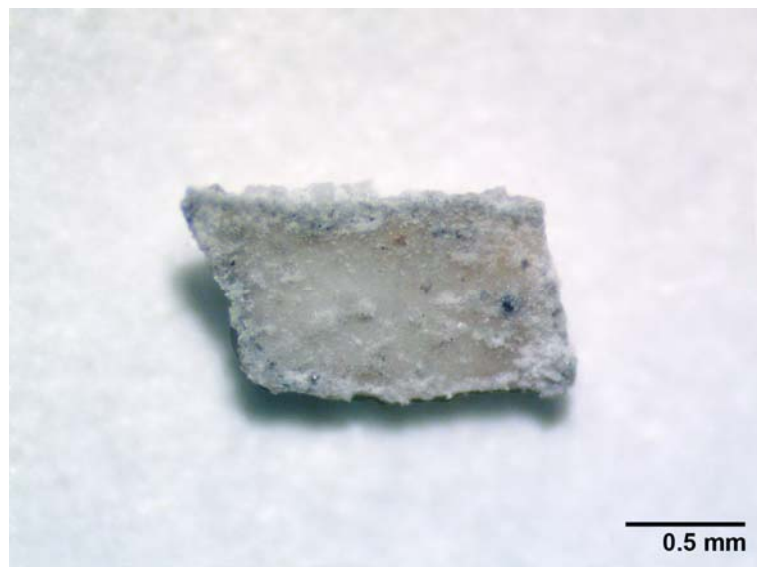
sample 43: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

82

Optical microscopy on cross section

sample 43: cross-section photograph with indication of the layers (white reflected light).
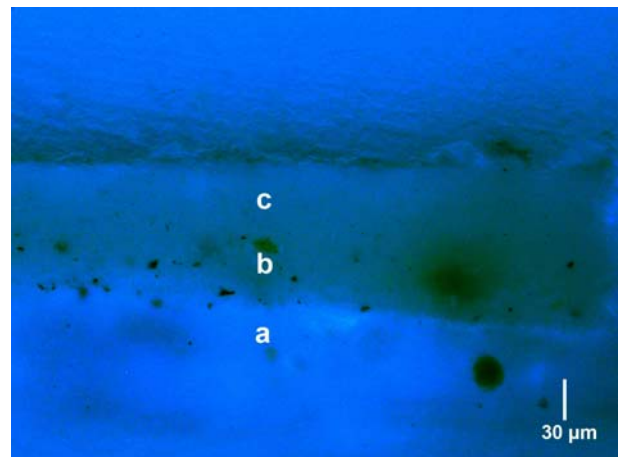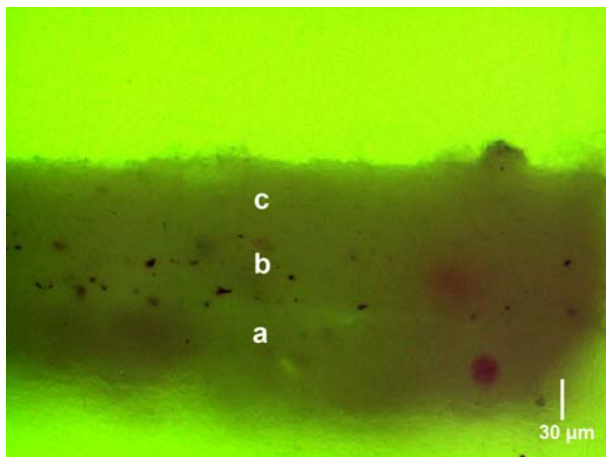
sample 43: detail (reflected light, on the left SWB filter, on the right UV filter).

FT-IR spectroscopy

layer	compounds	signals (cm^{-1})	estimated quantity
c	calcite	2513, 1795, 1399, 869, 711	++++
	hydromagnesite	3389, 1642, 798, 744	+
	brucite?	3689	++
	silicati	1070, 1002, 449	+

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

83

sample 43: FT-IR spectrum of the layer (**c**).

Scanning Electron Microscopy (SEM-EDS)

Analysis record abundant Calcium and, subordinately, Magnesium and Silicon; these data confirm the presence of calcium and magnesium carbonates and silicates.

sample 43: BSE image.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

84
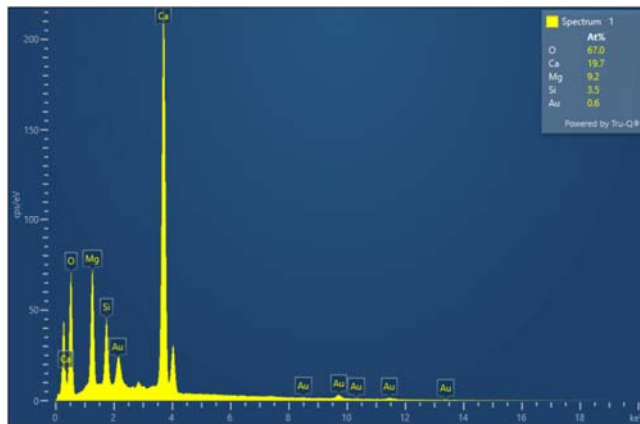
sample 43: EDS spectrum n.1
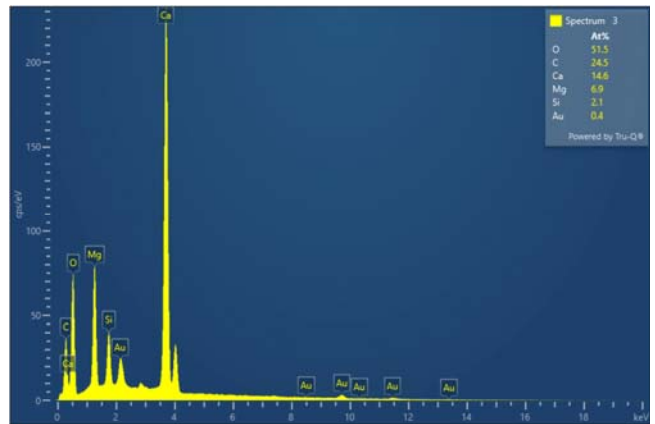
sample 43: EDS spectrum n.3

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (μm)	description and composition
c	white		40-70	lime based paint layer containing silicates
b	pale grey		35-60	lime-based paint layer slightly pigmented by Carbon Black and Yellow Ochre
a	white		-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

85

Code	Sample type	Sampling zone	Adopted analisys
44	black-greenish pictorial fragment	northern arm, background of the vault	ST, OM-RL, HT, FT-IR

sample 44: sampling point.

Stereoscopic microscopy

1 mm

sample 44: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

86

Optical microscopy on cross section

sample 44: cross-section photograph (white reflected light).
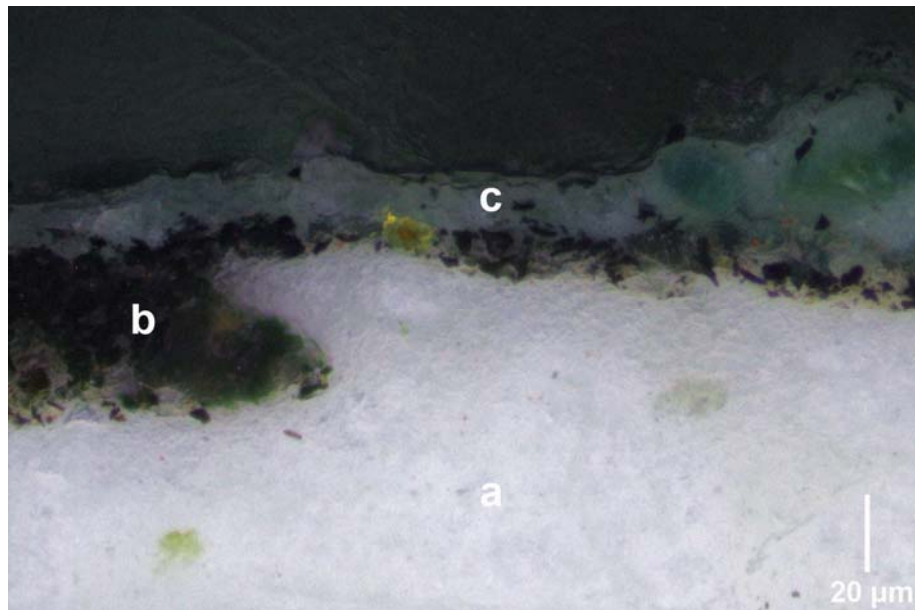
sample 44: detail with indication of the layers (white reflected light).

sample 44: detail (reflected light, on the left SWB filter, on the right UV filter).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

87

FT-IR spectroscopy

layer	compounds	signals (cm⁻¹)	estimated quantity
c	calcite	1795, 1406, 871, 711	++++
	Green Earth	3694, 3646, 3600, 1114, 1079, 977, 958, 679, 495, 462, 439	+
	hydromagnesite	3649, 3509, 1471, 1406, 1114, 852, 794, 744, 592	+
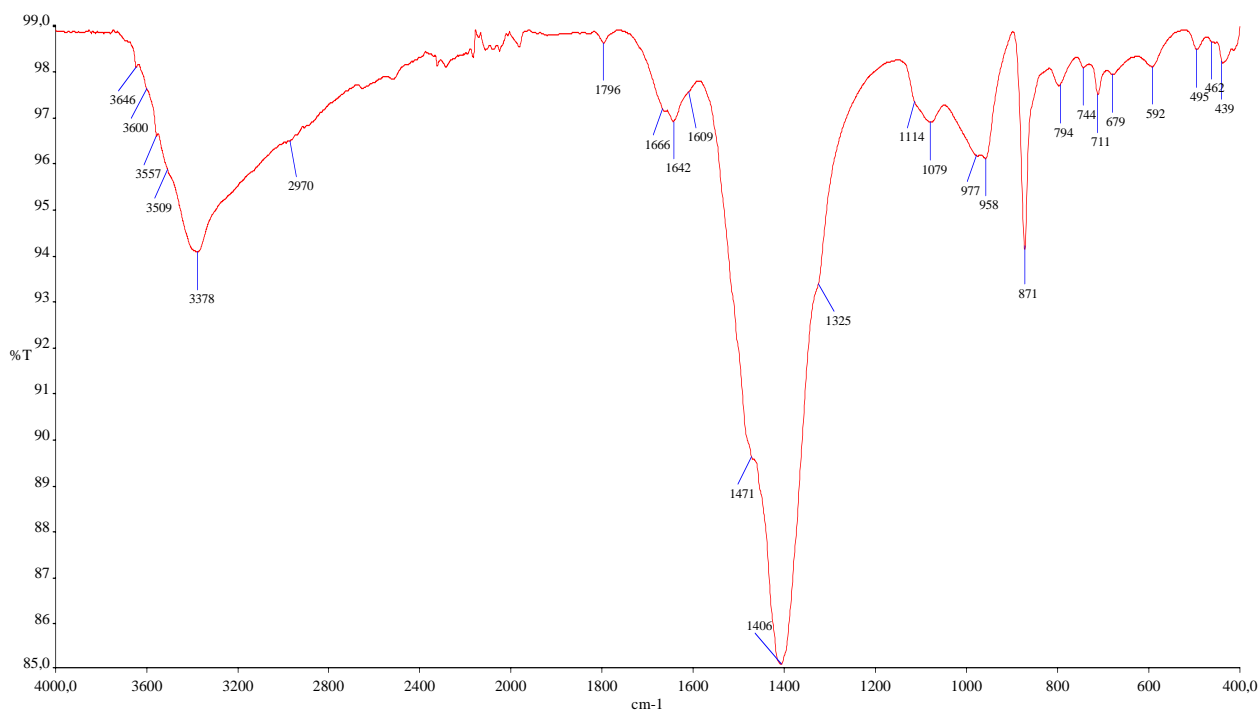
sample 44: FT-IR spectrum of the layer (**c**).

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (µm)	description and composition
c	green	-	20-40	lime-based paint containing Green Earth, few particles of Carbon Black and scarce hydromagnesite
b	black	-	10-20	lime-based paint layer of Carbon Black and Green Earth
a	white	-	-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

88

Code	Sample type	Sampling zone	Adopted analisys
45	blue pictorial fragment	northern arm, background of the vault	ST, XRF, OM-RL, HT, FT-IR
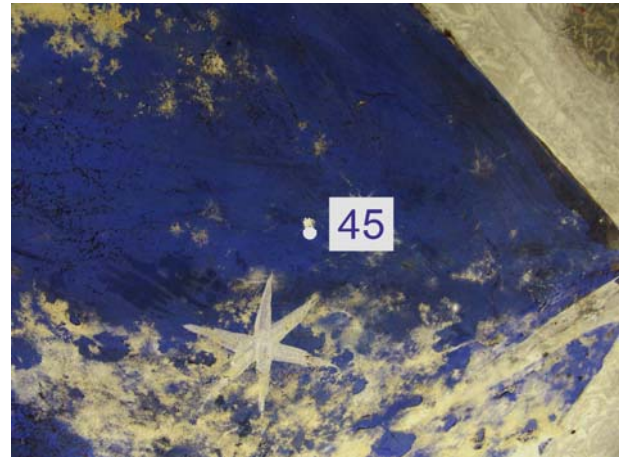
sample 45: sampling point.

Stereoscopic microscopy

0.5 mm

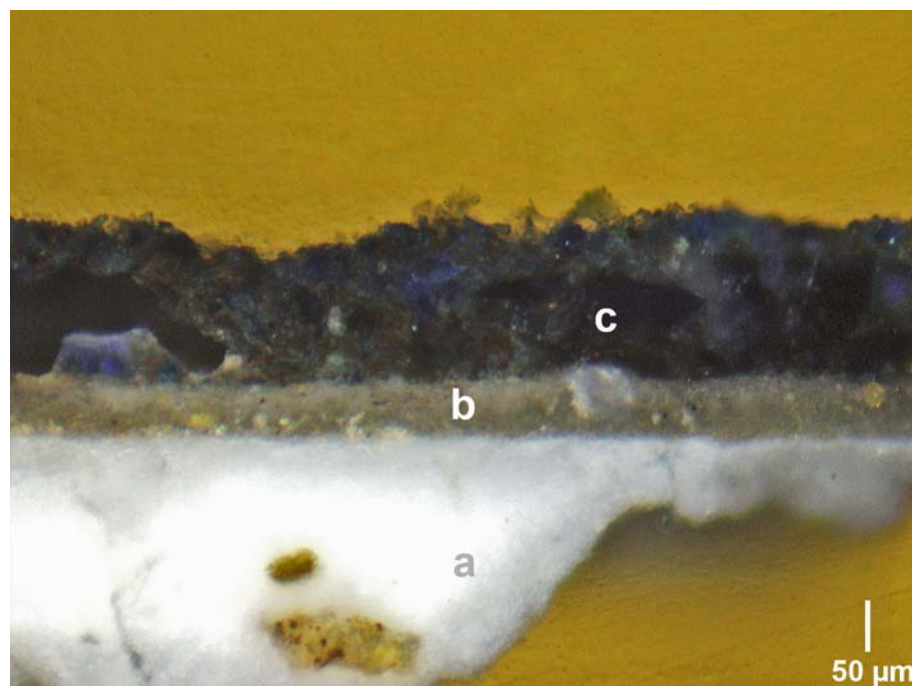sample 45: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

89

XRF measurements

| layer	Chemical Elements				possible compound
	main	**secondary**	**minority**	**in traces**	
blue	Ca		Si S K	Al Fe	calcite, Ultramarine Blue
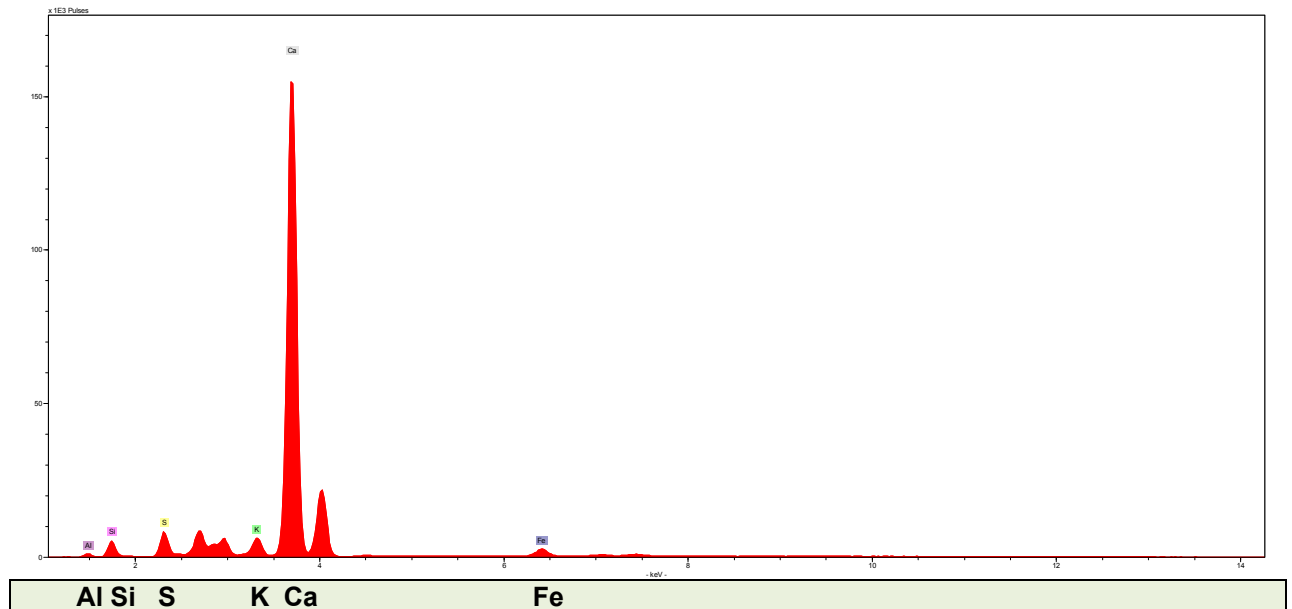
sample 45: 15 kV XRF spectrum of the blue layer.

Optical microscopy on cross section
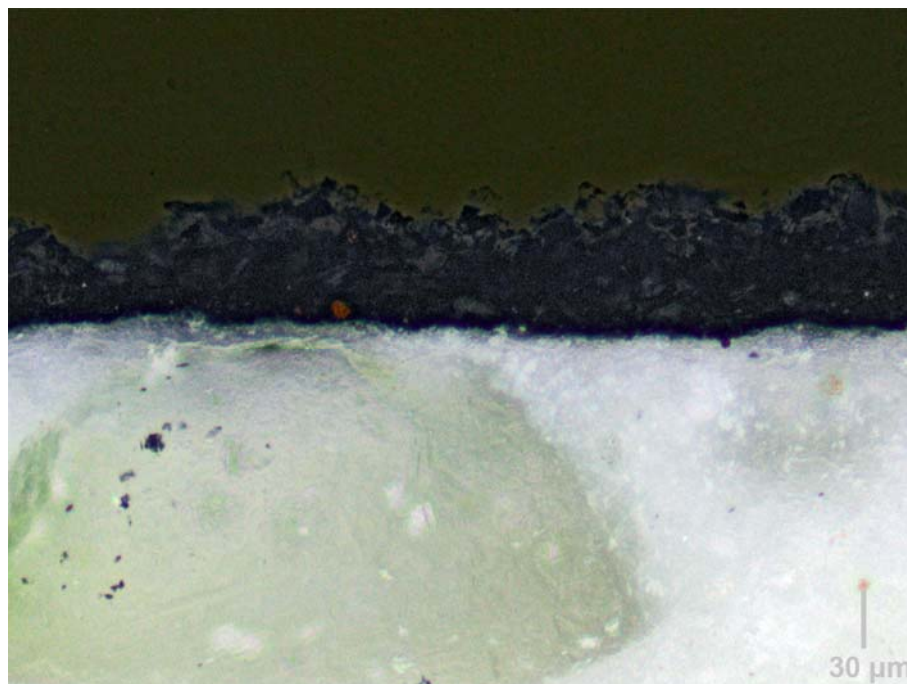
sample 45: cross-section photograph (white reflected light).

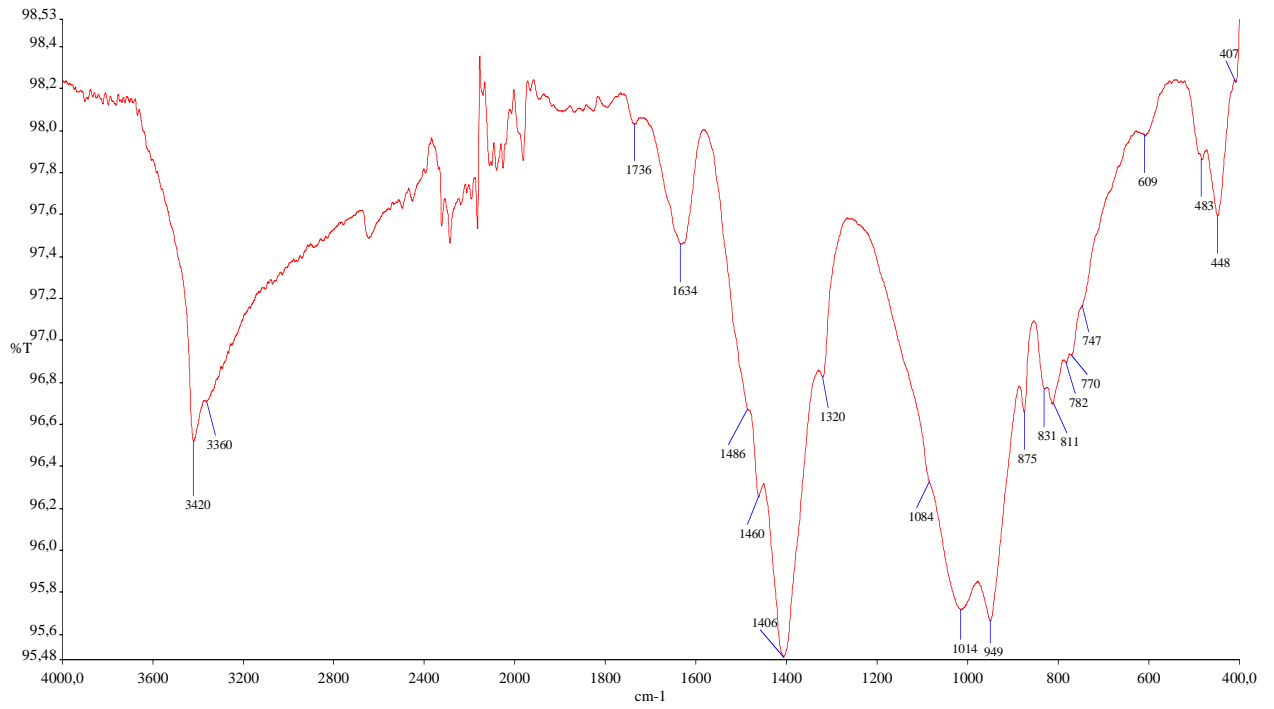Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

90
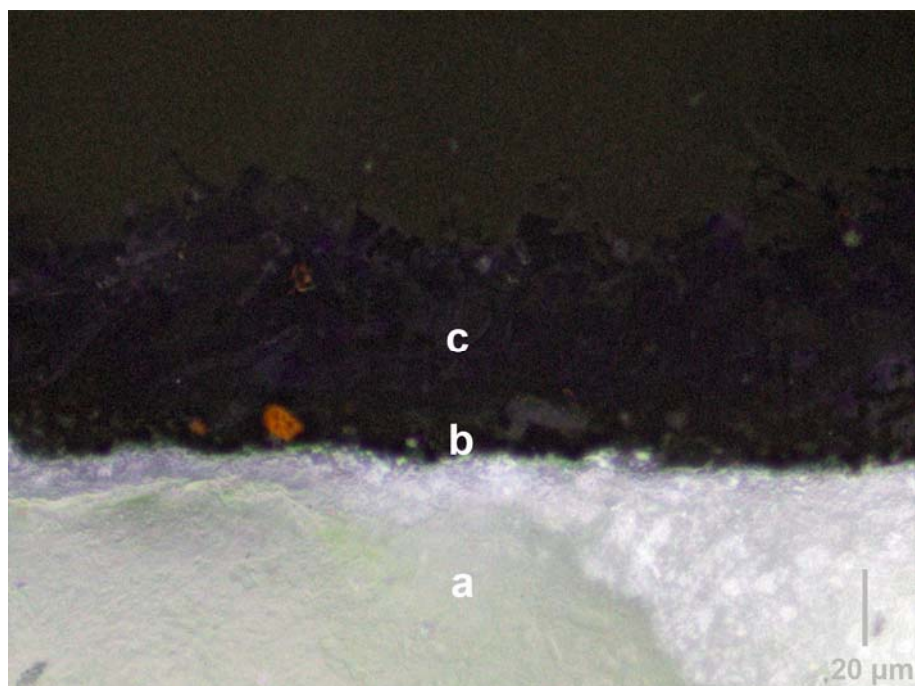
sample 45: detail with indication of the layers (white reflected light).
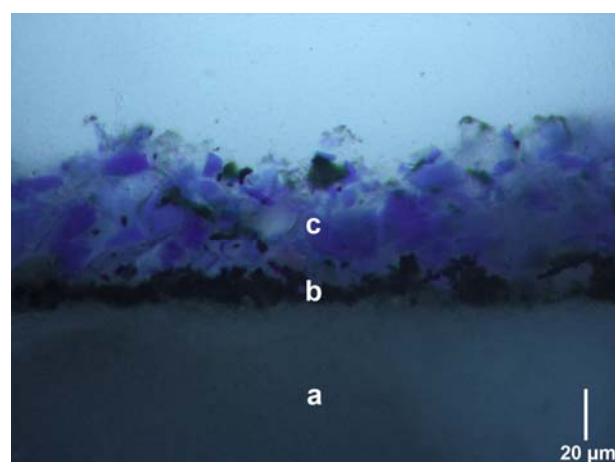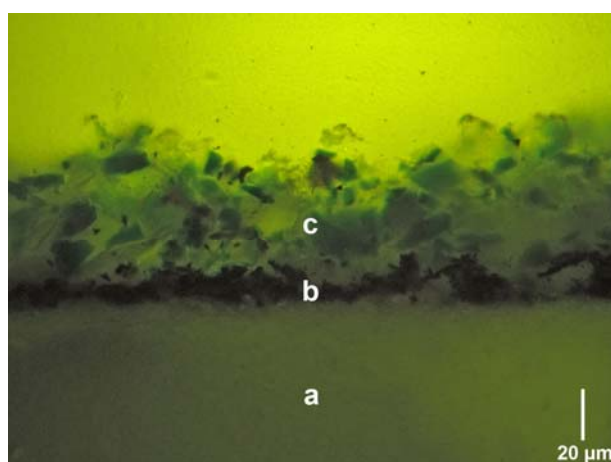
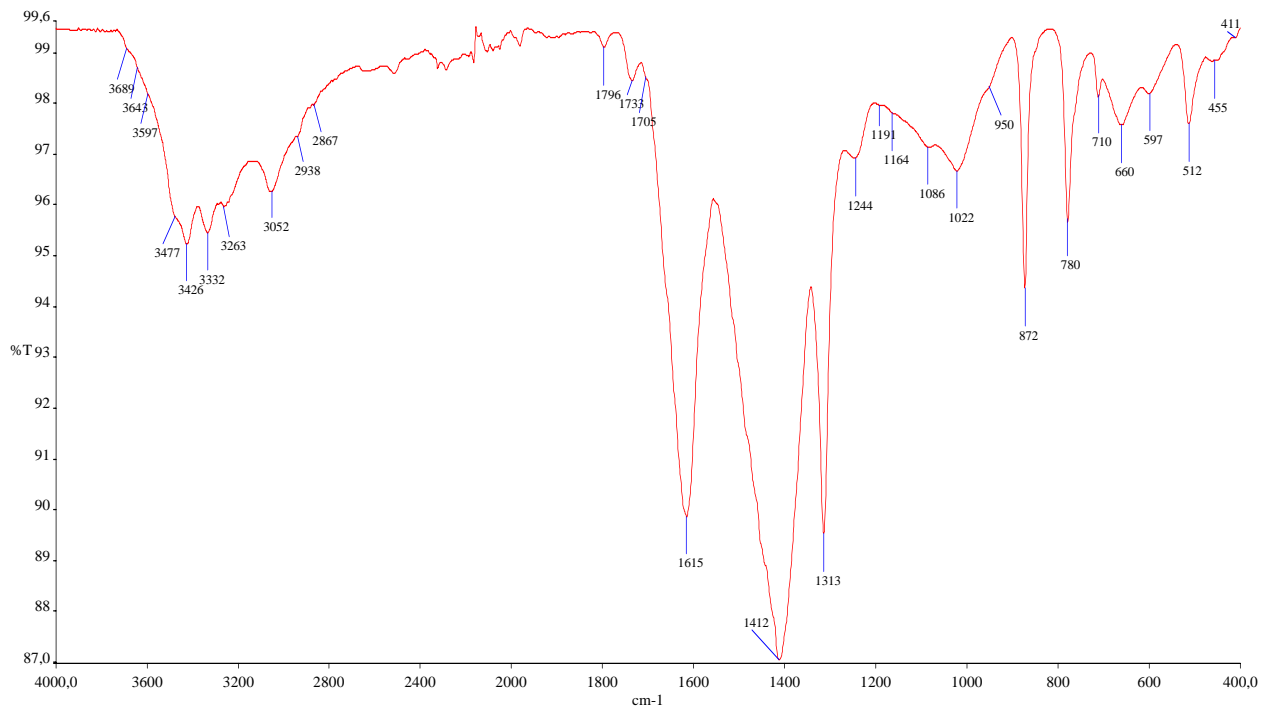sample 45: detail (reflected light, on the left SWB filter, on the right UV filter).

FT-IR spectroscopy

layer	compounds	signals (cm^{-1})	estimated quantity
c	calcite	1796, 1410, 871, 710	++++
	Ca-oxalates	1631, 1322, 777, 661, 519	++
	Ultramarine Blue	1101, 993, 445	++
	organic compound	2961, 2930, 2853, 1743	traces
c blue pigment	Ultramarine Blue	1113, 963, 801, 697, 657, 580, 542, 442	

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

91
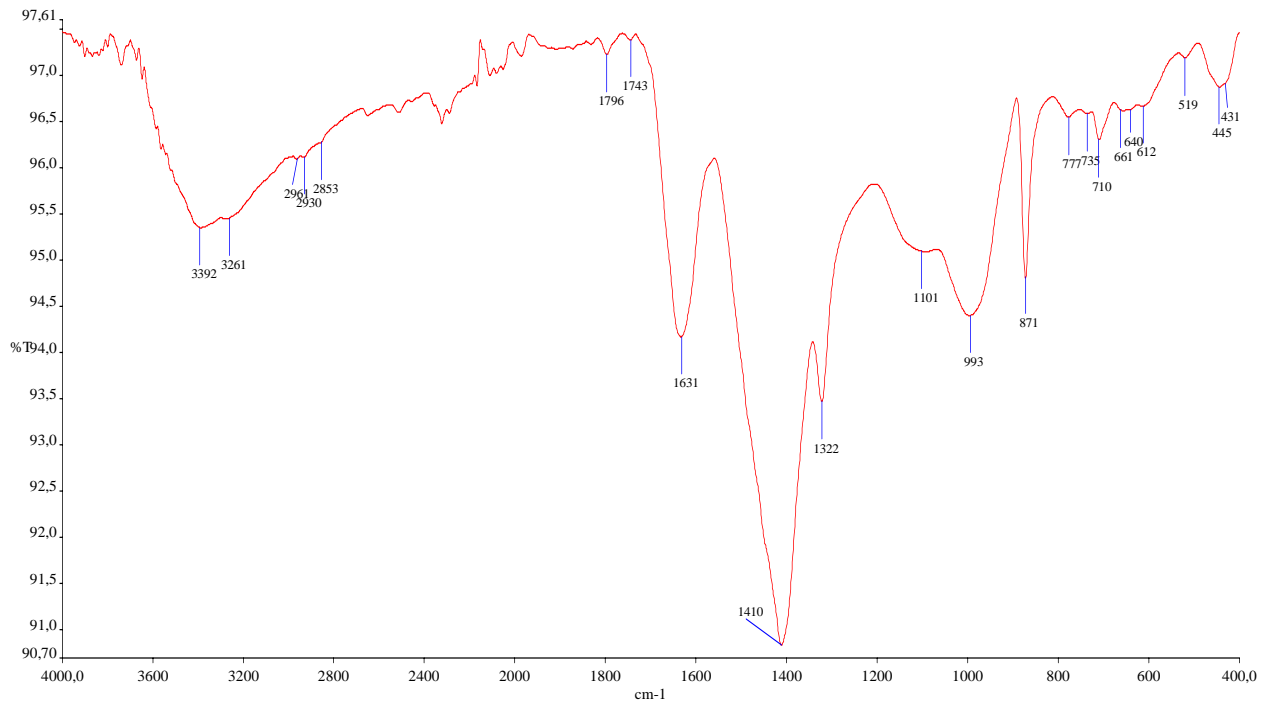
sample 45: FT-IR spectrum of the layer (**c**).

sample 45: FT-IR spectrum of a blue pigment's grain (layer **c**).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

92

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (µm)	description and composition
c	blue		25-60	lime-based paint layer containing Artificial Ultramarine Blue; Ca-oxalates and traces of an organic compound are also present
b	black		15-35	lime-based paint layer of Carbon Black with few particles of Red Ochre
a	white		-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

93

Code	Sample type	Sampling zone	Adopted analisys
46	blue pictorial fragment	north arm, northern side, Apostle's cloak on the right side	ST, XRF, OM-RL, HT, FT-IR
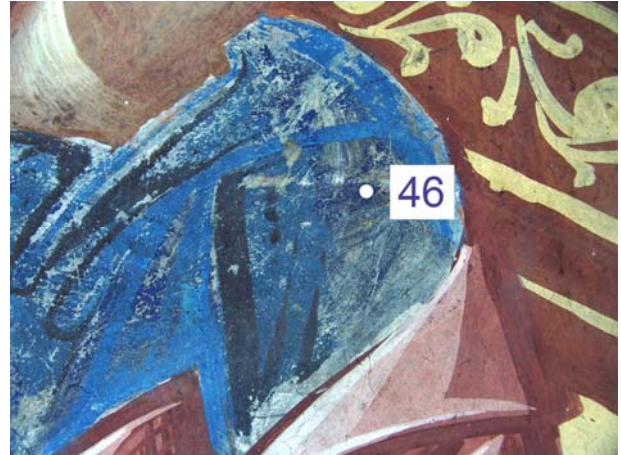
sample 46: sampling point.

Stereoscopic microscopy
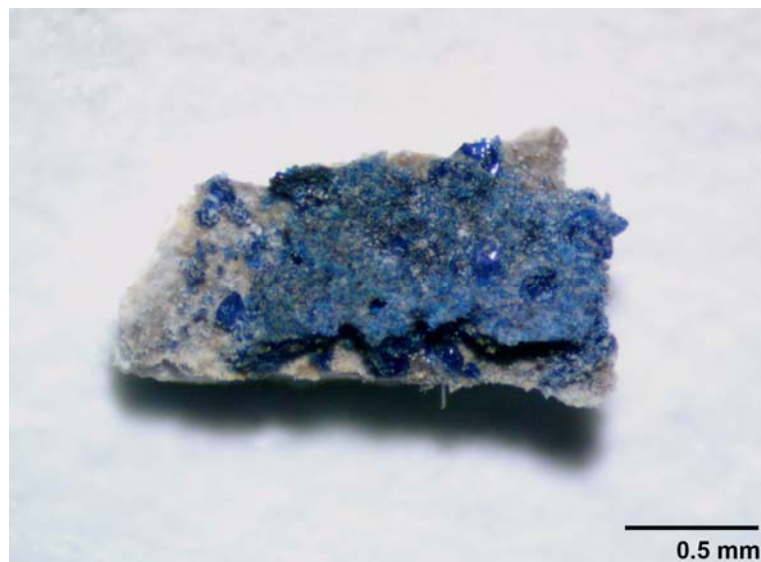
sample 46: photograph under the stereomicroscope.

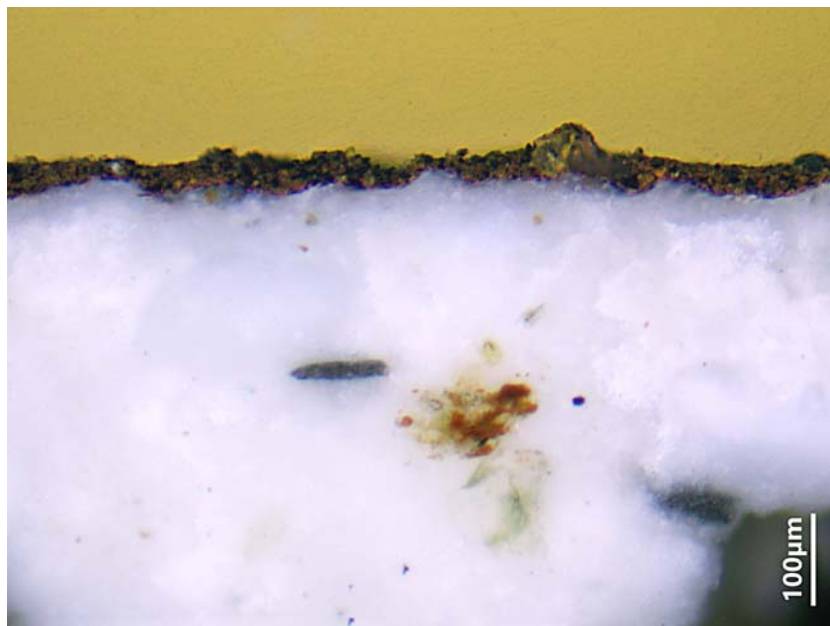Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

94

XRF measurements

| layer	Chemical Elements				possible compounds
	main	**secondary**	**minority**	**in traces**	
blue	Ca	Cu	Si S Co	K Mn Ni As Pb	calcite, Azurite, Smalt

Si S   K Ca   Mn Fe Co Ni Cu   As Pb
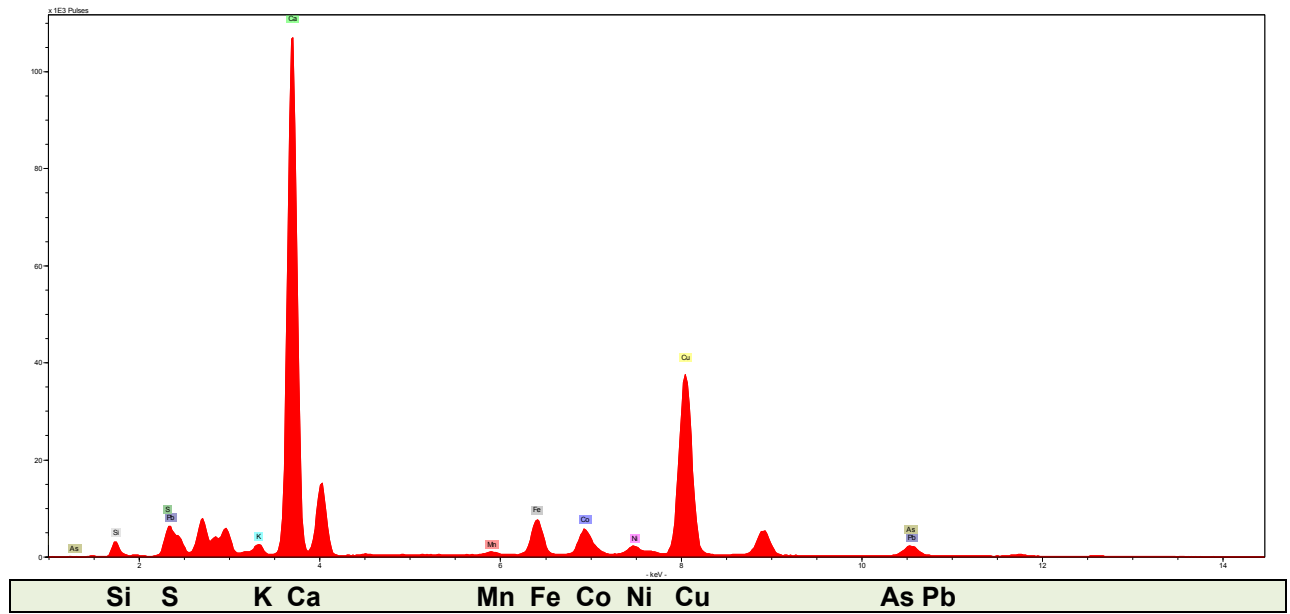
sample 46: 15 kV XRF spectrum of the blue layer.

Optical microscopy on cross section

sample 46: cross-section photograph with indication of the layers (white reflected light).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

95
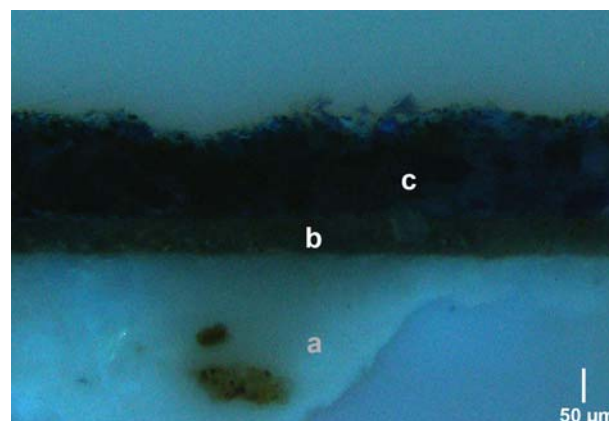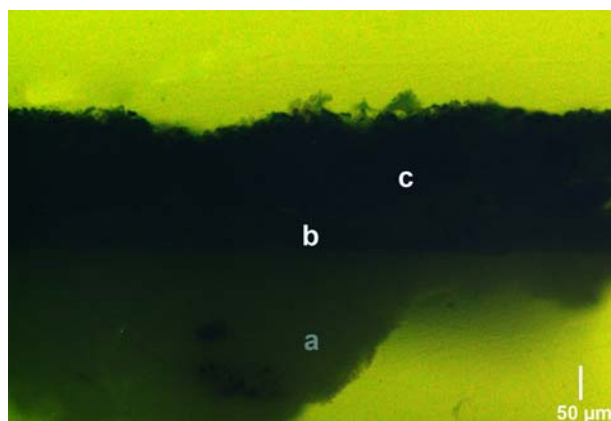
sample 46: detail (reflected light, on the left SWB filter, on the right UV filter).
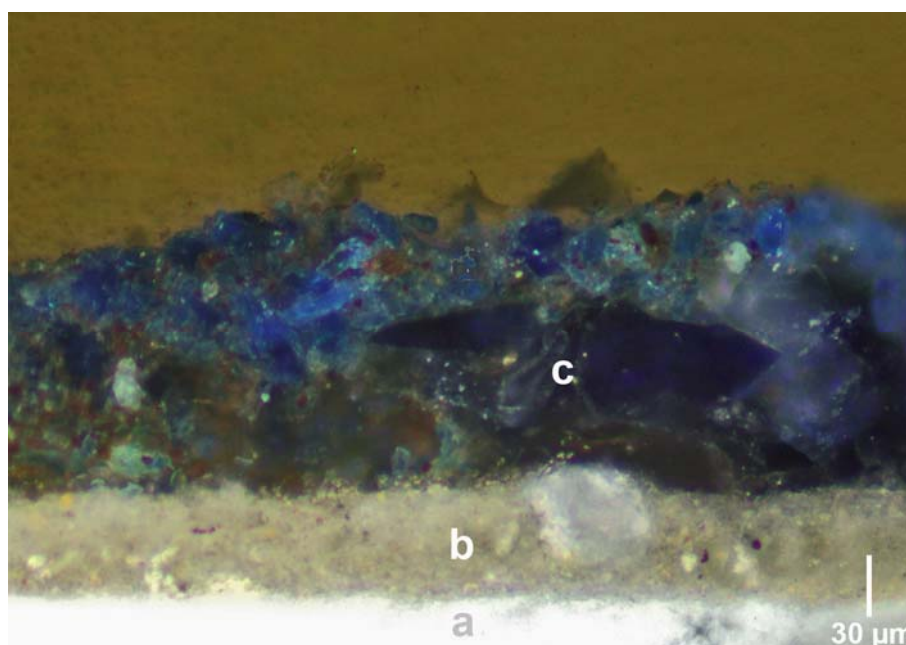
sample 46: detail (white reflected light).

FT-IR spectroscopy

layer	compounds	signals (cm^{-1})	estimated quantity
c	Azurite	3420, 3360, 1486, 1460, 1406, 1084, 949, 831, 811, 770, 747, 483, 448	++++
	Smalt	1014, 782, 448	++
	calcite	1406, 875	++
	Ca-oxalates	1634, 1320	++
	organic compound	1736	traces
b	calcite	1796, 1412, 872, 710	++++
	Ca-oxalates	3477, 3426, 3332, 3263, 3052, 1615, 1313, 780, 660, 597, 512	+++
	natural earths (ochres)	3689, 3643, 3597, 1022	+
	organic compound	2938, 2967, 1733-1705, 1244	traces

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

96

sample 46: FT-IR spectrum of the layer (**c**).

sample 46: FT-IR spectrum of the layer (**b**).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

97

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (µm)	description and composition
c	blue/green		0-130	paint layer containing Azurite and Smalt; some Azurite particles are turned green; Ca-oxalates and traces of an organic compound are also detected
b	gray		35-65	lime-based paint layer rich in Ca-oxalates and slightly pigmented by few particles of Carbon Black and Yellow Ochre
a	white		-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

98

Code	Sample type	Sampling zone	Adopted analisys
48	brown pictorial fragment	west arm, northern side, middle Apostle's hand	ST, XRF, OM-RL, HT, FT-IR

sample 48: sampling point.

Stereoscopic microscopy

0.5 mm
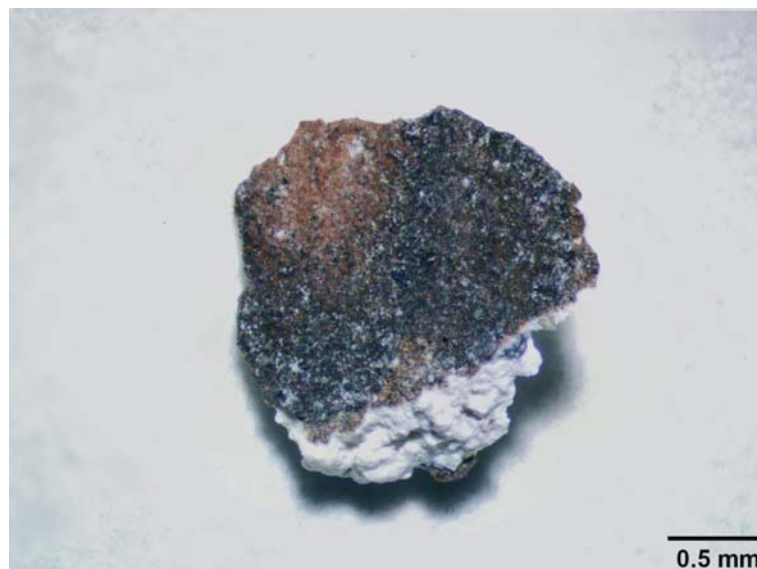
sample 48: photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

99

XRF measurements

layer	Chemical Elements				possible compounds
	main	**secondary**	**minority**	**in traces**	
brown	Ca	Fe	Si S K	Al Ti	calcite, ochres
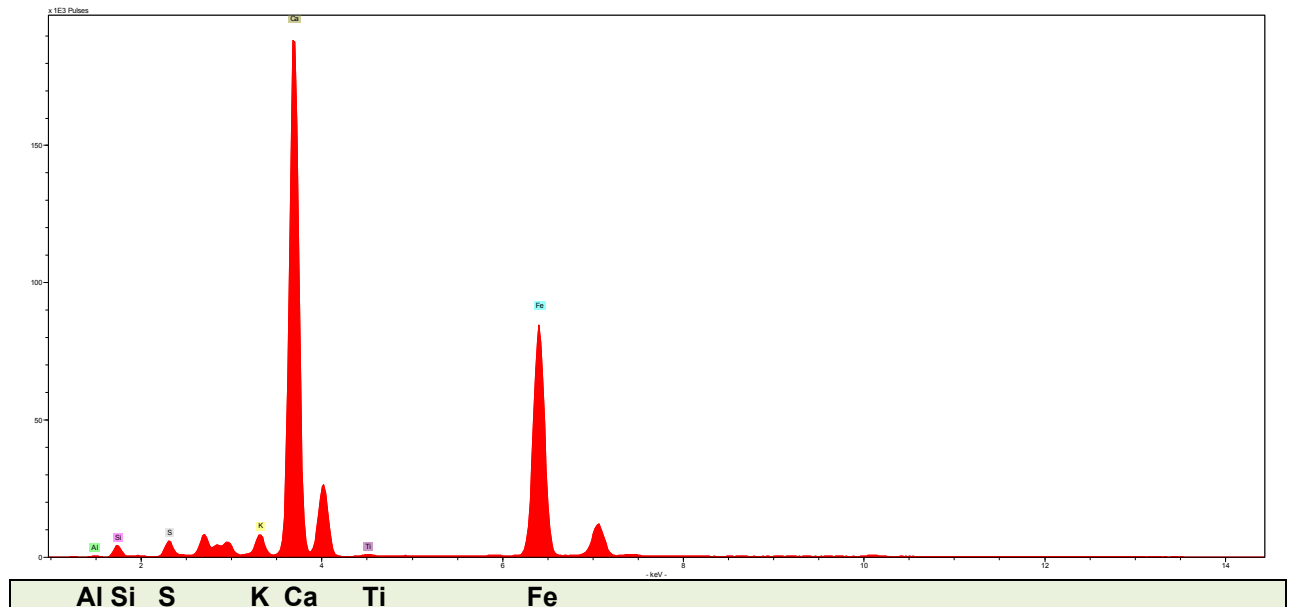
sample 48: 15 kV XRF spectrum of the brown layer.

Optical microscopy on cross section

sample 48: cross-section photograph (white reflected light).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

100
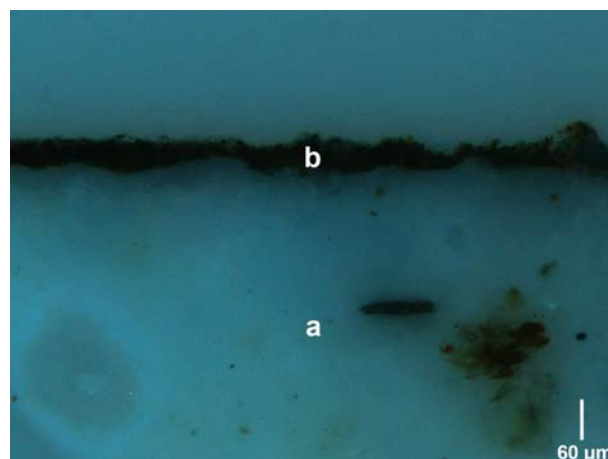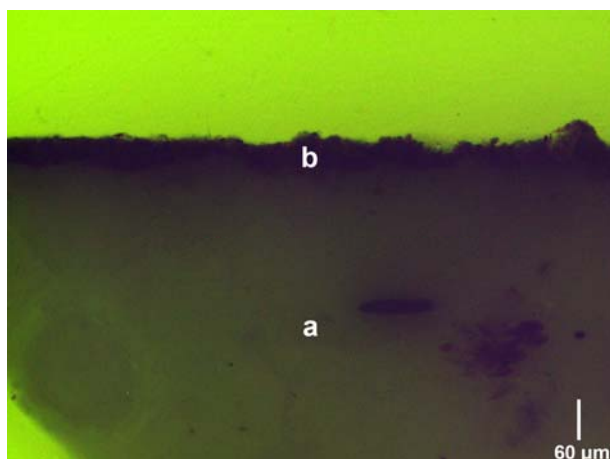
sample 48: reflected light (on the left SWB filter, on the right UV filter).
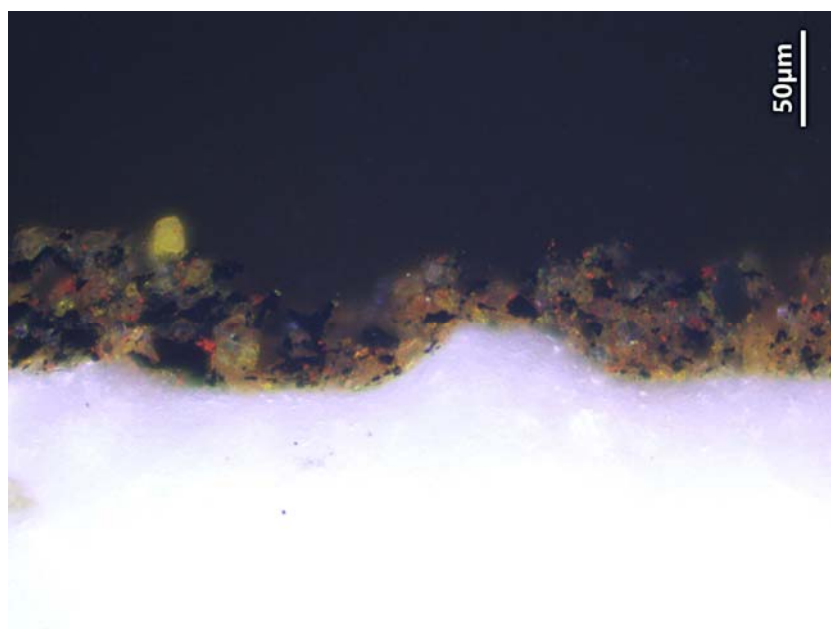
sample 48: detail (reflected light).

FT-IR spectroscopy

layer	compounds	signals (cm^{-1})	estimated quantity
b	calcite	2510, 1795, 1409, 872, 711	++++
	Ca-oxalates	1634, 1322, 782	++
	natural earths (ochres)	3697, 3646, 3623, 1026, 1004, 913, 529, 465, 438	++
	quartz	1165, 1081, 798, 782,	+
	phosphates?	958	+

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

101
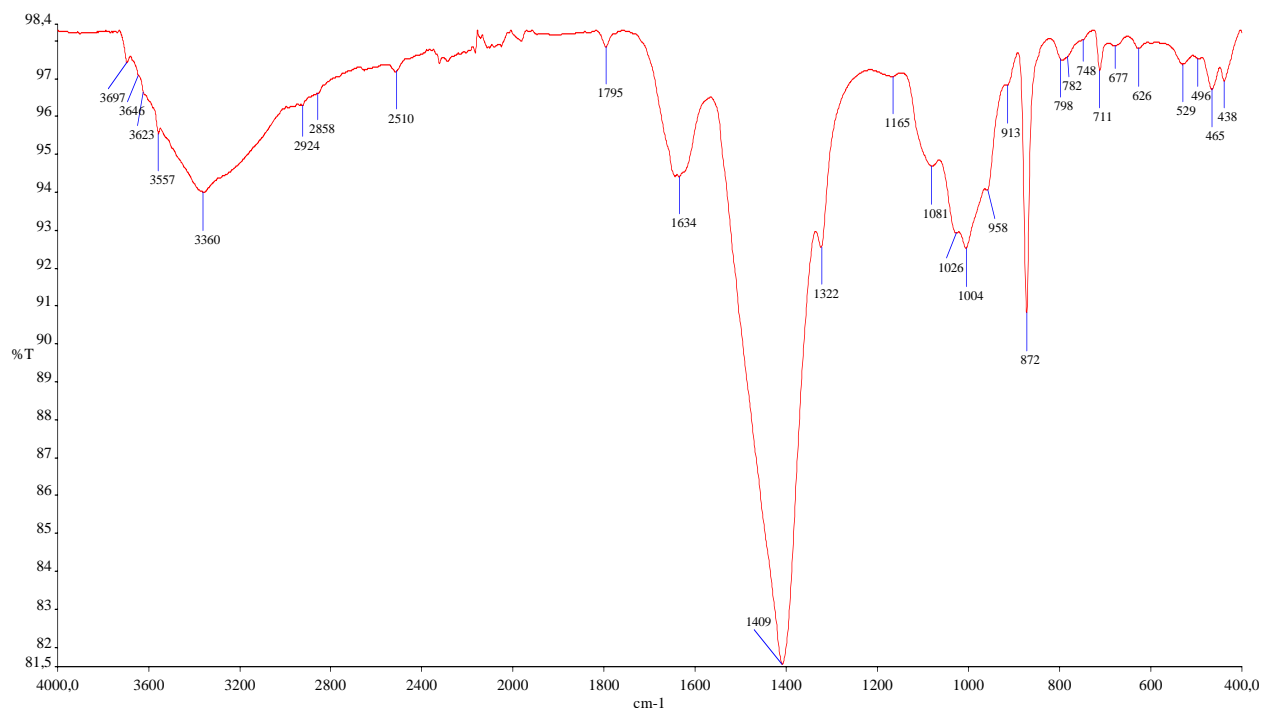
sample 48: FT-IR spectrum of the layer (**b**).

Description of the stratigraphic sequence:

layer	color	UV fluo.	thickness (µm)	description and composition
b	brown		20-60	lime-based paint layer containing Yellow Ochre, Red Ochre, Carbon Black and Bone Black?
a	white		-	plaster

Results of the histochemical tests: negative

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

102

Code	Sample type	Sampling zone	Adopted analisys
M1	fragments of white restoration mortar	west arm, southern side	ST, OM-TL
M6		vault	

sample M1: sampling point.

sample M6: sampling point.

Stereoscopic microscopy

sample M1

sample M6

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

103

Optical microscopy on thin section

Sample **M1** consists entirely of a gypsum groundmass ($CaSO_4*2H_2O$) with a micritic texture, recognisable by its grey or white 1st-order interference colour. Numerous small anhydride inclusions ($CaSO_4$), characterised by high birefringence and iridescent appearance, are dispersed within it; their size ranges from 50 to 100 µm. No aggregates are observed, while some pores of primary origin and subcircular shape are clearly visible, resulting in low porosity. A 120-150 µm thick layer of organic nature is present on the surface.

Mortar **M6** also consists of gypsum without aggregate but, unlike sample M1, does not contain anhydride. Porosity is low and is determined by elongated vacuoles.
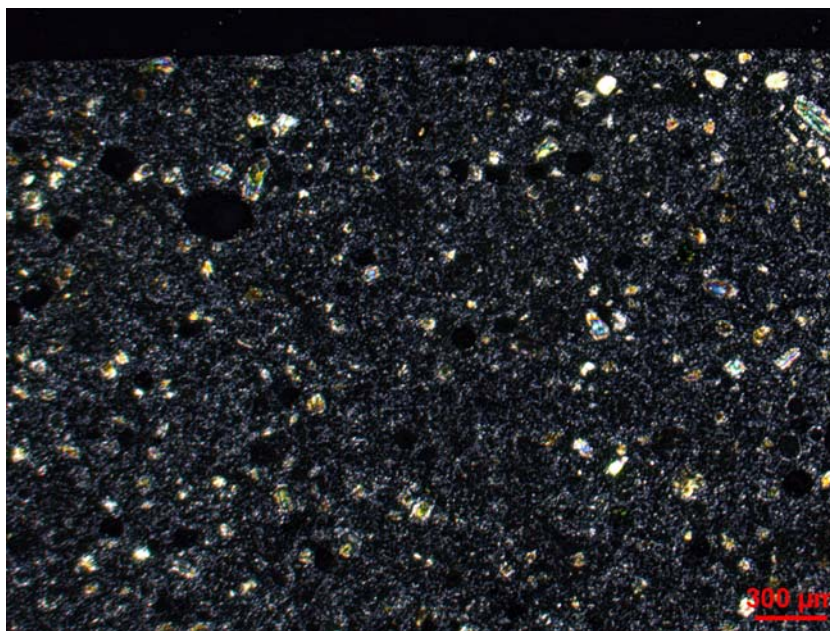
sample M1: thin-section photograph (transmitted light, X polars).
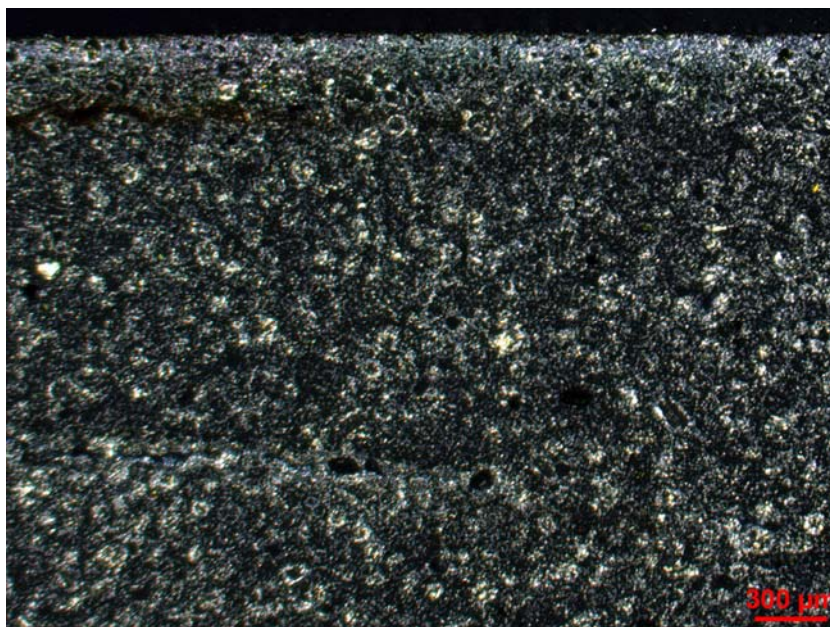
sample M6: thin-section photograph (transmitted light, X polars).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

Code	Sample type	Sampling zone	Adopted analisys
M2	fragments of reddish restoration mortar	west arm, southern side	ST, OM-TL
M3		west arm, northern side	

sample M2: sampling point.

sample M3: sampling point.

Stereoscopic microscopy

sample M2

sample M3

Optical microscopy on thin section

Samples M2, M3

Samples have the same compositional and textural characteristics.

MICROSCOPIC FEATURES OF THE BINDER		
1	Mineralogic composition	calcium carbonate ($CaCO_3$) originated from the carbonation process of an air-hardening lime
2	Structure	homogeneous
3	Texture	micritic (dimension of calcite crystals 4-10 µm)
4	Interactions with the aggregate	absent

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

105

5	Porosity	
5.1.	o tipology	voids
5.2.	o ubication	intergranular and intragranular
5.3.	o % (by volume)	very high (~35%)
5.4.	o origin	primary (voids naturally present within the aggregate or caused by shrinkage of the binder during setting and hardening)

MICROSCOPIC FEATURES OF THE AGGREGATE

1	Size	
1.1.	o dimensional range (estimated values)	The grain size varies from coarse silt to coarse sand (0.03-0.8 mm) but it mainly falls in the medium sand and fine sand classes (0.2-0.4 mm); it spreads in the different fractions as listed below:

granulometric classes	%
coarse sand (0.5-1 mm)	10
medium sand (0.25-0.5 mm)	30
fine sand (0.125-0.25 mm)	30
very fine sand (0.062-0.125 mm)	15
coarse silt (0.031-0.062 mm)	15

1.2.	o sorting	low
2	Shape (rounding and sphericity)	rounding: angular; sphericity: low
3	Surface morphology	faceted
4	Orientation	absent
5	Distribution	homogeneous
6	Composition (% by volume) (estimated values)	The aggregate have a silicatic and carbonatic composition; in order of decreasing abundance it spread as listed below:

rocks or mineral types	%
• pyroclastic volcanic rock fragments (red pozzolan containing piroxenes and plagioclases fenocristals and vulcanic glass)	65
• sedimentary rocks fragments identified as micritic, microsapritic and sparitic limestones	20
• metamorphic rock fragments classified as schists, quartzites and argillites	10
• effusive volcanic rocks fragments (lavas)	5

7	Admixtures	-
8	Binder/Aggregate Ratio (by volume)	~1:3

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione
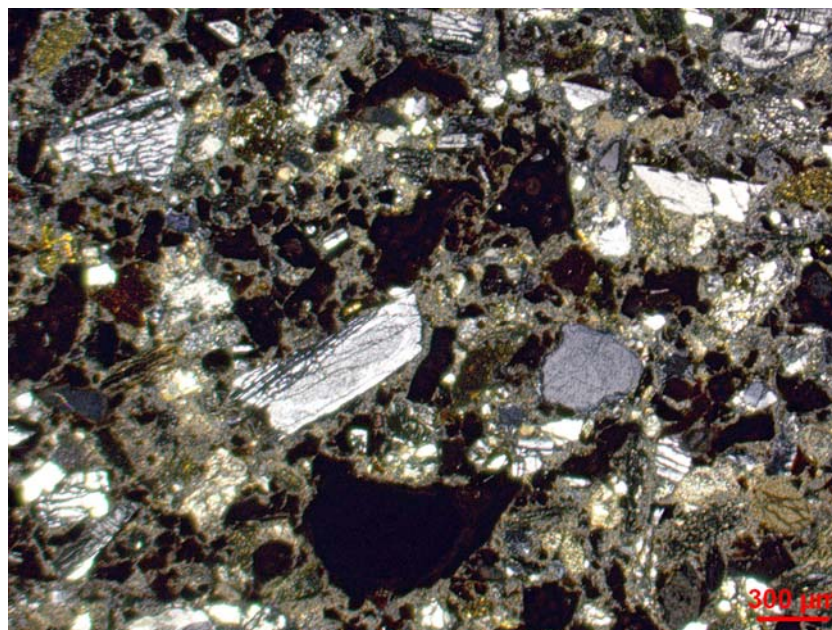
106

CONCLUSIONS		
1	Mixture characterization	It is a mortar consisting of air-hardening lime mixed with an aggregate composed of approximately 65% of red pozzolan and 35% by volume of a carbonate-silicate sand, presumably of fluvial origin. The aggregate has an average size between 0.2 and 0.4 mm and a maximum diameter of 0.8 mm. The binder/aggregate ratio is around 1:3 by volume.
2	Secondary processes and decay products	No neoformation phases attributable to degradation processes are observed.

A layer of carbonated aerial lime is observed on the surface of sample **M3**.
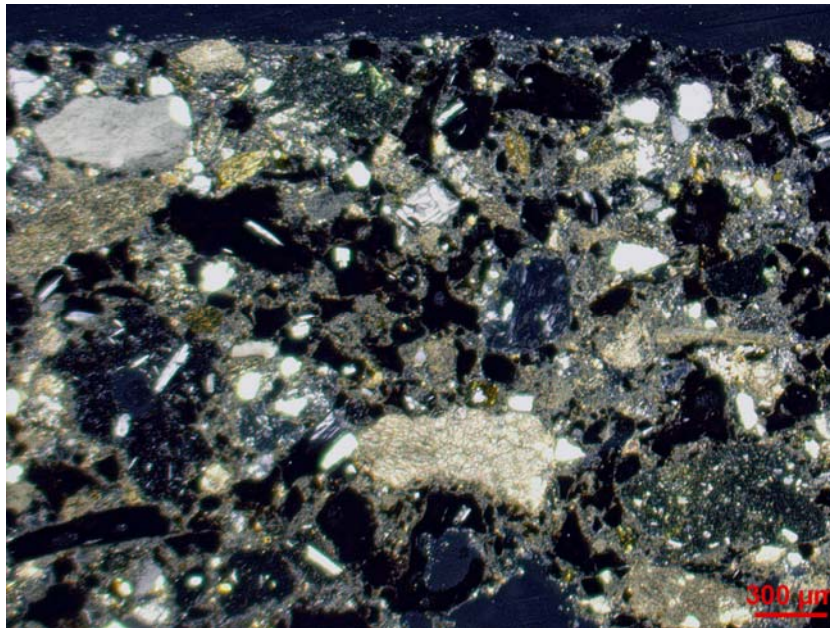
sample M2: thin-section photograph (transmitted light, X polars).

sample M3: thin-section photograph (transmitted light, X polars).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

107

Code	Sample type	Sampling zone	Adopted analisys
M4	fragment of reddish restoration mortar	west arm, northern side	ST, OM-TL

sample M4: sampling point.

Stereoscopic microscopy

sample M4

The sample consists of two layers, an outer whitish-pink layer and an inner red-brown layer; both are approximately 4 mm thick.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

108

Optical microscopy on thin section

Outer layer

MICROSCOPIC FEATURES OF THE BINDER		
1	Mineralogic composition	calcium carbonate ($CaCO_3$) originated from the carbonation process of an air-hardening lime
2	Structure	lumpy
3	Texture	micritic (dimension of calcite crystals 4-10 µm)
4	Interactions with the aggregate	absent
5	Porosity	
5.1.	o tipology	voids and microcracks
5.2.	o ubication	intergranular and intragranular
5.3.	o % (by volume)	very high (~35%)
5.4.	o origin	primary (voids naturally present within the aggregate or caused by shrinkage of the binder during setting and hardening)
MICROSCOPIC FEATURES OF THE AGGREGATE		
1	Size	
1.1.	o dimensional range (estimated values)	The grain size varies from coarse silt to coarse sand (0.03-0.68 mm) but it mainly falls in the fine sand class (0.125-0.25 mm); it spreads in the different fractions as listed below: <table><tr><td>granulometric classes</td><td>%</td></tr><tr><td>coarse sand (0.5-1 mm)</td><td>10</td></tr><tr><td>medium sand (0.25-0.5 mm)</td><td>20</td></tr><tr><td>fine sand (0.125-0.25 mm)</td><td>35</td></tr><tr><td>very fine sand (0.062-0.125 mm)</td><td>20</td></tr><tr><td>coarse silt (0.031-0.062 mm)</td><td>15</td></tr></table>
1.2.	o sorting	low
2	Shape (rounding and sphericity)	rounding: angular; sphericity: low
3	Surface morphology	faceted
4	Orientation	absent
5	Distribution	homogeneous

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

109

6	Composition (% by volume) (estimated values)	The aggregate have a silicatic and carbonatic composition; in order of decreasing abundance it spread as listed below:

rocks or mineral types	%
• pyroclastic volcanic rock fragments (red pozzolan containing piroxenes and plagioclases fenocristals and vulcanic glass)	55
• sedimentary rocks fragments identified as sparitic limestones	35
• metamorphic rock fragments classified as schists, quartzites and argillites	5
• effusive volcanic rocks fragments (lavas)	5

7	Admixtures	-
8	Binder/Aggregate Ratio (by volume)	~1:3

CONCLUSIONS		
1	Mixture characterization	It is a mortar composed of air-hardening lime and an aggregate consisting of approximately 55% of red pozzolan and the remaining 45% by volume of a calcitic sand obtained by crushing a sparitic limestone. The average size of the aggregate falls into the fine sandstone class and ranges between 0.125 and 0.25 mm; their maximum diameter is 0.68 mm. The binder/aggregate ratio is close to 1:3 by volume.
2	Secondary processes and decay products	No neoformation phases attributable to degradation processes are observed.

Inner layer

This layer shows compositional and textural characteristics quite similar to samples **M2** and **M3**.
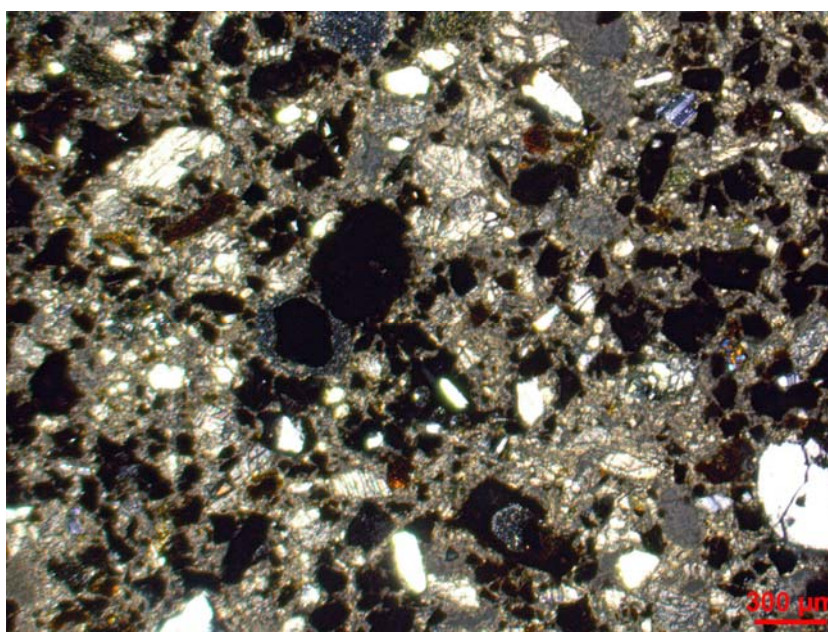
sample M4 - outer layer: thin-section photograph (transmitted light, X polars).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

110
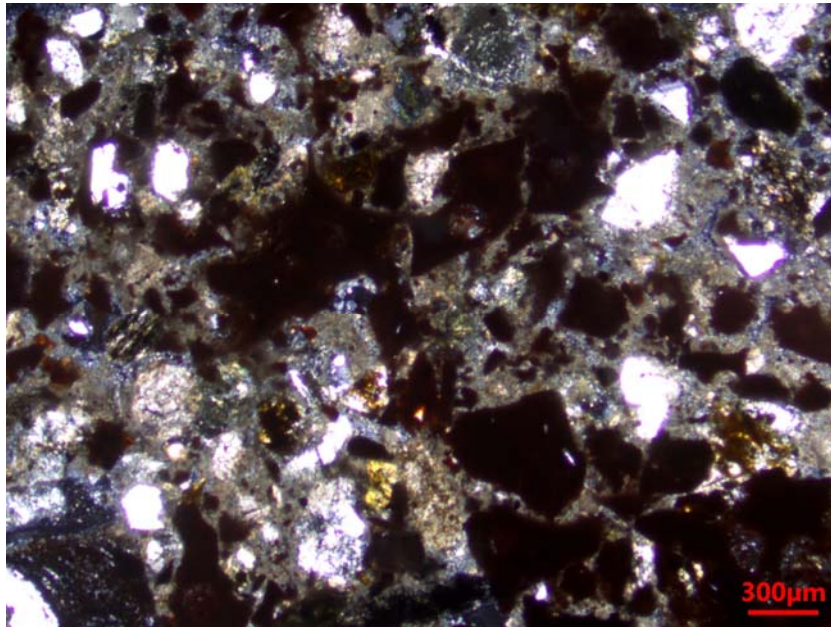
sample M4 - inner layer: thin-section photograph (transmitted light, X polars).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

111

Code	Sample type	Sampling zone	Adopted analisys
M5	fragments of reddish restoration mortar	west arm, vault	ST, OM-TL
M8		west arm, vault	

samples M5, M8: sampling point.

Stereoscopic microscopy

sample M5

sample M8

The two samples have the same compositional and textural characteristics and therefore belong to the same mortar.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

112

Optical microscopy on thin section

MICROSCOPIC FEATURES OF THE BINDER		
1	Mineralogic composition	calcium carbonate ($CaCO_3$) originated from the carbonation process of an air-hardening lime
2	Structure	homogeneous
3	Texture	micritic (dimension of calcite crystals 4-10 µm)
4	Interactions with the aggregate	absent
5	Porosity	
5.1.	o tipology	voids
5.2.	o ubication	intergranular and intragranular
5.3.	o % (by volume)	very high (~35%)
5.4.	o origin	primary (voids naturally present within the aggregate or caused by shrinkage of the binder during setting and hardening)
MICROSCOPIC FEATURES OF THE AGGREGATE		
1	Size	
1.1.	o dimensional range (estimated values)	The grain size varies from coarse silt to coarse sand (0.03-1 mm) but it mainly falls in the medium sand and fine sand classes (0.15-0.35 mm); it spreads in the different fractions as listed below:

granulometric classes	%
coarse sand (0.5-1 mm)	10
medium sand (0.25-0.5 mm)	30
fine sand (0.125-0.25 mm)	25
very fine sand (0.062-0.125 mm)	20
coarse silt (0.031-0.062 mm)	15

1.2.	o sorting	low
2	Shape (rounding and sphericity)	rounding: angular; sphericity: low
3	Surface morphology	faceted
4	Orientation	absent
5	Distribution	homogeneous
6	Composition (% by volume) (estimated values)	The aggregate have a silicatic composition; in order of decreasing abundance it spread as listed below:

rocks or mineral types	%
• pyroclastic volcanic rock fragments (red pozzolana containing piroxenes and plagioclases fenocristals and volcanic glass)	100

7	Admixtures	-
8	Binder/Aggregate Ratio (by volume)	~1:3.5

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione
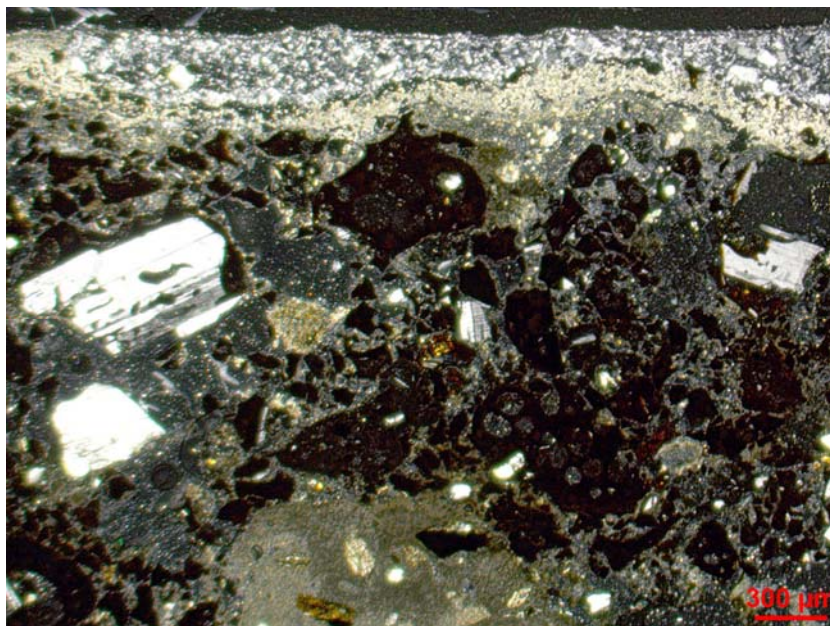
113

CONCLUSIONS		
1	Mixture characterization	The mortar consists of carbonated aerial lime and red pozzolan mixed according to a binder/aggregate ratio close to 1:3.5 by volume. The aggregate size varies between 0.03 and 1 mm but mostly falls in the range of 0.15-0.35 mm (medium and fine sandstone grain size classes).
2	Secondary processes and decay products	The sample is hard and shows no signs of degradation.

Sample **M5** shows a surface layer of carbonated lime about 100 µm thick

Sample **M8** shows a surface layer of carbonated lime, 150-250 µm thick, over which rests a layer of gypsum with a sparitic texture and small tabular crystals; the composition and texture of this latter layer seem to correspond to those of sample **M6**.
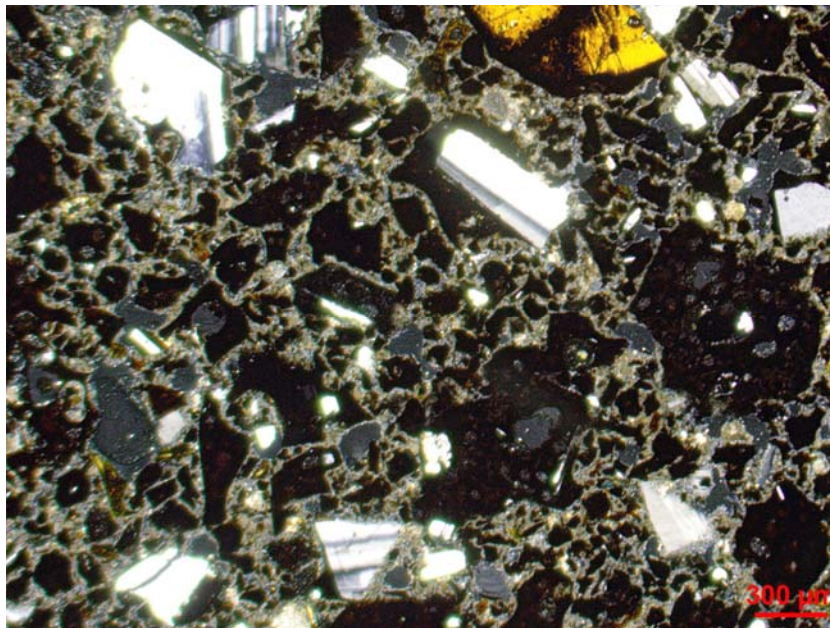
sample M5: thin-section photograph (transmitted light, X polars).

sample M8: thin-section photograph (transmitted light, X polars).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

Code	Sample type	Sampling zone	Adopted analisys
M7	fragment of gray restoration mortar	west arm, vault	ST, OM-TL

sample M7: sampling point.

Stereoscopic microscopy

sample M7 photograph under the stereomicroscope.

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione

115

Optical microscopy on thin section

MICROSCOPIC FEATURES OF THE BINDER		
1	Mineralogic composition	calcium carbonate ($CaCO_3$) originated from the carbonation process of an air-hardening lime
2	Structure	lumpy
3	Texture	micritic (dimension of calcite crystals 4-10 µm)
4	Interactions with the aggregate	absent
5	Porosity	
5.1.	o tipology	voids and microcracks
5.2.	o ubication	intergranular
5.3.	o % (by volume)	low (~15%)
5.4.	o origin	primary (caused by shrinkage of the binder during setting and hardening) and secondary (due to degradation processes)
MICROSCOPIC FEATURES OF THE AGGREGATE		
1	Size	
1.1.	o dimensional range (estimated values)	The grain size varies from coarse silt to medium sand (0.03-0.7 mm) but it mainly falls in the fine sand and very fine sand classes (0.1-0.25 mm); it spreads in the different fractions as listed below:

granulometric classes	%
coarse sand (0.5-1 mm)	10
medium sand (0.25-0.5 mm)	15
fine sand (0.125-0.25 mm)	35
very fine sand (0.062-0.125 mm)	30
coarse silt (0.031-0.062 mm)	10

1.2.	o sorting	low
2	Shape (rounding and sphericity)	rounding: angular or subrounded; sphericity: medium or low
3	Surface morphology	smooth or faceted
4	Orientation	absent
5	Distribution	homogeneous

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione
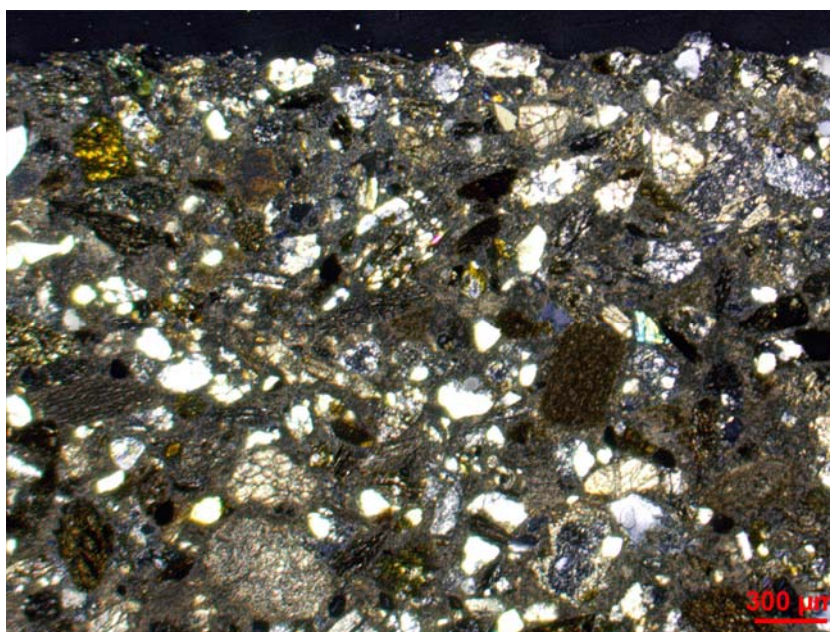
116

6	Composition (% by volume) (estimated values)	The aggregate have a carbonatic and silicatic composition; in order of decreasing abundance it spread as listed below:

rocks or mineral types	%
• sedimentary rocks fragments identified as micritic, microsparitic and sparitic limestones, marly limestone	35
• metamorphic rocks fragments classified as schists, quartzites and argillites	30
• feldspars crystals	15
• fragments of effusive volcanic rocks with microporphyric texture and intrusive volcanic rocks (granites?)	15
• fragments of quartz-rich silico-clastic sedimentary rocks (siltstones and fine-grained sandstones)	5
• chert, anphiboles, serpentinites	traces

7	Admixtures	-
8	Binder/Aggregate Ratio (by volume)	~1:3

CONCLUSIONS		
1	Mixture characterization	It is a mortar of air-herdening lime and river sand, mixed according to a binder/aggregate ratio close to 1:3 by volume. The sandy aggregate is composed of fragments of different lithotypes of sedimentary, metamorphic and volcanic origin with sizes predominantly between 0.1 and 0.25 mm.
2	Secondary processes and decay products	No signs of degradation are observed.

sample M7: thin-section photograph (transmitted light, X polars).

Dr. Geol. Davide Melica – Consulenza e Diagnostica per il Restauro e la Conservazione