

Article

The “Restoration of the Restoration”: Investigation of a Complex Surface and Interface Pattern in the Roman Wall Paintings of *Volsinii Novi* (Bolsena, Central Italy)

Claudia Pelosi ^{1,*}, Filomena Di Stasio ², Luca Lanteri ¹, Martina Zuena ³, Marta Sardara ³ and Armida Sodo ³

¹ Laboratory of Diagnostics and Materials Science, DEIM Department, University of Tuscia, Largo dell'Università, 01100 Viterbo, Italy; llanteri@unitus.it

² DIBAF Department, University of Tuscia, Largo dell'Università, 01100 Viterbo, Italy; f.distasio92@gmail.com

³ Science Department, University of Rome 3, Via della Vasca Navale 84, 00146 Roma, Italy; martinazuena@gmail.com (M.Z.); marta.sardara@uniroma3.it (M.S.); armida.sodo@uniroma3.it (A.S.)

* Correspondence: pelosi@unitus.it; Tel.: +39-0761357673

Abstract: (1) Background: The present paper reports the results of the analyses performed on the wall paintings of Room E of the *Domus delle Pitture* (Room of the Paintings) in the Roman archaeological site of *Volsinii Novi* (Bolsena, Viterbo, Central Italy) aimed at supporting the recently concluded restoration. (2) Methods: ultraviolet fluorescence photography was conducted to evaluate the conservation state. Painting materials were investigated via portable X-ray fluorescence spectrometer (p-XRF), μ -Raman spectroscopy, cross-section analysis under polarizing microscope, scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), and Fourier transform infrared (FTIR) spectroscopy. (3) Results: This analysis revealed the presence of traditional pigments used in Roman wall paintings, such as ochres, earths, and Egyptian blue. Additionally, it identified pigments from previous restoration containing titanium and chromium, along with other materials present in the surface and interface of the wall painting containing arsenic, copper, lead, and vanadium, where a bluish alteration was observed. In these samples, μ -Raman spectroscopy detected calcium oxalates but also copper arsenates, likely conicalcrite and/or duftite. (4) Conclusions: This result is highly relevant from an analytical point of view and in relation to the restoration decisions. Addressing the irregular bluish stains on the wall paintings poses challenges in understanding, requiring a decision on whether to remove or retain them.

Keywords: wall paintings; Roman period; X-ray fluorescence spectroscopy; μ -Raman spectroscopy; scanning electron microscopy–energy dispersive spectroscopy; restoration; degradation materials



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1. Introduction

The object of the present paper is the investigation of the wall paintings of the so-called Room E of the *Domus delle Pitture* (House of the paintings) in the Roman archaeological site of *Volsinii Novi*, currently Bolsena, in the district of Viterbo (Central Italy) [1] (Figure 1). The focus of this paper is to analyze the surface materials, which have not been previously examined in depth, to support the recently concluded restoration work [2].

Roman wall paintings have been extensively studied, and numerous scientific papers aiming to characterize pigments, binders, plasters, and degradation materials can be found in the literature, as summarized in some relevant reviews on this specific topic [3–5]. In a recent study, it was estimated that approximately 250 scientific papers have been published over the last 20 years regarding the analysis of materials used in Roman wall paintings [6], indicating considerable interest in this area of research. However, in the case of *Volsinii Novi*, only a few fragmentary analyses have been found in the archives of the École française de Rome, often not specifically referring to specific rooms or walls within the archaeological

site. Therefore, it has become particularly relevant to investigate the artwork to properly plan the restoration, especially the cleaning intervention of the surfaces.

The results of the scientific analyses are reported for the first time in the present paper, which aims to characterize the painting materials (pigments and binders) and, most importantly, to understand a peculiar bluish–green layer visible on the surface of the walls in Room E (Figure 2).

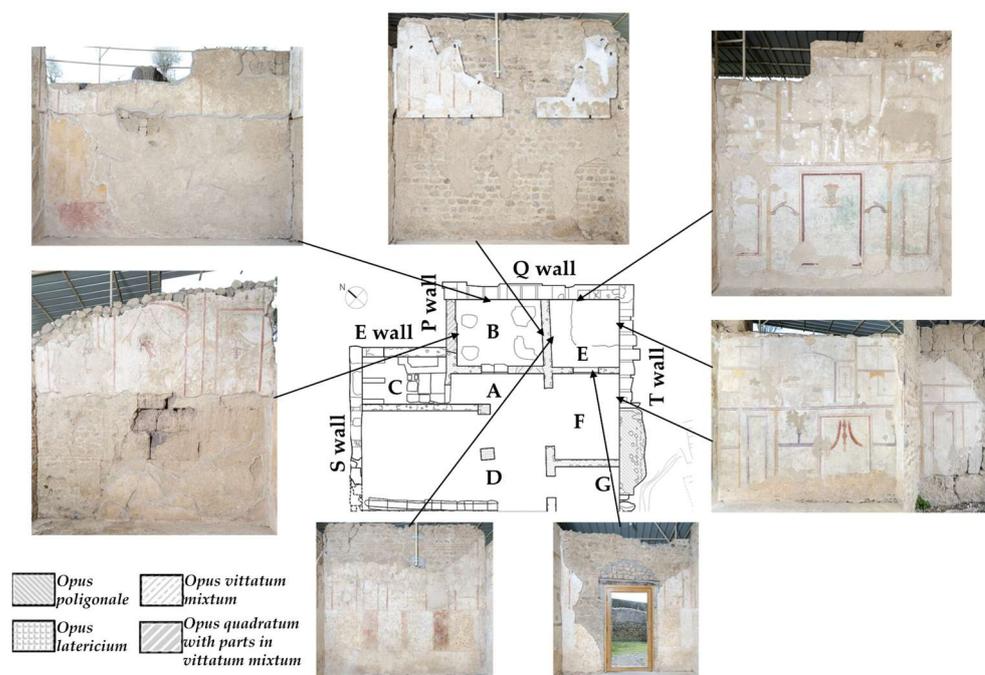


Figure 1. The *Domus delle Pitture* with a graphical map (in the center of the image) of the rooms and the main walls delimitating the area. A, B, C, D, E, F and G are the letters used to indicate the different rooms of the house. The different construction techniques (*Opus*) used in the Roman period are also highlighted by graphical representation.



Figure 2. View of the northeast wall of Room E (object of our study and restoration). (A) the wall painting before restoration showing the bluish–green areas on the surface; (B) a detail of the paintings better highlighting the bluish–green layer, and (C) a more detailed view showing the previous inpainting made by *puntinato* (dotted) and *rigatino* (vertical lines), this last developed by Cesare Brandi in the mid-1900s [7].

This bluish–green layer appears superimposed on the most well-preserved pictorial phase of Room E and appears unevenly distributed (Figure 2).

This bluish layer extends diagonally from the upper right corner of the median register to the lower left part of the pictorial surface, resembling an accidental pigmentation. Upon observing the photographic documentation found during bibliographic and archival research, the progression and design with which the bluish–green layer appeared seem to be consistent from the moment of discovery of the paintings until today [8]. Since its discovery, as the pictorial surface was affected by a biological attack, the layer was initially interpreted as a biodeterioration pattern. This hypothesis was further considered valid after measuring the degree of humidity of the wall and noting that the trend followed that of the graphs corresponding to the measurements. However, the biocidal treatment and interventions on the environment made in the 1982–1983 restoration yielded minimal results. For this reason, experts put forward an alternative hypothesis suggesting that the layer not removed, initially thought to be a biological attack, might be a chemical alteration caused by the oxidation of a mineral present within the wall. Although suggested, no appropriate analyses were ever carried out to confirm this hypothesis [9].

Considering the complex situation regarding the distribution of painting layers and the conservative history, as detailed in the Materials and Methods section, the objective of the Unitus restoration has been the recovery of the artwork. It represents a palimpsest resulting from a series of modernizations carried out in antiquity, whose levels and iconography had been partly eliminated in the first intervention following the discovery (in 1968) and partly hidden in the last (in 2012) [10,11]. The Unitus restoration was supported by a diagnostic and analytical campaign mainly aimed at characterizing the bluish–green layer that, upon careful observation during our restoration, surprisingly seems to constitute a further painting layer positioned between the second and the third pictorial phases. As an investigation method, preliminary ultraviolet fluorescence photography was conducted to evaluate the conservation status and the restoration materials. The bluish layer was investigated using a portable X-ray fluorescence spectrometer (p-XRF) and μ -Raman spectroscopy. Further investigation involved cross-section analysis under a polarizing microscope and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS). Finally, Fourier transform infrared spectroscopy was applied to study binders and possible degradation materials.

2. Materials and Methods

2.1. Archaeological Contest

The wall paintings in the *Domus delle Pitture* exhibit different phases realized in various Roman periods, along with three recent restorations. These factors make reading the paintings particularly challenging. Within Rooms B, E, and F, three different pictorial phases can be observed based on the stylistic characteristics: the initial phase dating back to 50 B.C.–50 A.D.; a second phase executed before 200 A.D.; and a third phase between 220 and 240 A.D (see Figure 1).

The careful observation of the walls revealed that Rooms E and F originally formed a single room. This deduction is based on the analysis of the paintings on the southeast wall labeled as T, which match those on wall Q on the northeast side of Room E. On the other hand, the paintings on the northwest and southwest walls are clearly different.

When the dividing wall between rooms E and F was built, the existing walls were covered with painted plaster intended to harmonize with the new decorative apparatus. The term *ante quem* is, therefore, provided by the reconstruction of the wall in *opus vittatum mixtum* (divisions B–E and E–F), which, by cutting the room, mutilated the decoration of the long wall T to the northeast and destroyed that present on the partition that originally separated the same point room B from E. In the left corner of the back wall (northeast) of room E, there is no indication that the painting continued further toward room B, as on the right wall. Furthermore, the new wall is not based on any previous wall structure, as demonstrated by the surveys conducted by the *École Française de Rome*, unlike, for example, wall T, which delimits the room to the southwest and houses the oldest decoration.

In summary, the decorative pattern is the same on the back wall (northeast) and the right wall (southeast) of room E and on the left end of the back wall of room F. The partition in *opus vittatum mixtum*, built to divide the two rooms, effectively altered the previous decoration, subsequently overlaying it with a new pictorial program, which partly obscured the previous decoration of the second phase (room E–F) and first phase (room B), where present [8].

2.2. Previous Restorations

The archaeological site of *Volsinii Novi*, located in Poggio Moscini, a hill in the town of Bolsena, underwent conservation and restoration interventions following the first discoveries in the 1960s of the 20th century that modified the original appearance and characteristics of the wall paintings. To comprehend today's situation, it was very important to investigate the past restoration treatments and the materials used, as synthesized in this subparagraph.

Specifically, the paintings were discovered between 1967 and 1968 and immediately restored by the École Française de Rome (French School in Rome) and Istituto Centrale del Restauro (Central Institute of Restoration, ICR) [12]. This intervention aimed to recover the second pictorial phase in Room E and remove the third phase painting characterized by false marble decoration. The choice of removing the third phase was likely due to aesthetic reasons. In fact, the paintings of the second phase were considered more valuable stylistically. A 1969 report indicates that the intervention on the wall paintings of Room E mainly addressed cleaning and consolidating the surfaces [13]. The cleaning intervention involved water and, in some areas, acetic acid. The consolidation was performed via injections of calcium caseinate to fix the plaster and using Paraloid® B72 (a copolymer based on ethyl methacrylate and methyl acrylate) to fix the edges and the painting layer.

The lacunae were grouted with cement, and protective cords were created along the edges of the painted walls. Additionally, small gaps in the paint film were reintegrated with colored earths added to Primal®, a 100% pure acrylic resin in water dispersion belonging to a generation of acrylic resins from Dow Chemicals (formerly Rohm & Haas, Midland, MI, USA). It is commonly used in the restoration sector for water-based paints and as a wall fixative for interiors and exteriors. Finally, a roof with gutters was installed during the same period, comprising plasticized material mounted on a metal frame. Extending beyond the limits of the rooms, its purpose was to facilitate wall evaporation and ensure the conservation of the wall paintings sustainably.

In 1981, an inspection by officials from the École Française de Rome and the Superintendence highlighted the precarious state of conservation of the wall paintings due to the infiltrating and capillary rising humidity present in situ [14,15]. To solve this problem, in that same year, a cavity was created between the external walls of Room E and the surrounding ground to aid water evaporation from the tuff blocks outward. Furthermore, the existing roof was expanded to redirect rainwater away from the gutters, preventing its seepage into the archaeological structures. These interventions aimed at improving the microclimate conditions within Room E, specifically addressing raising damp and wall water infiltration. The microclimatic reclamation works were followed by direct interventions in the paintings [9]. These interventions consisted of (1) removal of the cement grouting along the edges of the lacunae, (2) consolidation of the wall paintings, (3) removal of the protective layer applied during the 1968 restoration, (4) cleaning of the surfaces, (5) grouting of the lacunae and little cracks, (6) inpainting with watercolors, (7) biocidal treatment on the surfaces, and (8) application of a final protective.

The consolidation phase involved three operations: (1) injections of Paraloid® B72 to re-establish the cohesion of the mortars; (2) injections of pozzolan and lime for the re-adhesion of the detachments considered more serious between the plaster and the wall support; and (3) injections of Vinnapas® (Wacker, Munich, Germany) a vinyl acetate co- and terpolymer dispersion for the re-adhesion of the remaining areas [9]. The cleaning was performed by using a mixture named AB57® developed by ICR. AB57® is based on ammonium bicarbonate, sodium bicarbonate, ethylene diamine tetra acetic acid (EDTA),

carboxymethyl cellulose, and quaternary ammonium salts. It is a formulation that has been studied by the ICR and has been used for several decades to clean frescoes and stone surfaces. It belongs to the non-harmful chemical cleaning methods of surfaces used in the field of conservative restoration. The surfaces were protected by applying a layer of Paraloid® B72, which was also intended to revive the inpainting.

Later, in 2012, a new restoration was started and never concluded by the Academy of Fine Arts “Lorenzo da Viterbo” (Viterbo, Italy) [10,11]. From the limited information obtained from the only two publications available, it seems that the restoration had the objective of reproducing the original pictorial surface. However, the criteria and choices guiding the various operations likely resulted in misreading the paintings. This led to the creation of a particularly invasive chromatic inpainting, which was methodologically questionable and irreversible. By analyzing the chromatic range used for the inpainting, both neutral and dotted (*puntinato*) inpainting, it was hypothesized that the intervention aimed to give continuity and partly hide the traces of bluish pigmentation present on the surfaces, reading the latter as residues of what must have originally been the authentic color of the background. Furthermore, the choice was also to hide the stratigraphy, and the traces of the executive technique were kept visible until then, thus overshadowing the conservative history of the archaeological artifact.

Starting from the knowledge of the conservation history of the wall painting derived from the archive documents and published papers, a diagnostic campaign was undertaken with the aim of characterizing the materials, with a special focus on the areas appearing bluish–green in color and visible in different zones of the surface. This bluish–green layer is superimposed on the second pictorial phase of Room E and appears unevenly distributed (Figure 2).

2.3. Ultraviolet Fluorescence Photography (UVF)

This technical photography was performed before the restoration activities with the aim of revealing the status of the painting surfaces. UVF photography was performed using a Nikon (Tokyo, Japan) D5300 digital camera equipped with a 17–35 mm lens and with an exposure time of 30 s. The fluorescence was stimulated by using two CR230B-HP 10W LED (Madatec, Milan, Italy) projectors with a peak emission at 365 nm, positioned at about 45° with respect to the surface to be acquired. In front of the camera lens, two filters, UV-IR cut and filter A, were used to remove the UV and IR components of the spectrum. The spectra of the two filters had been previously published [16,17].

2.4. X-ray Fluorescence Spectroscopy (XRF)

XRF spectroscopy was performed on site by a portable apparatus supplied by Assing (Monterotondo, Rome, Italy). The instrument used was a Surface Monitor II equipped with an Ag anode operating at 40 kV and 76 μ A and an Amptek X-123 Si Pin detector (Amptek, Bedford, MA, USA) that revealed elements from S to U with a resolution of 146 eV. The work distance was 94 mm from the artwork surface, and the spot area was 2.0 mm in diameter. The acquisition time was set at 60 s. XRF measurements were gathered from 21 points (X1–X21) to cover the entire palette visible on the painting surface and, above all, to characterize the chemical elements of the bluish–green areas (Figure 3, red points). Both original and restoration colors were examined on the northeast and southeast walls of Room E.

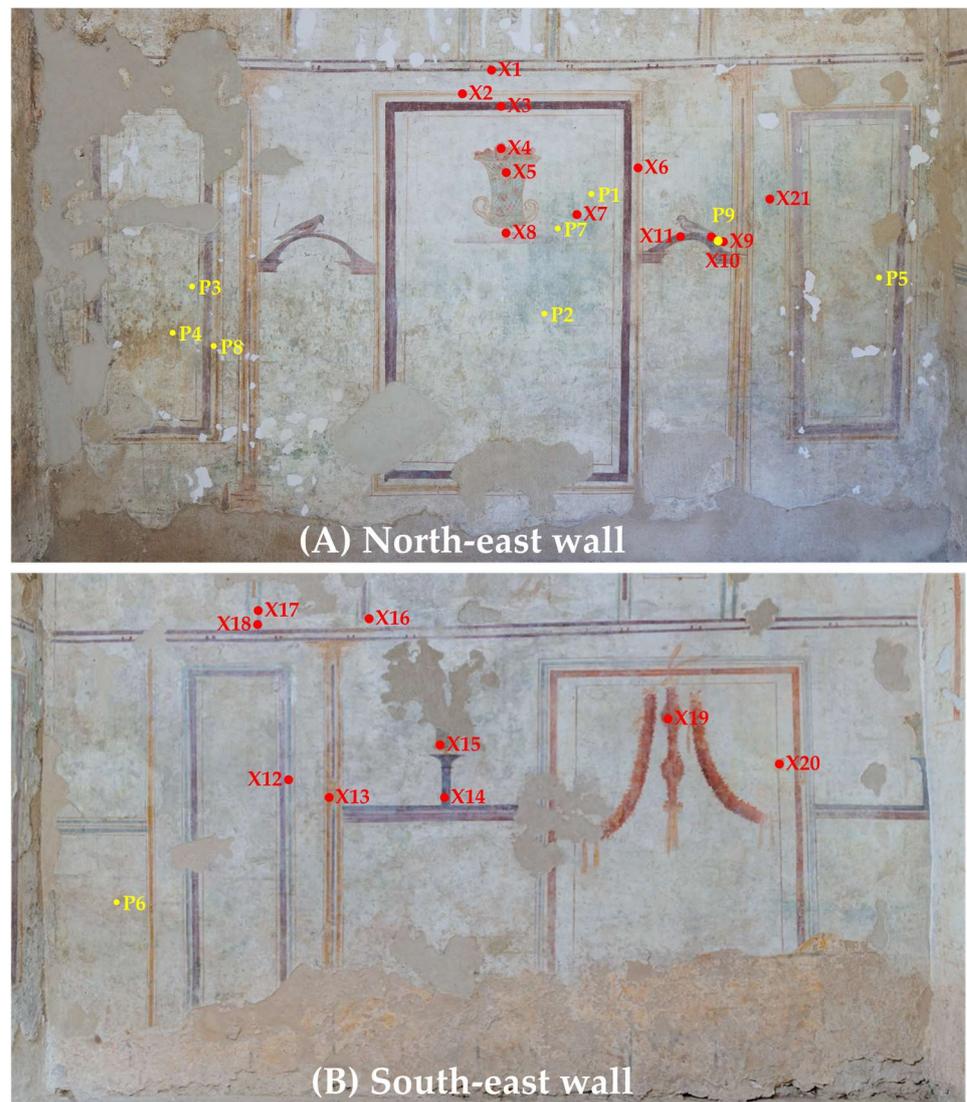


Figure 3. Photographs of the two examined walls in Room E with the points of XRF measurements (X1–X21) in red color and the sampling points (P1–P9) in yellow.

2.5. Micro-Sampling for Laboratory Analysis

After a careful on-site examination and analysis, micro-sampling was conducted with the aim of investigating the stratigraphy of the wall paintings and enhancing understanding of the bluish–green patina distributed on the surfaces and particularly concentrated on the northeast wall, which was the focus of our restoration work. For this reason, nine micro-samples were collected from the artifact, making sure to avoid damaging the wall painting while obtaining samples useful for laboratory analysis.

The points of sampling are shown in Figure 3 in yellow. Samples were not only obtained at the beginning of the restoration work but also during various steps, according to the requirements of the intervention.

The micro-samples were examined using cross-sections under optical and scanning electron microscopes, Fourier transform infrared spectroscopy, and micro-Raman spectroscopy.

Table 1 summarizes the characteristics of the samples and the analyses performed on each one.

Table 1. A summary of micro-samples' characteristics and analyses performed on each sample.

Micro Sample Nr.	Sample Description	Performed Analysis
P1	Bluish–green surface layer (XRF point X7)	FTIR
P2	Light green layer apparently superimposed to P1 (XRF point X7)	FTIR
P3	Bluish–green layer	FTIR
P4	Light brown surface layer	FTIR
P5	Micro-fragment for stratigraphic analysis (XRF point X21)	OM, SEM-EDS
P6	Micro-fragment for stratigraphic analysis and comparison with P5	OM, SEM-EDS
P7	Bluish–green surface layer (XRF point X7)	OM, SEM-EDS, μ -Raman
P8	Bluish–green surface layer	OM, SEM-EDS, μ -Raman
P9	Blue color of the bird's tail (XRF point X9)	μ -Raman

2.5.1. Optical Microscopy

The cross-section of samples P5–P8 was observed with a polarizing microscope Zeiss Axioskop (Carl Zeiss, Oberkochen, Germany) equipped with transmitted and reflected light and UV radiation using a vapor mercury lamp.

Images were acquired by means of a Zeiss AxioCam directly connected to a laptop computer and were processed using the AxioVision Version 1.0 dedicated software.

2.5.2. Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS)

The same samples, P5–P8, were further examined using a scanning electron microscope coupled with energy dispersive spectroscopy (SEM-EDS) to map the chemical elements directly on the cross-sections.

For SEM-EDS analysis, a Jeol JSM 6010 LA scanning electron microscope (Tokyo, Japan) was used, operated at 20 kV as the acceleration voltage of the electrons. Before the SEM-EDS analysis, the samples were placed on aluminum stubs, secured with carbon tape, and metalized with gold using a sputter coater Balzers Union MED10 (Cae, Austin, TX, USA), operating under vacuum.

2.5.3. μ -Raman Spectroscopy

The μ -Raman investigations were conducted employing a Renishaw (Wotton-under-Edge, UK) InVia Reflex Raman spectrometer equipped with two diode lasers: one at 532 nm and another at 785 nm, generating power outputs of 100 mW and 180 mW, respectively. Utilization of a diffraction grating, with specifications of 1800 grooves/mm for the 532 nm excitation wavelength and 1200 grooves/mm for the 785 nm excitation, facilitated the dispersion of backscattered light; a Peltier-cooled (-70 °C) 1024×256 -pixel CCD detector was used. Fine adjustments of integration time and accumulation numbers were executed for each analyzed point, aiming to diminish fluorescence while optimizing the signal-to-noise ratio. After a series of preliminary trials, it was observed that the optimal results were obtained using the green source (at 532 nm) and employing the $50\times$ objective. Tailored to the specific response of each individual sample, spectra were acquired with an acquisition time of about 5–10 s, utilizing 30 accumulations within the spectral range of 100 – 3500 cm^{-1} . The WiRE™ software Version 5.6 played a pivotal role in configuring measurements, acquiring data, and performing baseline subtraction. Subsequently, the acquired spectra underwent further processing using the Origin software Version 9 (Origin Lab Corporation, Northampton, MA, USA).

2.5.4. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was performed using a Nicolet Avatar 360 spectrometer (Thermo Fisher Scientific Waltham, MA USA) equipped with a diffuse reflectance accessory (DRIFT), a Michelson interferometer, and a detector based on deuterated triglycine sulfate (DTGS). Spectra were obtained by grinding about 10 mg of the sample with spectrophotometric grade potassium bromide (KBr), which was also used as background material. Spectra were processed with Omnic 8.0 software supplied by Thermo Fisher Scientific.

3. Results

3.1. Ultraviolet Fluorescence Photography (UVF)

The first investigation carried out on the wall painting surfaces was the UVF photography focused on the northeast wall of Room E, where the restoration activities were addressed (Figure 4).

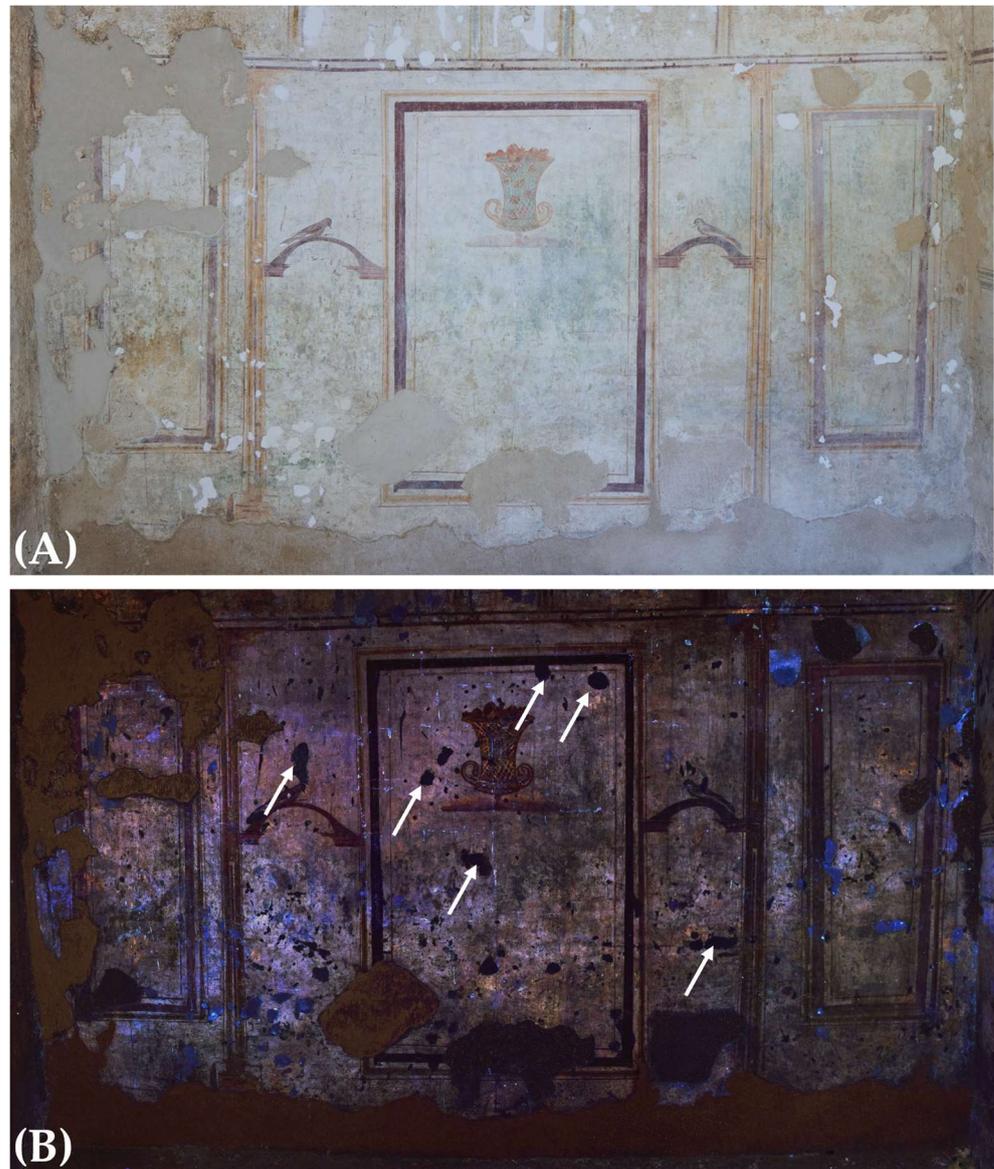


Figure 4. Photographs of the northeast wall in Room E before the last restoration: (A) RGB image and (B) ultraviolet fluorescence photograph. White arrows in the UVF image indicate the restoration inpainting applied in 2012.

The UVF image shows a surface characterized by various kinds of fluorescence due to the various interventions performed over time on the wall painting, revealing a complex situation. Compared to the RGB image, UV fluorescence highlights a light blue response corresponding to the white grouting and the dotted lines made with gypsum. The dotted lines, generally traced by the restorers for delimitating different areas of the surface during treatment, can be referred to as part of the incomplete 2012 intervention. The dotted line that divides the central vase into two parts seems to define different conservation statuses between the right and left parts of the wall paintings.

Specifically, the left side appears very heterogeneous, with an evident orange fluorescence mainly concentrated in the upper part, presumably due to the protective resin spread on the pictorial surface during the 1980s intervention. In the lower part, on the other hand, the presence of an uneven situation is an indication of an unfinished intervention attributable to the works carried out in 2012.

The large grouting has no fluorescence, suggesting the presence of modern plaster materials used in the 1981 restoration to substitute the previous cement. Additionally, the UVF image reveals some small, completely black areas (see white arrows in Figure 4) attributable to the 2012 restoration inpainting. In fact, in 2012, the restoration was not concluded, leaving some grouting white without inpainting (exhibiting light blue fluorescent) while others were retouched (black under UV).

The right side of the UVF image shows a more homogeneous situation resulting from the 2012–2015 intervention, which in this part of the surface was almost completed. An orange fluorescence is perceptible, probably attributable to the resin spread during the works in the 1980s. However, especially on the right side, this fluorescence is obscured by a greenish substance lacking any fluorescence, possibly stemming from the extensive chromatic inpainting undertaken during the 2012 restoration.

It is interesting to note that the bluish–green areas, mainly visible in the central part of the wall, have no fluorescence.

3.2. X-ray Fluorescence Spectroscopy (XRF)

After the preliminary study using UVF photography, on site X-ray fluorescence spectroscopy was performed to detect the main chemical elements present on the painting surface. The overall results of the XRF analysis are summarized in Table S1 in Supplementary Material.

Focusing attention on the bluish areas, the main detected element is copper, and it appears associated with lead. In fact, the increase in lead content would seem directly linked to the increase in copper content by observing point by point, suggesting an intentional presence of both elements in the points examined. The diffused presence of copper, whose higher counts are detected in the bluish–green inhomogeneous areas of the surfaces, led to the hypothesis that these areas constituted a further painting phase covering the second one. The incorrect reading and interpretation of this bluish–green color led to a wrong treatment in the past, first with the use of a biocide, then with acid compounds, and finally, with the attempt to hide it, likely contributing to an alteration of the original materials creating the current situation.

The XRF analysis allowed for the detection of other elements on the painting surface. Specifically, as can be observed by the data in Table S1, calcium, iron, and strontium are constantly present in all examined points, with different relative counts. In some points, titanium was also revealed (points X6, X12, X13, X16, X17, and X18). In the restoration area (green color), chromium was further detected together with Ti.

Calcium and strontium are elements of the plaster, while iron is an element of the pigments based on iron oxide and green earths. The presence of copper in the blue areas suggests the use of Egyptian blue and leads to the probable addition of lead white, which was used to lighten the various colors and achieve whites. Iron may also be an element present in the aggregates of the plaster.

When present in low counts, titanium can be associated with some iron minerals as an impurity, but this may be due to contamination from restoration pigments that often contain TiO₂. An exception is point X17, where the high content of Ti suggests a potential use as a restoration material. This hypothesis is further supported by the presence of chromium and the lack of lead, copper, and strontium, which are present in the other examined points.

3.3. Optical and Electronic Microscopy to Investigate the Sample Cross-Sections

The analysis of cross-sections was focused on the bluish–green areas, particularly visible in the northeast wall of Room E. Some images of the cross-sections obtained via the optical microscope are shown in Figure 5.

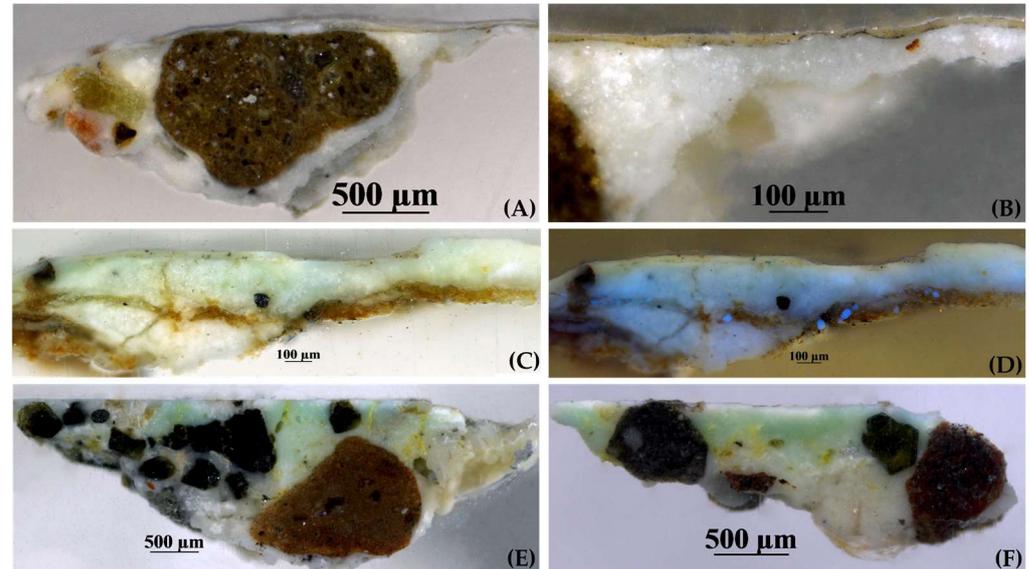


Figure 5. Micro-photographs of sample cross-sections at the optical microscope. (A) sample P5, magnification 25 \times , reflected light; (B) detail of (A) at 100 \times ; (C) sample P6, 100 \times , reflected light; (D) sample P6, 100 \times , UVF; (E) sample P7, 25 \times , reflected light; (F) sample P8, 25 \times , reflected light.

From the observation of the cross-sections, it can be derived that the plaster is made of lime and pozzolana, whose large dark grains are particularly evident in samples P5, P7, and P8. The surface of sample P5 appears light yellow and covers a thin and discontinuous black layer that seems to be constituted by a dirty deposit. So, it can be supposed that the yellow hue is an inpainting applied over an uncleaned surface. The other samples show similar surface and interface appearance with the presence of a bluish–green color in the upper part of the cross-sections. However, the bluish–green zone is not well-defined, but the color appears diffused in the plaster support. A pale-blue fluorescence appears under UV radiation that could be attributed to the various restoration materials and consolidants used in the previous restorations. In the cross-sections of samples P7 and P8, yellow zones localized in correspondence with micro-cracking are observed, which deserve further investigation. After this preliminary observation of the cross-sections under an optical microscope, two samples were selected for further investigation using scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS). P7 and P8 were chosen because the bluish–green zone in these samples was more visible compared to sample P6. In Figures 6 and 7, the examined areas of the two cross-section samples are shown in detail.

The cross-section of sample P8 in Figure 8 refers to the other half of the micro-fragment produced during the cutting of the embedded micro-sample, which resulted in some differences from the sample cross-section displayed in Figure 5. The EDS point analysis was addressed to investigate the composition of the yellow zones that are lighter in backscattered electrons, suggesting the presence of chemical elements with higher atomic numbers. In these zones, the EDS revealed the presence of Pb as the main element with minor amounts of Cu, As, and V (Supplementary Figures S1–S3).

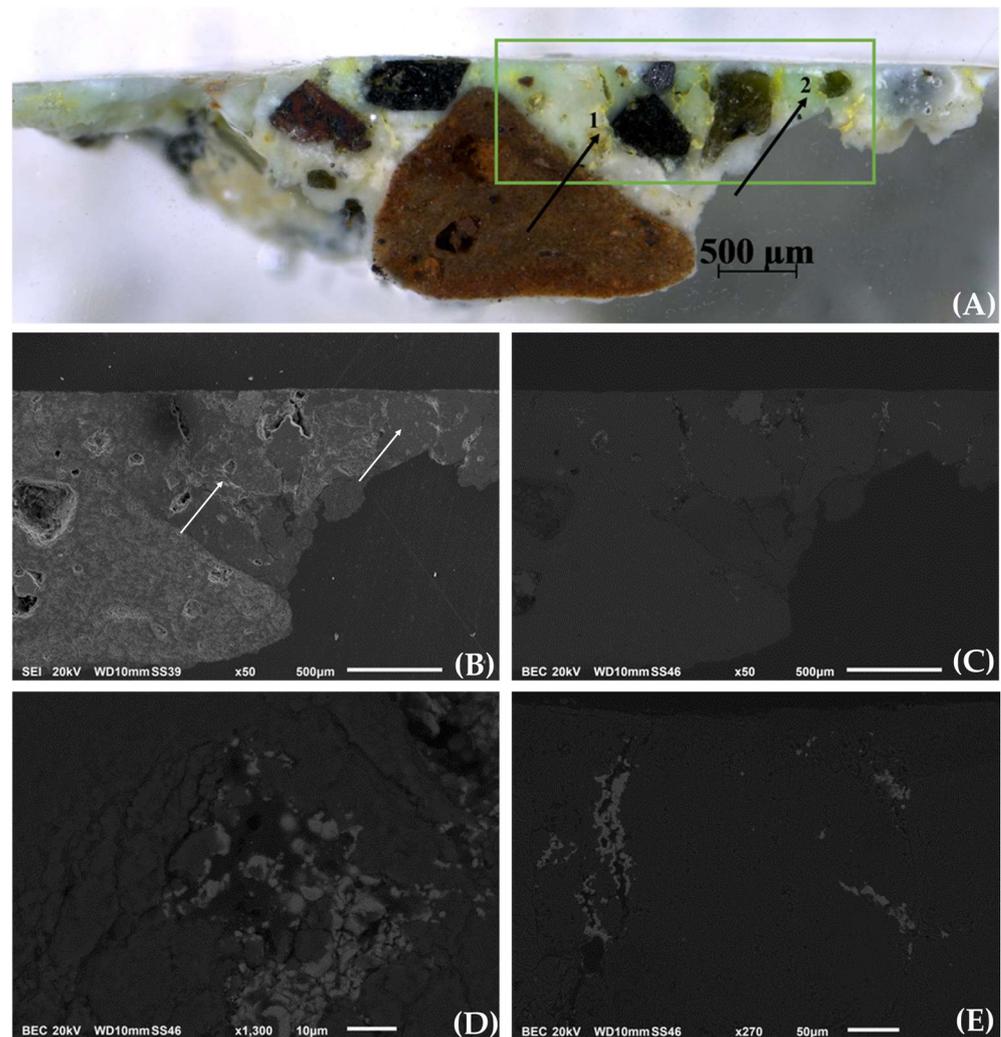


Figure 6. Micro-photographs of sample P7 cross-section at the microscope. (A) magnification 25 \times ; reflected light with the two areas (1 and 2) investigated using SEM-EDS; (B) P7 cross-section under SEM observation in secondary electrons, the arrows indicate the 1 and 2 studied areas; (C) the same shown in (B) but in backscattered electrons; (D) detail of area 1 in backscattered electrons; (E) detail of area 2 in backscattered electrons.

On the other hand, in the light green-bluish zone, the EDS analysis revealed systematically the presence of only Cu, as well as the elements of the plaster (Supplementary Figures S4 and S5). To focus the SEM-EDS investigation in the bluish zones, an area of sample P8 was selected, where Pb, Cu, As, and V were revealed by point analysis. This area is shown in Figure S6 and in Figure 8A,B. Additionally, chemical mapping was performed with the aim of correlating the above-detected elements (Figure 8C).

In the chemical mapping shown in Figure 8C, the main elements of interest were displayed. Apart from the plaster component, Pb, Cu, V, and As are highlighted.

The main evidence from the mapping indicates that these elements are correlated, suggesting that they are associated with chemical compounds.

The next step to try to identify the compounds responsible for the bluish and yellow colors visible in the P7 and P8 cross-sections containing Pb, Cu, V, and As has been to apply μ -Raman spectroscopy to these samples.

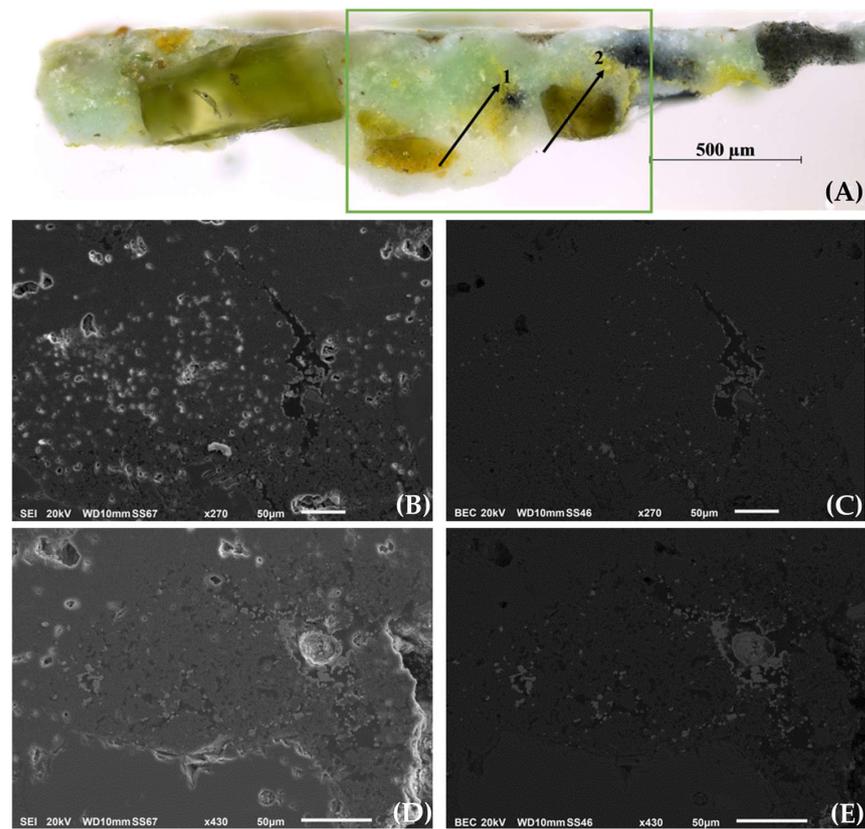


Figure 7. Micro-photographs of sample P8 cross-section at the microscope. (A) magnification 25×; reflected light with the two areas (1 and 2) investigated using SEM-EDS; (B) detail of area 1 in secondary electrons; (C) the same shown in (B) but in backscattered electrons; (D) detail of area 2 in secondary electrons; (E) detail of area 2 in backscattered electrons.

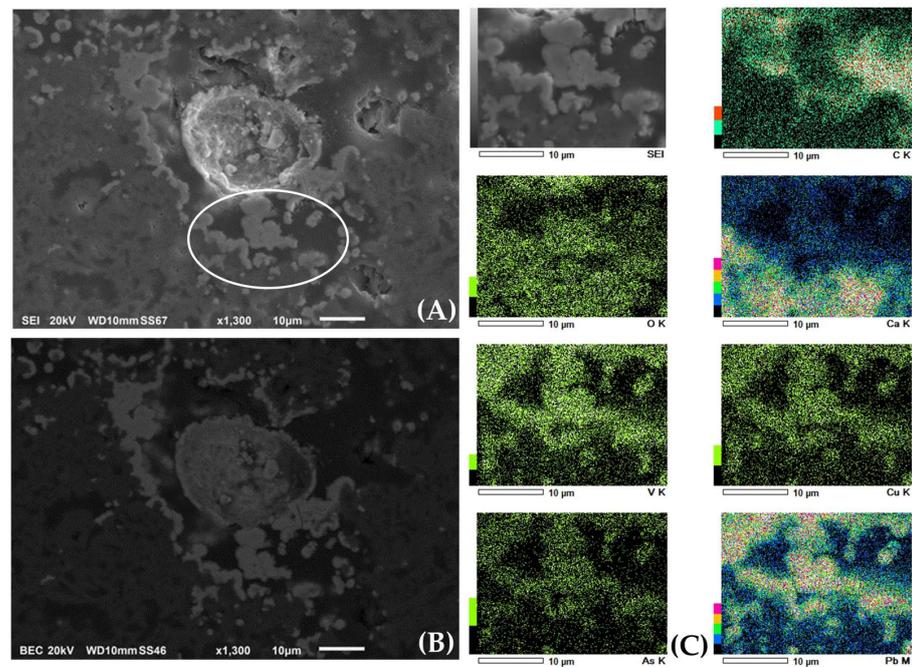


Figure 8. SEM micro-photographs of sample P8 cross-section: (A) secondary electrons with the area selected for the chemical mapping in the white circle; (B) the same shown in (A) but in backscattered electrons; (C) chemical mapping of the area shown in (A); magnification 4.300×. The colors' scale used in the mapping is reported on the left side of each map.

3.4. μ -Raman Spectroscopy

The bluish patina in samples P7 and P8 and the blue color in sample P9 were examined via μ -Raman spectroscopy. Upon initial visual inspection, the surface of the samples P7 and P8 to be investigated appears green; under the μ -Raman microscope, grains of different colors are observed, including white, green, yellow, blue, and black. In all three fragments, within the white areas, the characteristic bands of calcite (CaCO_3) at 156, 280, 712, and 1085 cm^{-1} [18] are perfectly identifiable, as well as the bands of calcium oxalate (CaC_2O_4), specifically in the form of monohydrate oxalate, whewellite, identified by the bands at 1461 and 1489 cm^{-1} . However, due to the low quality of the obtained spectra, the presence of dihydrate oxalate, weddellite [19], cannot be excluded.

The green areas correspond to augite $\text{Ca}(\text{Mg, Fe, Ti, Al})(\text{Si, Al})_2\text{O}_6$ with characteristic peaks at 184, 227, 325, 353, 392, 531, 666, 768, 822, and 1008 cm^{-1} [20]. Some black spots give the Raman spectra of carbon black with the typical bands at 1366 and 1590 cm^{-1} .

All Raman spectra collected from the investigated samples focusing on yellow, green, and blue-colored areas exhibit the same identical fingerprint, characterized by bands at 304, 361, 485, 787, and 837 cm^{-1} (Figure 9). Interesting are the results obtained from some yellow–blackish areas, which revealed peaks at 159, 362, 786, and 837 cm^{-1} . Bands in the ranges of $300\text{--}450\text{ cm}^{-1}$ and $770\text{--}880\text{ cm}^{-1}$ are attributable, respectively, to the bending and symmetric stretching of the arsenate group [21]. From the spectroscopic analysis conducted on these bands and the referencing literature, it seems that these bands could be associated with a copper arsenate; particularly, considering the position of the Raman bands, this could be associated with conichalcite, $[\text{CaCu}(\text{AsO}_4)(\text{OH})]$ and/or with duftite, $[\text{PbCu}(\text{AsO}_4)(\text{OH})]$. Both these compounds are quite common green arsenate minerals, often found associated [22,23].

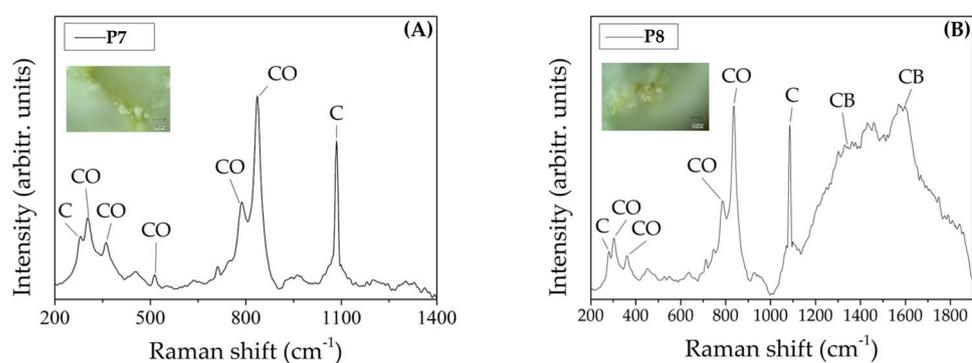


Figure 9. μ -Raman spectra: (A) sample P7 and (B) sample P8. C: calcite; CB: carbon black; CO: conichalcite/duftite. The scale bar in the images is 20 μm .

At present, it is not possible to formulate hypotheses regarding the origin, especially whether the compound derives from the degradation processes of originally present materials or if it was intentionally applied as a painting material. However, it is interesting to note that some works of the literature [24] focusing on the pigment palette of Roman wall paintings in a volcanic environment highlight the presence of copper arsenates without expanding on their possible origin. Other works of the literature pertaining to different artistic realities and epochs also report evidence of this [23].

Sample P9, upon microscopic observation, exhibits areas of various colors: blue; light blue; purple; dark green; white; black; and golden yellow. The blue, light blue, and purple areas consist of Egyptian blue ($\text{CaCuSi}_4\text{O}_{10}$, peaks at 118, 164, 194, 377, 431, 473, 568, 761, 786, 985, 1011, 1082 cm^{-1}), lead white [$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$], peak at 1047 cm^{-1}), and carbon black (Figure 10) [18].

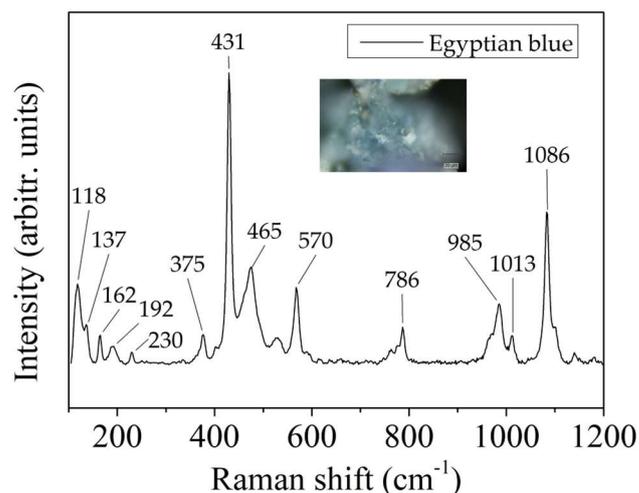


Figure 10. μ -Raman spectrum of Egyptian blue as detected in sample P9. The scale bar in the image is 20 μm .

In the purple section, alongside Egyptian blue and white lead, an additional compound identified as linarite $[\text{PbCu}(\text{SO}_4)(\text{OH})_2]$, with peaks at 631 and 913 cm^{-1} , was detected [25]. Within the light blue areas, cristobalite (SiO_2 , peaks at 229 and 415 cm^{-1}) and lead white were identified in one instance, while linarite and lead white were found in another [26]. The white color corresponds to lead white; silica (SiO_2) and calcite (CaCO_3) were detected in some regions [18]. Finally, the golden spot encompasses various compounds such as K-feldspar, white lead, calcite, and carbon black.

3.5. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used to try to detect organic and inorganic compounds, and in this case, with a specific focus on the bluish–green layer.

The spectra of samples P1–P4 reveal the presence of calcium carbonate (main signatures at cm^{-1} : 2515, 1795, 1635, 1457, 875 and 712), silicates with the large band at around 1030 cm^{-1} and gypsum in P4 (signatures at cm^{-1} : 3549, 3403, 2232, 2121, 1685, 1621, 1144, 1124, 672, 603, 461) (Figures 11 and 12).

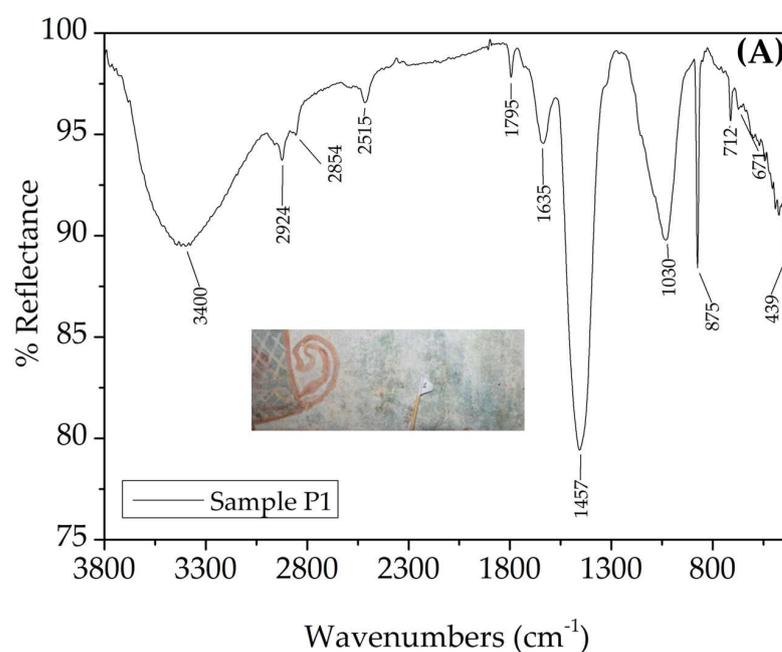


Figure 11. *Cont.*

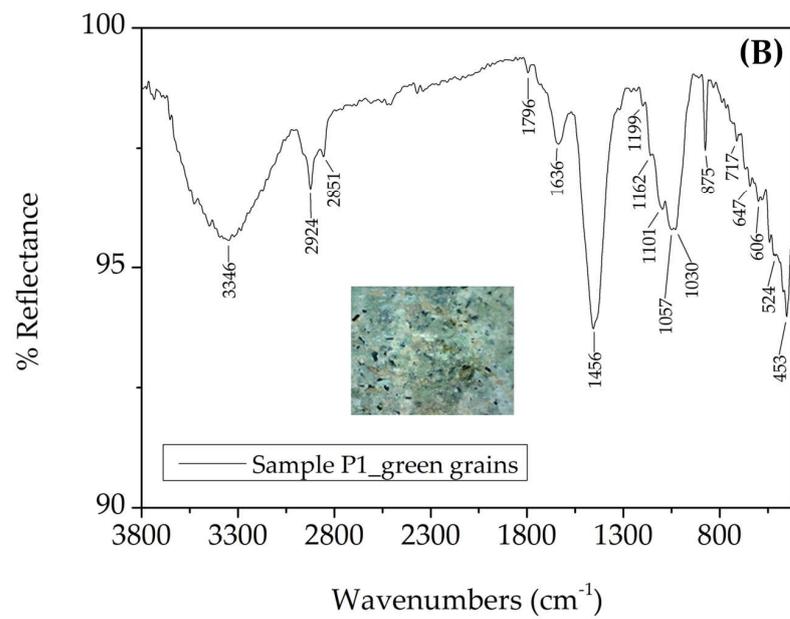


Figure 11. FTIR spectra of sample P1 (bulk) (A) and of the green grains (B) isolated from the micro-sample powder. The surface of the sampling area is also shown inside the spectra windows.

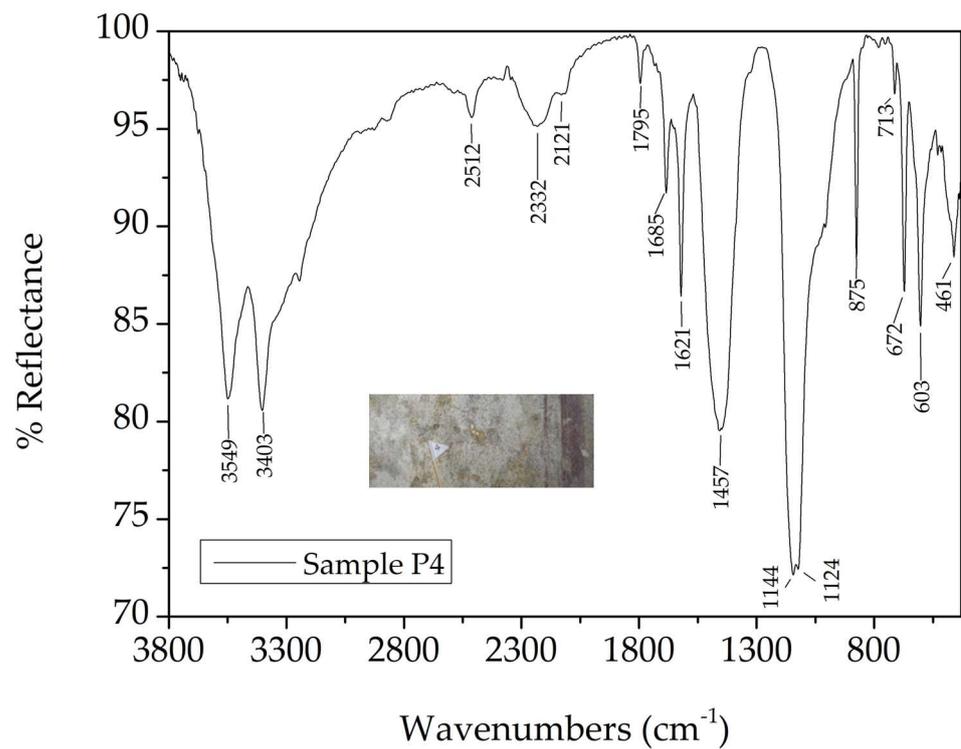


Figure 12. FTIR spectrum of sample P4. The surface of the sampling area is also shown inside the spectra windows.

Sample P4 can be associated with restoration grouting. Some peaks in the spectrum reveal the presence of organics, specifically those at 2924 and 2851 cm^{-1} , which are attributable to the C-H stretching.

In the spectrum of the isolated green grains, additional bands are observed at lower wavenumbers, between 1199 and 453 cm^{-1} . The bands at 1199–1101 cm^{-1} , if associated with those at 2924–2851 cm^{-1} , may refer to organics, probably the polysaccharides gum

(such as gum Arabic), a binder used in watercolors during the past restoration inpainting [27,28].

The spectrum shown in Figure 11B is rich in signals, allowing for the detection of other materials. The peaks at 1319 and 770 cm^{-1} can be associated with Ca-oxalates, and those at 3528, 1435 (partially overlapped with that of calcium carbonate), 1053, and 833 cm^{-1} can be associated with lead white [29,30]. Lastly, the peaks at 1030, 670, 647, 601, 548, 524, and 453 cm^{-1} are due to various silicates, including those constituting green earth [31,32].

Samples P2 and P3 exhibit FTIR spectra similar to those in sample P1 (see Supplementary Materials, Figures S7 and S8).

4. Discussion

The analysis of the wall painting materials of the so-called Room E in the Roman archaeological site of *Volsinii Novi* was aimed at supporting the recently concluded restoration activities, focusing on the back wall (the northeast wall) of the room. Before starting this analysis, careful archive research was conducted to understand the conservation history of the paintings and the various treatments they underwent over time. One of the most challenging problems was understanding the nature of the unevenly distributed bluish–green areas on the surfaces. These areas appeared on the paintings since their discovery but were interpreted in different and sometimes incorrect ways.

The first step of the diagnostic campaign was conducted by means of UVF photography, a non-invasive technique widely used in the field of restoration of cultural heritage as it revealed the state of conservation of the surfaces [33–36]. This technique showed a bad state of preservation of the paintings characterized by several grouting, lacunae, and differences due to the past interventions, e.g., the ones that started in 2012 and were never completed. The bluish–green layer appears dark under UV, indicating the absence of fluorescent materials such as organic binders or fluorescent organic dyes [37]. The hypothesis made to explain this behaviour could be the loss of the binder due to the degradation caused by acid treatment and other not specified operations performed in the past restoration that caused the pigment alteration.

To investigate the composition of the bluish–green areas on the surface of the wall painting, on-site analysis XRF spectroscopy was applied. This technique is widely used in the non-invasive chemical investigation of artworks, especially in the case of immovable objects or in the case of impossibility to sample materials from the artifacts [38–40]. XRF analysis revealed the presence of Ca, Fe, Pb, and Cu as main elements in all examined points, suggesting the use of iron-based pigments, lead white and Egyptian blue. This led to the hypothesis that the bluish–green layer was probably distributed on the entire surface to cover the second pictorial phase. Additionally, in the restored areas, Ti and Cr were detected as main elements, indicating the use of modern pigments commonly used for the inpainting.

From the results obtained by XRF analysis, it is evident that in the bluish–green areas, the chromophore elements were Cu and Pb. In light of this result, attention was then focused on these areas by taking some micro-samples for laboratory analyses using optical and electronic microscopy, μ -Raman, and FTIR spectroscopies, all techniques widely used in the investigation of wall painting materials [6,41–43]. Optical microscopy revealed that the light bluish–green color diffused into the plaster instead of appearing as a surface pictorial layer and that the yellow hue is concentrated around the micro-cracking of the plaster. This observation suggests the possibility that the bluish–green color is due to an alteration of the original materials of the wall painting. To investigate this aspect further, SEM-EDS analysis was performed on the cross-sections of the two samples where the bluish–green color was more visible. EDS point analysis confirmed the presence of Pb and Cu but also revealed As and V. Moreover, mapping analysis showed a correlation among these elements. To summarize the SEM-EDS analysis, the following can be derived:

- (1) the main elements in the mortar are certainly C, O, Ca, and Si, confirming the presence of calcium carbonate and silicates;
- (2) in the very light and widespread green–bluish areas within the mortar, which are observed above all in the superficial parts of the cross-sections, copper (Cu) is constantly detected, in addition to the elements indicated in point 1;
- (3) in the more limited yellow areas, Pb, As, Cu, and V are constantly present, along with Ca, O, C, and Si. Arsenic is probably not present in the most superficial layer, and for this reason, it was not revealed by XRF spectroscopy. It must be said that if arsenic is present in low concentration, it is not easy to detect by XRF spectroscopy due to the main line ($K\alpha$) overlapping with the $L\alpha$ line of lead, which is the main element. Moreover, the $K\alpha/K\beta$ ratio of As is high, resulting in a very low intensity of $K\beta$.

Based on SEM-EDS and μ -Raman spectroscopy, it is plausible that a compound of copper and arsenic (conichalcite or duftite) may be present, but the presence of a compound of vanadium and lead is also possible. However, other compounds among these elements cannot be excluded. Since neither the elements found nor the Raman spectra can be traced back to pigments traditionally used in Roman times or to modern synthetic pigments (such as Cu acetoarsenites, which constitute Emerald and Scheele green or vanadium compounds), it can be concluded that the materials found on the wall painting are most likely derived from alterations of the original pigments due to various treatments undergone by the surfaces. Some authors have suggested the possibility that arsenic is associated with copper-based minerals [24,43,44]. Compounds of Cu and As can also be formed by degradation of Egyptian blue containing these elements, which by reaction produced copper arsenates [45]. The use of copper vanadate and other V and Cu compounds (in the 13th and 15th centuries) to create green backgrounds, often altered to yellow, is also documented in the literature [44,46]. However, the possible provenance of vanadium from the original plaster materials cannot be excluded since it is a chemical element contained in rocks of volcanic origin [47,48].

To summarize the discussion, a possible hypothesis may be made about the formation of the bluish layer as follows: the second pictorial phase was probably covered by a sort of monochromatic painting based on lead white and Egyptian blue for receiving a third phase, removed immediately after the excavation. The removal process associated with the treatment made in the past on this painting probably altered the residues of the original monochromatic layer, leaving surface areas of the bluish–green appearance.

The relevance of the obtained results can be seen in the following points:

- (1) After decades of hypotheses and erroneous treatments of the bluish–green layer of Room E in the archeological site of *Volsinii Novi*, it was finally understood that it was an original layer exhibiting degradation patterns whose origin is not yet completely clarified;
- (2) The recently concluded restoration was able to restore this layer, previously partially hidden, giving it the correct reading as a residual of an original painting.

To complete this analysis, FTIR spectroscopy was also applied to the micro-samples. This technique provided information about the plaster (made of lime and silicate materials, such as pozzolan) and some other compounds, such as Ca-oxalates and organics, presumably the polysaccharidic binders of the retouching pigments. FTIR confirmed the presence of lead white and iron-based pigments (ochre and earths).

5. Conclusions

The work presented in this paper may be considered a sort of reconstruction of the historical events that interested the wall paintings of Room E in the archaeological site of *Volsinii Novi* situated on the Poggio Moscini hill in the town of Bolsena (Central Italy, close to the homonymous volcanic lake) by combining information obtained from the archives and those gathered from our analyses. This work was carried out to support the recently completed restoration, which had to address a complex surface and interface pattern created by the prolonged period in the buried environment and further by various

past interventions after the excavation, which brought the paintings to light. The most challenging choice during the restoration concerned the decision on whether to remove the bluish–green inhomogeneous layer that covered the entire surface of the northeast wall of Room E, the object of our restoration activities.

But before making a decision, it was necessary to investigate the archive documentation and conduct an analysis to characterize this layer.

By combining the historical information that showed the existence of the bluish–green layer since the 1960s, immediately after the excavation, and the results of our analyses, which revealed the presence of pigments and degradation products compatible with the original materials, it can be derived that the bluish–green layer is definitively demonstrated to be an original pictorial phase that today appears degraded but worthy of preservation and valorization.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/coatings14040408/s1>, Figure S1: EDS spectrum and concentration of the elements detected in the point 4 of area 1, sample P7; Figure S2: EDS spectrum and concentration of the elements detected in the point 5 of area 1, sample P7; Figure S3: EDS spectrum and concentration of the elements detected in the point 7 of area 1, sample P7; Figure S4: EDS spectrum and concentration of the elements detected in the point 6 of area 1, sample P7; Figure S5: EDS spectrum and concentration of the elements detected in the point 6 of area 1, sample P8; Figure S6: EDS spectrum and concentration of the elements detected in the point 3 of area 2, sample P8; Figure S7: FTIR spectrum of sample P2; Figure S8: FTIR spectrum of sample P3; Table S1: Results of XRF analysis. The detected elements are reported in a decrescent order of counts.

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