

MULTITECHNICAL APPROACH FOR THE CHARACTERIZATION OF THE STRATIGRAPHY OF BLUE AREAS IN THE WALL PAINTINGS IN THE CHAPEL 11 AT THE “SACRO MONTE DI VARALLO”, ITALY

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Abstract

Chapel n. 11(1591) represents ‘the Massacre of the innocents’ and is one of the most dramatic of the 45 chapels at the UNESCO World Heritage site of the “Sacro Monte di Varallo” (Vercelli, Italy). The University of Applied Sciences and Arts of Southern Switzerland (SUPSI) in collaboration with “Ente Sacri Monti” is carrying out several investigations to acquire the necessary knowledge about original, added and degradation materials present on the wall paintings of chapel 11, to develop a conservation strategy and a restoration plan. Starting from on site visual examination, the analytical investigation campaign included non-invasive investigations (portable microscope, technical photography and portable X-ray fluorescence spectroscopy) and laboratory analyses on samples (Fourier transform infrared spectroscopy, observations by polarized optical microscope and Scanning electron microscopy with energy dispersive X-ray spectroscopy). Selected datasets resulted from the investigation on plaster, blue polychrome and on repainting are presented in this paper.

Keywords: *Wall painting; Technical photography; FTIR; XRF; SEM-EDS; FTIR; Varallo; IR, Vis and UV reflectography; Smalt; Azurite*

Introduction

The UNESCO world Heritage site ‘Sacro Monte di Varallo’ (Vercelli, Italy) was conceived in the late 15th century by Bernardino Caimi (friar of the Franciscan order) with the idea of reproducing the holy places of Palestine in Varallo. The site consists of a complex of 45 chapels each illustrating an episode of the life of Christ with wall paintings and life-size polychrome sculptures. Supported by the Bishop of Milan and by the ideas developed at the Council of Trento, over the years, the holy complex of Varallo became a model for the other Sacri Monti built in the nearby regions.

Chapel 11 represents ‘the Massacre of the innocents’ and contains both polychrome terracotta sculptures and wall paintings. It was commissioned by the Savoy duke Carlo Emanuele I and it was built by the D’Enrico brothers starting in 1586. The walls were decorated in 1590 by the Della Rovere brothers, called the Fiammenghini [1-3].

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The current appearance of the wall paintings compared with that documented by historical pictures by the photographer Giuseppe Pizzetta in 1898 and 1910 [4] and contained in the Soprintendenza archives [5], one dated earlier than 1930 and the other one earlier than 1933, show that Chapel 11 was restored and repainted extensively. It is known from historical record that the wall paintings were restored at least twice, including the latest known interventions by the painter Emilio Contini in 1955, who was at that time director of the Sacro Monte complex.

A project for the conservation-restoration of chapel 11 started in 2015 and included a preliminary investigation campaign with non-invasive (technical photography, portable microscopy and X-ray fluorescence analysis) and invasive (Fourier transform infrared spectroscopy, Scanning electron microscopy and energy dispersive X-ray spectroscopy and polarized light microscopy), methods used to characterize original, added and deterioration materials. The investigation focuses on the study of painting materials used by the Fiamminghini brothers's and re-paintings to assess if original paintings remained under the repainting and if it would be possible to reveal them.

This paper focuses on the results obtained from few selected datasets acquired by means of the above mentioned methods, during the investigation campaign performed on the wall paintings. In particular, the characterization of the Fiamminghini plaster and their painting techniques with highlights on blue pigments are described, as well as the main features of the latest restoration intervention (1955).

Experimental

Analytical Methods

Following a methodology widely used for cultural heritage, non-invasive methodologies were used for in situ wall paintings characterization, including imaging and point analysis. The imaging systems consisted of portable microscope and technical photography. Technical photographs were recorded with illumination in different electromagnetic radiation ranges (abbreviated as UV - ultraviolet, Vis - visible and IR - infrared) and in different configurations, giving the following outputs:

- Reflected Vis
- Reflected IR (IRr)
- Reflected UV (UVr)
- Vis fluorescence induced by UV (UVf)

Portable X-ray fluorescence spectroscopy (p-XRF) was used for the *in situ* elemental analysis of the artistic materials.

For the invasive laboratory analysis, the wall paintings were sampled in different locations of the chapel, selected on the basis of indications given by the imaging and non-invasive methods. The data recorded on site were complemented with laboratory molecular analysis (attenuated total reflectance Fourier transform infrared spectroscopy, ATR-FTIR), microscopic observation of samples (cross sections and thin sections) under polarized light microscope (PLM) and Scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDS). PLM was used to characterize the pictorial layers stratigraphy and to determine the plaster composition (aggregate particle size, texture, binder, etc.), while SEM-EDS was above all valuable for mapping elemental distribution within the painting stratigraphy.

This paper presents a selection of the analytical results obtained by crossing the photographic and XRF records captured from the vertical walls and the vault with those obtained by the invasive measurements performed on four samples taken from analogous same location. In Figure 1a-b and in table 1 the locations of non invasive measurement, the sampling points and the corresponding analyses used are summarized.

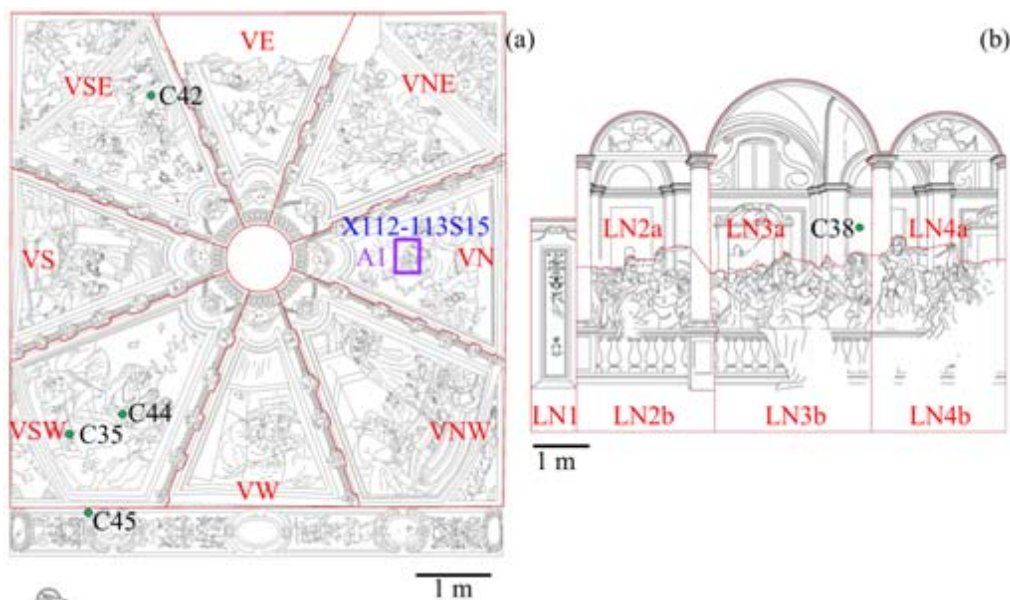


Fig. 1. Location of measured areas (A1) and sampling points (C35, C38, C42, C44 and C45) on the chapel sectors (abbreviation: V, vault; L, vertical walls; N, S, W, E, North, South, West and East respectively; the same nomenclature is used for table 1a. vault. b. north wall).

Table 1. Samples and measurement points name, location and analyses used.

Name	Location	Analyses
A1	VN	Technical photography
X_112-113_S15	VN	XRF analysis
C35	VSW	Cross section (PLM)
C42	VSE	Cross section (PLM)
C44	VNE	FT-IR
C45	VSE	Thin section (PLM)
		FT-IR
C38	LN3a	Portable microscope

Analytical Instruments

A portable microscope Dinolite AM4113T_FVW (equipped with Vis and UV LED bulbs) was used to observed details and understand stratigraphy.

Technical pictures were taken with a modified Canon 5D Mark II camera (inbuilt UV/IR block filter removed). A tungsten Lowel V (500W) lamp was used for illumination with Vis and IR radiations, while a filtered low-pressure mercury arc lamp (maximum emission at 365nm, Schott DUG11 interference filter) for UVr and UVf acquisitions. The camera was equipped with the following filters: IDAS-UIBAR UV/IR blocking filter for VIS, Schott RG830 high-pass filter (near-IR/Vis/UV blocking) for IRr, IDAS-UIBAR plus Schott KV418 UV blocking filter for UVf and Schott DUG11 interference filter for UVr acquisitions were used.

A Niton XL3t 900 Thermo Scientific was used as p-XRF analyzer, equipped with an X-ray tube (maximum voltage 50kV), an Ag anode and a semiconductor detector SI-PIN, which allows a resolution of 195eV in absence of He system. Measuring time was 30 seconds.

ATR-FTIR was performed with a Perkin Elmer UATR (Single Reflection Diamond) ‘Spectrum two’ spectrometer on solid samples. The system utilizes a MIR source, a diamond

crystal, an OptKBr beam-splitter and a LiTaO₃ based detector. Spectra were acquired within the 4000 – 400cm⁻¹ range at 4cm⁻¹ resolution and 1 minute accumulations.

A Zeiss Axioskop 40 polarizing microscope was used for thin and polished sections observation; it utilizes a Zeiss AxioCam MRC camera and an AxioVision Software Rel. 4.5. for capturing images. The samples were incorporated in epoxy resin (Araldite) under vacuum, paying special attention to avoid the acquisition of a secondary porosity during the preparation. Thin and polished sections were prepared by dry polishing and according Logitech standard procedures [6].

SEM-EDS images and analyses were performed by a large Angle SDD-EDS mounted on JEOL 6010LA system. Back scattered electron (BSE) images were acquired at 15.00kV voltage and at 45 and 200X magnifications. EDS spectra and maps (K-lines) were acquired on relevant locations using the following acquisition conditions: Volt 15.00kV, Process Time T3, Live time 90.00 sec.

Results and Discussion

The plaster

Figure 2 shows the sampling location (a-b) and the microscopic image of the back of the C38 sample (c), taken by portable microscope. The medium size grained aggregate appears dark in color. A better comprehension of the aggregate's nature is given by the observation of thin sections. Figure 2d shows the sampling location and the PLM images of the C45 sample thin section (e, crossed Nichols and f, parallel Nichols).

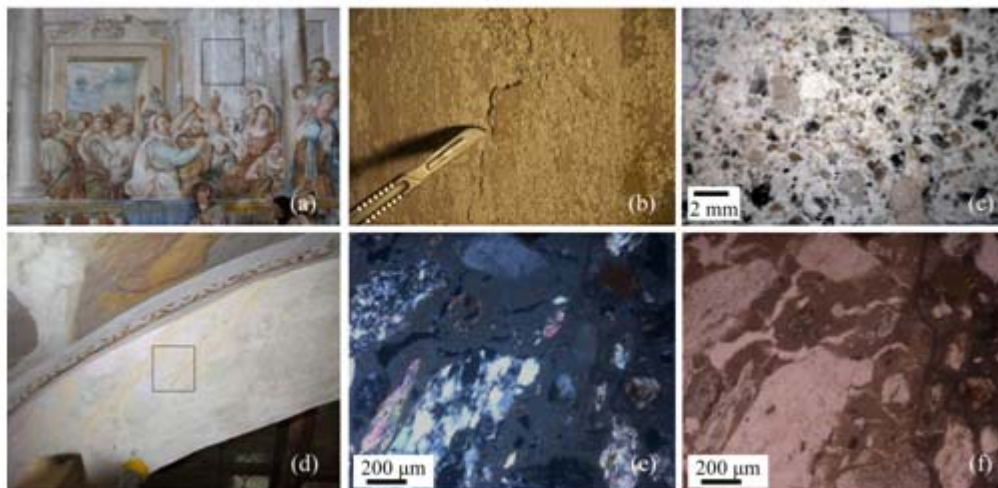


Fig. 2. Foto and Microscopic image: a. North wall, overall area of C38 sampling location; b. Detail of C38 sampling location; c. back of C38 sample, observed by portable Dino-Lite at 50X, showing color and size of aggregates; d. West arch, under vault's south-west sector, C45 sampling location; e. Photomicrograph of the C45 thin section, transmitted light, crossed nicols. On the left two siliceous-rich metamorphic rock fragments are visible. Crystals of quartz, mica and feldspar are also present; f. Photomicrograph of the C45 thin section, transmitted light, parallel nicols. Shrinkage cracks can be observed.

The PLM analysis shows that the plasters are characterized by binder/aggregate ratio > 1. Elongated fissures are also observed and interpreted as a consequence shrinkage, due to the high value of the binder/aggregate ratio (Fig. 2f). The dolomitic lime binder has micritic texture and inhomogeneous structure. The aggregate is prevalently siliceous metamorphic sand (siliceous-rich rock fragments, quartz, feldspar and mica crystals) with a few grains of pyroxene and amphibole (Fig. 2e).

PLM images of cross sections in reflected light of samples C35 and C42 (sampling locations in figure 1a and figure 3a-c, C42 cross section images in figures 4a and 4d, C35 cross section images in figures 6c-d) show the presence of 50 - 300µm size metamorphic aggregate. A mica particle parallel to the plaster layer and crossing the entire image is visible in figure 4c. The same can be observed in the SEM-EDS BSE images of figure 4b and 4d (sample C42) and figure 6a and b (sample C35).



Fig. 3. Sampling locations: a. Vault’s south-west sector C35 sampling location; b. Vault’s south-east sector, C42 sampling location; c. detail of C42 sampling location.

The mineralogical-petrographic composition of the aggregates, which does not differ much from that found in previous studies about the Sacro Monte chapels plaster can be referred to the alluvial deposits of the nearby Sesia River [7].

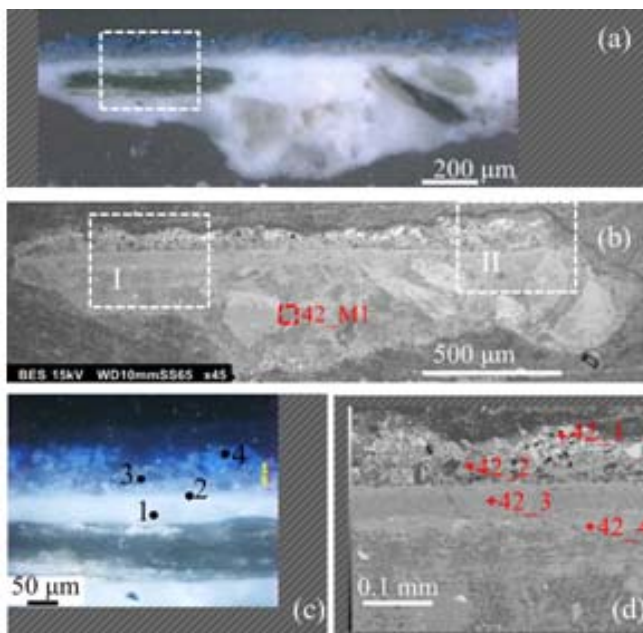


Fig. 4. SEM-EDS BSE images: a. Reflected light image of the C42 cross section (the white dashed square localizes the position of Fig. 4c.); b. SEM BSE image of C42 sample. The red squares localize the area investigated with elemental EDS analysis (results listed in table 2); the dashed white square I indicates the frames of the BSE image (shown in 4d); c. Reflected light image of a portion of sample C42 in cross section; d. Detail of the 4b image (SEM BSE); the red crosses localize the points analyzed by EDS, as listed in table 2 (see also Fig. 10).

Table 2. % mass of the elements found by EDS analysis in sample C35 and C42.

	C	O	Mg	Al	Si	Ca	Cu	K	Na	Ti	Fe	As	Cl
C42 1	25.86	7.21	0.51	0.40	1.38	2.30	43.82						0.53
C42 2	26.98	31.95		0.39	26.83	1.09	0.62	0.29				2.70	0.53
C42 3	17.92	32.26	18.72		0.85	15.75	0.68						0.49
C42 4	15.75	31.61		14.08	17.54			6.12	0.49		2.91		0.28
C42 M	34.64	34.19	8.93	0.35	3.2	10.95			0.46				0.68
C35 1	19.46	24.33	0.97	0.56	0.78	0.22	45.48						
C35 2	13.42	41.85		8.50	25.26			10.19	0.50				0.29
C35 3	16.93	40.80	5.81		0.38	31.15							0.21
C35 4	10.74	42.78		13.51	22.57	6.84			3.56				
C35 5	10.83	39.55	0.70	11.10	16.37	14.64				1.81	5.00		
C35 6	10.58	37.15	5.19	10.24	15.71	0.87					20.25		
C35 M1	9.02	36.60	4.93	9.85	15.08	0.91					19.32		
C35 M2	10.56	41.94		14.29	22.16	7.85			3.19				
C35 M3	33.75	38.90	8.04	0.36	0.80	13.63			0.34				0.61

The mortar binder was also characterized by ATR-FTIR analysis. Figure 8 shows the FTIR spectra of C44 and C45 samples (Fig. 1b for sampling location).

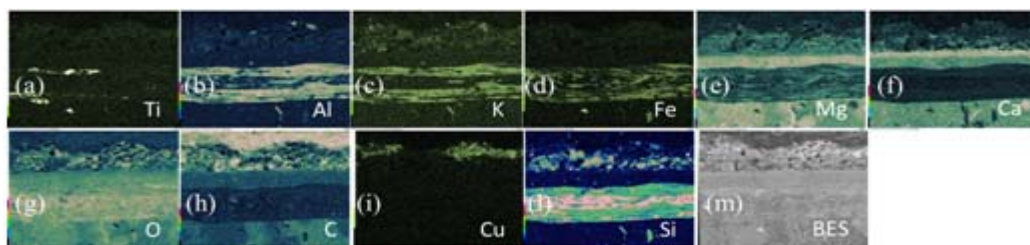


Fig. 5 Elemental distribution SEM-EDS maps (K-lines) on C42 sample for the major elements found: a. Ti; b. Al; c. K; d. Fe; e. Mg; f. Ca; g. O; h. C; i. Cu; l. Si; m. BSE image of the relevant C42 detail (see also Fig. 4d and Fig. 10).

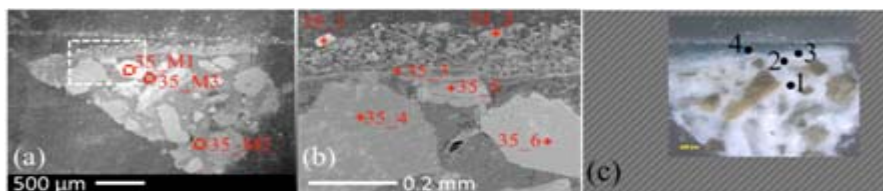


Fig. 6. SEM image: a. C35 sample, 45X. The small red squares indicates the areas investigated with elemental EDS analysis (results listed in table 2). b. Detail (BSE, 15.00kV, 200X) of the previous image, as indicated by the dashed white square. The red crosses localize the points analyzed by EDS (results listed in table 2). c. Reflected light image of C35 cross section.

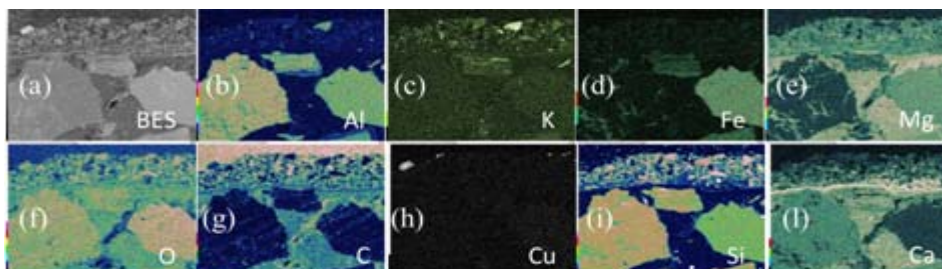


Fig. 7. SEM image: a. relevant BSE image of the C35 sample. b-m elemental distribution SEM-EDS maps on C35 sample for the elements; b. Al; c. K; d. Fe; e. Mg; f. O; g. C; h. Cu; i. Si; l. Ca.

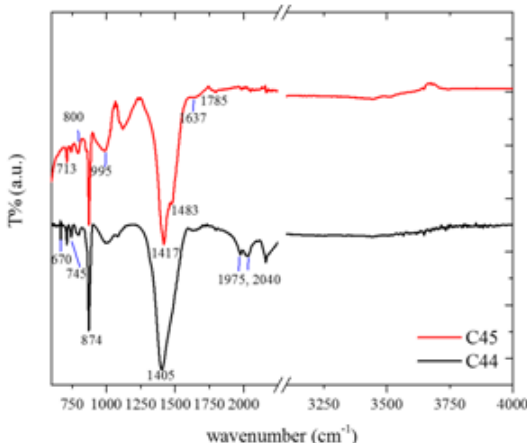


Fig. 8. FTIR spectra: a. C45 (red line) and C44 (black line) ATR-FTIR transmittance spectra.

The fundamentals bands of calcium carbonate can be observed at 713 (v4 in-plane bend), 874 (v2 out-of-plane bend), and at about 1405 – 1417cm⁻¹ (v3 symmetric stretch) [8], even if the band at 745cm⁻¹ suggests the presence of magnesium carbonate (v4) [9-12]. The use of magnesian lime binder was confirmed by SEM-EDS Mg maps and spectra made on C42 (Fig. 5e and C42_M1 in table 2) and C35 (Fig. 7e and 35_M3, table 2) samples. This information strongly suggests the predictable use of dolomitic material for the production of the mortar binder. Dolomitic lime stone is known to have been extracted at the Mount Fenara, close to the Varallo site [7].

Polychromies

Figure 9 shows the technical images captured from a detail of the wall paintings showing the Virgin and the infant Christ, located on the north sector of the vault (frame A1, Fig. 1a). The original paintings by the Della Rovere brothers are clearly identified and are only partly repainted. The overpaintings are limited to the yellow hues covering the forehead and some details of the Virgin’s face as well as the right hand, left arms and face of the child Christ (Fig. 9a).

The UVf image (Fig. 9d) clearly distinguishes the original from the repainting due to the strong yellow-green fluorescence emitted by the added paint. Portable XRF measurements (point X113S15 in Fig. 9a and table 3), show that the overpaint contains high amounts of zinc (Zn), lead (Pb) and barium (Ba).

Table 3. Elements detected by p-XRF on an original and on a repainted area (see Fig. 1a and Fig. 4a for points location).

	Pb	Zn	Ba	Ca	Fe	Sr	Cu	Ni	Bi
X112S15	+	+		+++	+	++	tr	tr	
X113S15	+++	+++	+		+	+	tr	tr	+

The strong defect-related [13] yellow-green UVf emission of ZnO (Zinc white) is well known and is clearly visible in association with the repainting. In addition, the simultaneous presence of Ba and Pb in addition to Zn suggests the use of other modern white pigments (lithopone and/or barium sulfate) and lead white, used in a mixture with a yellow pigment. On the other hand, despite the presence of residual Pb and Zn, the original white seems to be Ca-based, indicating the use of lime white (X112S15 in Fig. 9a and table 3).

The UVf photograph (Fig. 9d) also shows the presence of drippings on the surface, which may have been caused by water infiltration from the opening above and/or by a surface material used during a restoration (likely the 1955 intervention).



Fig. 9 Technical photography of virgin and child in Vault's north sector.
 a. Vis image with indication of p-XRF measurement points b. Raking light Vis image.
 c. IRr image. d. UVf image showing strong fluorescence associated with repainting.

The IRr photographs show that the opacity of the overpainting to the near-IR radiation (approximately 830-1000nm) does not allow the inspection of the original painted surface underneath (Fig. 9c). The original brushstroke directions (which follow the profile of the painted subjects) and thicknesses are well appreciated on the visible image in raking light (Fig. 9b), which also underlines the use of a notably thick paint in correspondence to the white borders of the Virgin veil.

The SEM-EDS elements distribution maps for the C35 and C42 samples show the presence of a white lime-wash just below the paint layers (Fig. 5f and Fig. 7l). This suggests that the Fiamminghini masters did not always paint directly on the plaster but applied a lime based white wash before the colors application. It is likely that this intermediate layer was used as a white base to cover the gray color of the plaster (given by the dark aggregates). At the same time, this lime layer must have helped in extending the wet state of the plaster, aiding to fix pigments through the carbonation process of the binder (calcium and magnesium hydroxides).

The SEM-EDS elemental distribution maps (Fig. 5 and 7) and the EDS analysis (C42_1, C42_2, C35_1, C35_2 in table 2) of the grains of composing the superimposed blue pictorial layers of both C42 and C35 offered the occasion to study the original painting technique used by the Fiamminghini brothers on blue dresses. Two layers of blue are visible by PLM cross section and BSE image of C42 samples (Fig. 4a-d) and, partially, on the PLM cross section and BSE image of C35 sample (Fig. 6 a-d).

The EDS analysis made on the grains of the top blue layer of both samples shows the presence of Cu, C and O, (C42_1 and C35_1 in table 2, points location in Fig. 4d and Fig. 6b) suggesting the presence of the mineral pigment azurite [$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$] applied over a layer composed of a different blue. The same analysis performed on this lower pictorial layer (C42_2 and C35_M2 in table 2, points location in Fig. 4d and Fig. 6b) shows the presence of Si, Co and K, as major elements, suggesting the presence of potassium cobalt silicate (smalt pigment), which was widely used at Varallo.

This evidences brought to the conclusion that, in both the sampling locations, the pigment azurite was over a layer of smalt. Only few azurite particles are visible over a smalt layer in sample C35 (Fig. 6a-d). It is important to notice that there is no interphase or separation layer between the azurite and smalt layer. This suggests that the two blue layers have been applied at the same artistic time. The Fiamminghini artists applied first a blue layer of smalt

and then the blue was reinforced by adding azurite probably to obtain a shimmering and vibrating effect for the Virgin dress. Visual examination support these findings as the blue area have a original aspect with only fine dashed lines were used for the pictorial rendering of the dress, typical mark of the Fiamminghini style and incompatible with any overpainting (Fig. 10).

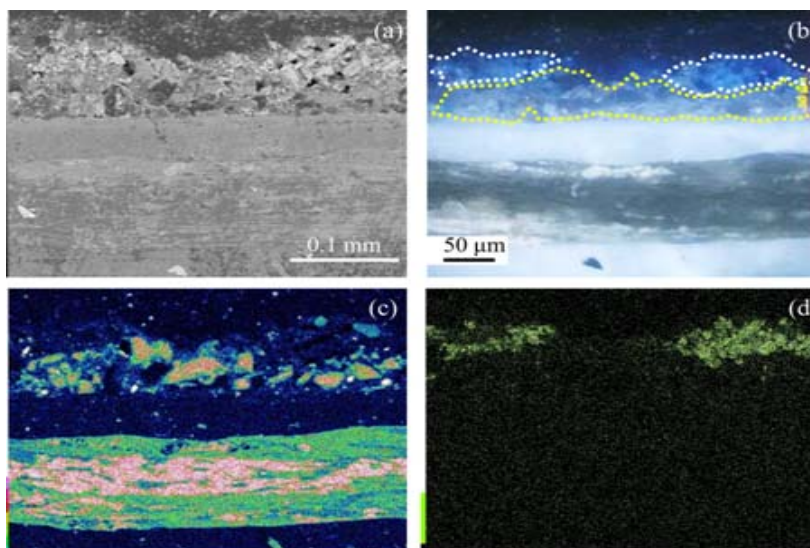


Fig. 10. SEM EDS and reflected light image: a. BSE detail of C42 cross section. b. Reflected light image of a detail of C42 cross section. The white dotted line indicates areas rich in Cu (see Fig. 10d) suggesting the presence of azurite while the yellow dotted line indicates areas rich in Si (see Fig. 10c) which, associated with other elemental maps (shown in Fig. 5), suggests the use of smalt. c. SEM-EDS map of Si (K-lines). d. SEM-EDS map of Cu (K-lines).

Conclusions

This paper reports on the results obtained from few selected datasets acquired by non invasive and invasive investigations of the wall paintings of the chapel 11 at the Sacro Monte di Varallo. The nature of the plaster used by the painters, the Fiamminghini brothers, was studied by means of SEM-EDS, PLM and ATR-FTIR. The plaster layer resulted composed of a mixture of siliceous and metamorphic aggregates in a magnesium lime binder. The aggregates composition can be referred to the alluvial deposits of the near Sesia River and the SEM-EDS analysis determined the presence of a magnesian component in the carbonate binder, thus suggesting that it comes from the Mount Fenera, close to the Varallo site. PLM and SEM-EDS images of cross sections of two samples of blue areas from the vault paintings clearly detected a limewash Ca-based layer over the wall paintings plaster, but under the paint layers. Probably this intermediate layer was used as a white primer to ease the application and the binding of the polychrome and to improve the visual effect by covering the gray color of the plaster given by the dark aggregates. The whitewash layer has also the function of slowing the setting time of the plaster allowing fixing the pigments within the calcium and magnesium hydroxides carbonation process.

SEM-EDS examination of cross-sections showed that both smalt and azurite are present in the Fiamminghini blue palette. These two pigments were found used together even if applied layered, probably for giving a vibrating and shimmering effect to the blue color.

The IR-opacity of the overpainting do not allow the visualization of the lower original layers (IRr) and/or impeding the understanding of the condition original pictorial layers. Anyway, when not clear by visual inspection, UVf photography helped enormously in identifying the location of overpainting, very often characterized by a strong yellow-green fluorescence, caused by the large used of ZnO based white pigment.

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