



# Production technique and multi-analytical characterization of a paint-plastered ceiling from the Late Antique *villa* of Negrar (Verona, Italy)

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Received: 12 December 2023 / Accepted: 25 March 2024  
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## Abstract

The research focuses on analyzing the production techniques and materials of a Roman paint-plastered ceiling from a Late Antique Roman *villa* near Negrar (Verona, Italy), recently uncovered. Stylistic features of the decoration, found in reworked collapse debris during the *villa*'s excavation, date the ceiling to the original construction phase in the 4<sup>th</sup> century CE. The paper presents the protocol we adopted for recovering and analyzing the painted decoration of the *villa*, which was in-laboratory recomposed in its original layout after a meticulous and systematic retrieval of fragmented materials. Micro-samples of mortar and pigment were then taken to fully reconstruct the execution technique and raw materials used in the paint-plastered ceiling, detailing the application of the *tectorium* and pigment preparation. Mortar samples were analyzed to define preparatory layer properties, using various analytical techniques including Transmitted-Light Polarized Optical Microscopy (TL-OM) and Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDS). Optical reflected-light microscopy detected guide incisions on the preparatory mortar, while Reflected-Light Optical Microscopy (RL-OM) revealed the microstratigraphy of pictorial micro-layers. Micro-samplings of painted decorations were conducted to define pigment palettes, determining their mineralogical composition through X-Ray Powder Diffraction (XRPD) analysis coupled with micro-Raman analyses for the determination of carbon-based compounds. The research aims to establish a comprehensive protocol for future endeavors, integrating archaeological reassembly with precise micro-analyses of pigments and mortars, deciphering the intricate layout of ancient, fragmented decorations. This study is the first of its kind in Northern Italy, overcoming challenges posed by fragmented and reworked artifacts in previous research, enabling detailed analytical studies like those conducted here. Moreover, this study of the paint-plastered ceiling of the Late Roman *villa* of Negrar aims to provide a new impulse for the knowledge of Late Antique painting techniques and materials, which were only marginally considered within Roman painting tradition so far.

**Keywords** Ancient pigments · XRPD · Raman · PLM: Late antiquity · Negrar

## Introduction

In recent years, the research on ancient wall-paintings has been reevaluating the traditional approaches conventionally focused on the autoptic analysis of the stylistic features and fashions of the painted decorations. In fact, ancient wall-paintings can be appreciated not only for their external appearance, but also considered as three-dimensional spaces inside which the history of creation of these man-made products is encrypted. Within this framework, in fact, most of the information regarding the making process and *savoir-faire* of the craftsmen in charge of the manufacture of these artistic products are archived. Essentially, these “black boxes”

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consist of two main elements: a) the preparatory mortars, usually distributed into multiple layers (*tectorium*), providing the support for b) the outer pigments, typically distributed in background layers and over-paintings.

Roman literary sources report numerous indications and suggestions regarding the best executive procedures and materials to be adopted in the wall-painting's realization. The number and composition of the mortars constituting the *tectorium* are described in detail by Vitruvius and Pliny (Vitr. 7.3.5-7; 7. 6; Plin. 36.176), as well as the correct and inappropriate ways of applying the layers constituting the *substratum* (Mora 1967; Allag and Barbet 1972; Daniele and Gratzu 1996; Mora et al. 1999; Vlad Borrelli 2015; Salvadori and Sbrolli 2021; Dilaria 2023). Furthermore, the authors meticulously delineated the chromatic characteristics and properties of both natural and artificial pigments employed in ancient times (Vitr. 7.7-14; Plin., 35) and elucidated the intricate dynamics of painterly relationships within workshops (Esposito 2011; Salvadori and Sbrolli 2021).

Nowadays, the scientific investigation of these aspects is carried out by describing in detail the petro-mineralogical and chemical features of the mortars (Vola et al. 2011; Jackson et al. 2011; Ramacciotti et al. 2018; Columbu et al. 2018a, 2022; Miriello et al. 2018; Ponce-Antón et al. 2020; Secco et al. 2020; Dilaria et al. 2023) and pigments used in the making of ancient wall-paintings (Coutelas 2011, 2021; Sitzia et al. 2020; Cavalieri and Tomassini 2021; Gliozzo et al. 2021; Columbu et al. 2022). Numerous case studies document the findings of archaeometric analyses conducted on ancient wall paintings, delving into the diverse "recipes" utilized by societies across the ancient Mediterranean. These studies explore and compare these techniques from both regional and diachronic viewpoints (Freccero 2005; Weber et al. 2009; Gutman et al. 2016; Columbu et al. 2018; Baraldi et al. 2019; Coutelas 2021; Dilaria et al. 2021; Baragona et al. 2022). On the other hand, fewer research considers the complete investigation of the wall-painting "making process" within a specific context (i.e. the decoration of the walls of a house), encompassing the thorough analysis of the different steps and materials involved in the production of a pictorial space, from a structural support to the laying of the exterior painted micro-layers. It goes without saying that most of these case studies are focused on the Vesuvian sites, where such an operation is eased by the extraordinary in-situ state of preservation of the paintings (Varone and Bearat 1997; Prisco 2005; Pique et al. 2015; Baraldi et al. 2019; Miriello et al. 2021). Analogous studies applied to specific contexts outside this region are certainly less consistent (Falzone et al. 2021; Bugini and Folli 1997; Calia and Giannotta 2005; Pecchioni et al. 2014; Brecoulaki et al. 2023; Urosevic et al. 2023).

A further issue concerns the chronological bias, as most of the scientific analyses on ancient wall-paintings are

framed within the apogee of the ancient wall painting tradition, namely the Hellenistic and Roman Era. Conversely, the Late Roman period, specifically the 4th and 5th centuries CE, is often viewed as a time of decline in pictorial tradition, receiving comparatively less scholarly attention (Tapete et al. 2013; Sebastiani et al. 2019).

In order to improve the state of art regarding making methods, and materials in use in the Late Roman wall-painting tradition, this study reports the results of the analytical investigations of a pictorial *nucleus* pertaining to the collapsed paint-plastered ceiling of the 4<sup>th</sup> century CE *villa* from Negrar in Valpolicella (Verona, Northern Italy, 45°32'18.1"N; 10°56'42.7"E). Beginning with an accurate methodology for retrieving fragmented *nuclei* of wall-paintings from primary collapses and proceeding with in-laboratory reconstruction of the original decorative layouts, the goal of the research is to establish a standardized protocol for future endeavors. This protocol aims to enable precise and comprehensive analysis of pigments and mortars, faithfully capturing the overall design of ancient, fragmented decorations. This approach is truly groundbreaking as previous analytical studies on wall-painting fragments from secondary deposits in Northern Italy have been constrained to sporadic samples (Lazzarini 1978; Mazzocchin et al. 2004, 2011; Roffia et al. 2005; Baraldi et al. 2006; Bugini et al. 2017), which cannot adequately represent the complete decorative scheme. This limitation arises from the inherent condition of the findings, which are often challenging to reassemble in their original layout. In this perspective, the current context perfectly suits to the purposes of our research targets, as it provides one of the few examples, for the Cisalpine, of wall painting preserved in situ; indeed, in this area, the pictorial evidence is mainly preserved in a fragmentary state and in secondary lying, unrelated to its original context (Salvadori et al. 2015; Didonè 2020). Moreover, it represents one of the very few cases of well-preserved Late Antique painted decorations in Northern Italy up to now.

## Archaeological background

### The Late Roman *villa* of Negrar

The history of the *villa* in Negrar began in 1885 with the discovery of mosaic fragments on a farm in the hamlet having the significant toponym of "Villa". These fragments were later sold to the municipality of Verona (De Stefani 1887). In 1922, archaeologist Tina Campanile conducted an excavation that revealed part of the residential sector of an ancient Roman *villa* with valuable mosaic floorings, a significant presence of fragments of painted plasters and the remains of raised masonries with portions of wall-paintings still preserved *in situ* (Campanile 1922).

Since 2019, the Soprintendenza Archeologia Belle Arti e Paesaggio is undertaking new excavations to investigate the layout of the building and its dating, taking advantage of the full range of modern scientific techniques that are currently applied to the archaeological research. The ongoing excavations revealed that the *villa*, probably realized around the first decades of the 4<sup>th</sup> century CE, covered an area of around 3000 m<sup>2</sup> and it was arranged on terraces following the natural slope of a hill. It included a residential area to the south with apsidal rooms and mosaic floors, a northeastern thermal quarter with different rooms and a western production sector, possibly for wine processing (Basso et al. 2024) (Fig. 1a).

A remarkable portion consists in the peristyle/portico bordered by columns, surrounding the central area. It was paved with mosaic on three sides and limestone slabs on the north. The peristyle occupied two terraces, with the northern part located at a higher elevation.

The recent excavations revealed important cores of painted plasters (*nuclei*) found within primary collapse debris originating from masonry structures and roofs. In detail, some fragments from a painted ceiling were found in the southern arm of the portico (Fig. 1b - *nucleus* 1, 45°32'17.512"N; 10°56'42.402"E). The second *nucleus* pertains to a massive collapse of the ceiling in the eastern side of the portico, exhibiting a progressive increase in thickness from the bottom of the access stairs of the northern arm to the second and third intercolumns of the peristyle (Fig. 1b - *nucleus* 2, 45°32'17.851"N; 10°56'43.567"E). The third comes from a collapsed wall within a side room of the portico (Fig. 1b - *nucleus* 3, 45°32'17.844"N; 10°56'43.789"E). The fourth pertained to a small remnant of a plinth still in situ, the decoration of which is badly preserved (Fig. 1b - *nucleus* 4, 45°32'17.981"N; 10°56'43.829"E).

Given their extremely fragile state of preservation, all painted *nuclei*, except for the one from the plinth, have been stabilized, removed from their original location, and safeguarded in the storage facilities of the University of Padova for subsequent laboratory analyses and reassembly.

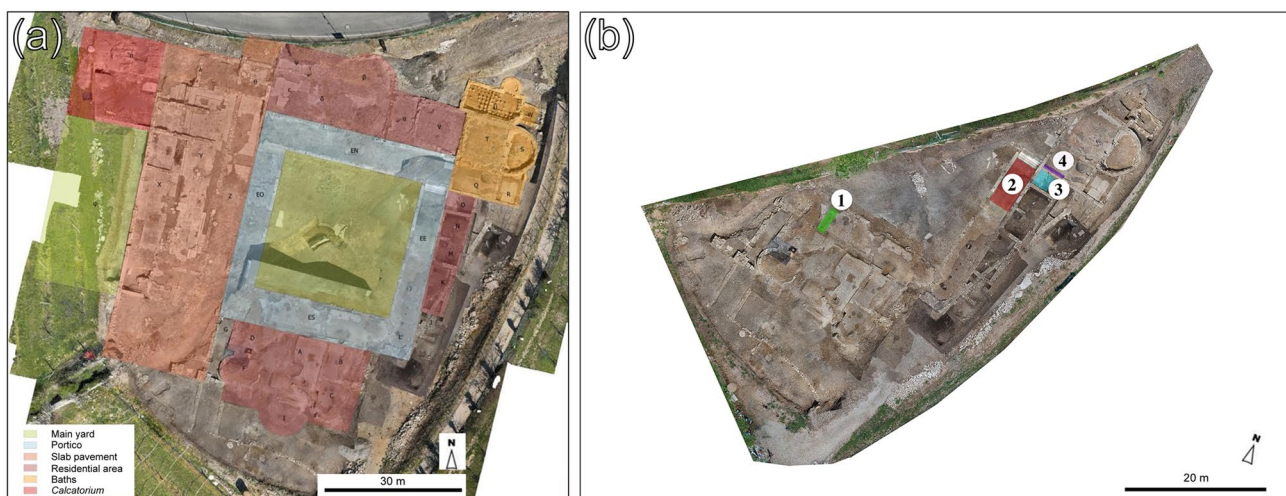
### The stylistic features and chronology of the collapsed paint-plastered ceiling

The focus of this paper is the analysis of the *nucleus* of wall-paintings found in primary collapse debris over the mosaic floor of eastern arm of the portico (*nucleus* 2). Traces of burnt residues from the roof were discovered on the underside of the ceiling's backing, proving that the collapse occurred as consequence of a fire (Fig. 2a-c).

After the excavation, the fragments constituting the decoration have been reassembled in laboratory. This allowed to recognize an orthogonal system of crosses of tangent lozenges framing squares having an inclination of 45° (Fig. 3). On each side, the outer limit of the decorative score is closed by a red band profiling another blue band, which is crossed by yellow stripes.

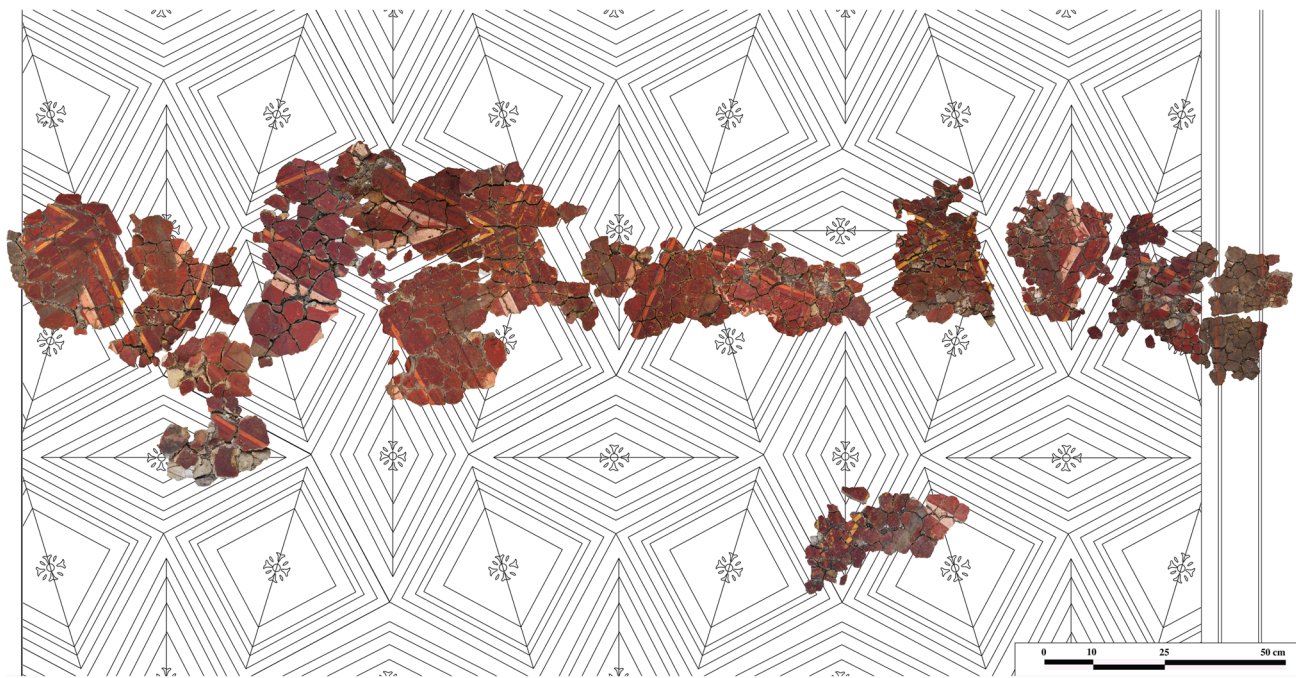
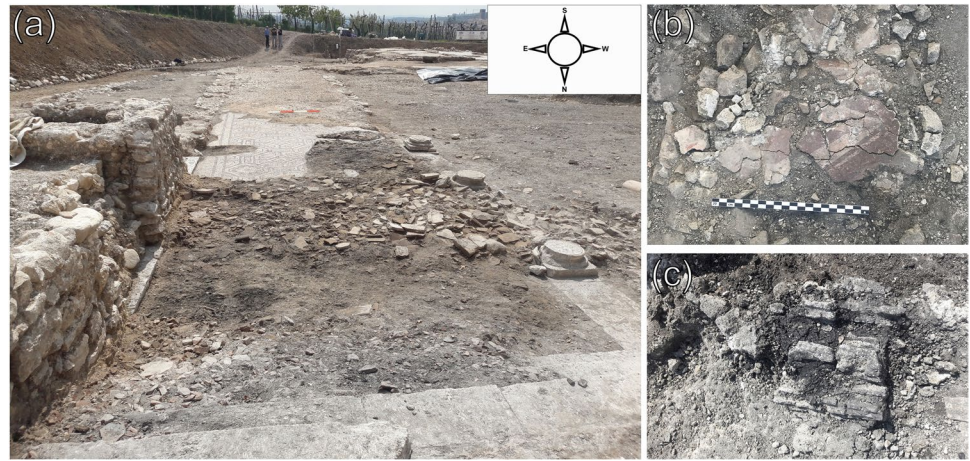
The assortment of various hues suggests the technique used to create the painted-plastered ceiling motif, indicating a departure from illusionistic portrayal towards a primary focus on ornamental design.

In fact, the alternation of colors is intended to reproduce an effect of complexity rather than three-dimensionality. The lozenges and squares are composed of an articulated sequence of two-colored bands and listels, with light tones towards the open peristyle and dark ones towards the inner masonries of the portico. The outer profile of lozenges and squared elements is defined with a yellow listel surrounding



**Fig. 1** Characterized zenithal orthomosaic of the *villa*. (a) Functional identification of different sectors; (b) the southern sector with indication of the *nucleus* of the southern arm of the portico (1) and of the eastern arm (2, 3, 4)

**Fig. 2** Eastern portico of the villa. (a) View from the north of *nucleus* 2 under excavation; (b) detailed photo of the collapse near the staircase; (c) detail of the back of the ceiling fragments with charcoal remains of firing and the negative traces of the wooden canes (reed leaves wattle)



**Fig. 3** Reconstruction of the wall-painting fragments and graphic reconstruction of the ceiling

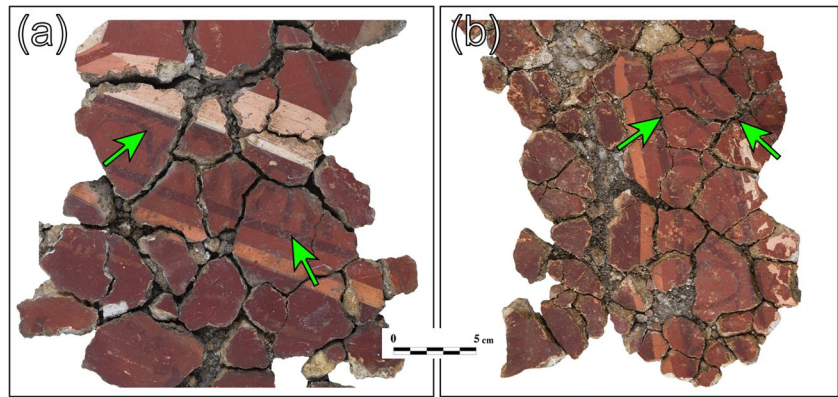
a stylized dusky red painted *kyma* (this derives from a common decorative element in the capitals of columns and other architectural features, Kirchof 2004). The sequence, in turn, surrounds the central motif, which features a two-colored palmette inscribed with two different shades of red: light red and dusky red, respectively. Both the lozenges and squares are framed by pink bands, with a white listel counterposed to greenish grey bands with a dusky red listel. A brown-yellow frame, crafted with short strokes alternating with pairs of beads, encircles the entire structure, converging at the corners where the lozenges and squares intersect. Diverse execution techniques are evident through the varied drafting styles of certain motifs. This variability is particularly

noticeable in the *kyma*, where some sections exhibit precise detailing while others display a less meticulous execution (Fig. 4a-b).

It must be outlined that some shades are not related to execution but rather to the exposure to heat during the firing of the building. This can be perceived in some portions of the decoration, where the yellow color of the listels shifts to reddish yellow (Fig. 5), as it will be described in detail in paragraph 4.3.

In general terms, the "orthogonal motif of adjacent lozenges and squares", that is a type of "repeated module" decorative system, is more common in the mosaic repertoire (type 161b from Balmelle et al. 1985) than in the wall-painting tradition.

**Fig. 4** (a-b) Details of the decorative execution of the painted lesbian *kyma*

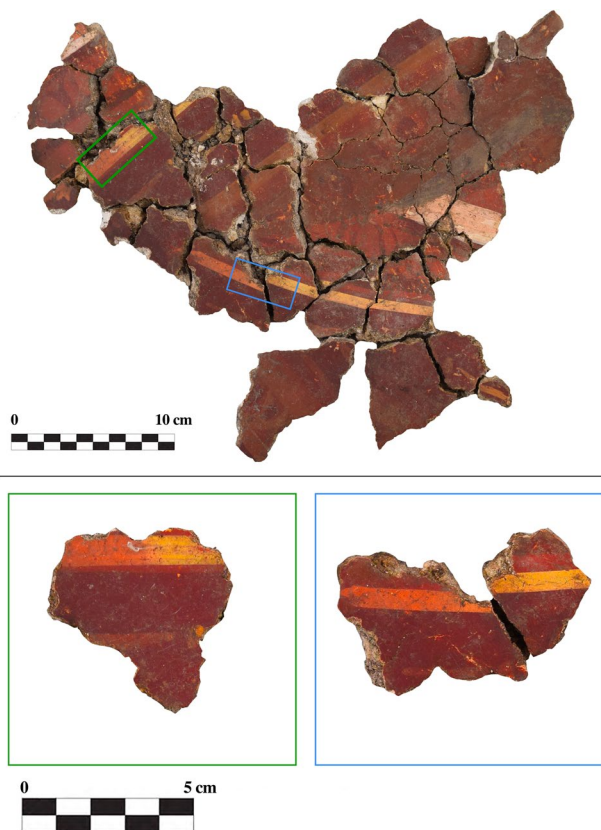


However, from the 1<sup>st</sup> c. CE, a progressive stylization of the three-dimensionality of the lacunars in favor of flatter and more monotonous solutions started, in mosaic as well as in the wall-painting production (Bragantini 2009; Barbet 2021).

Within the framework of the Italian peninsula, a close comparison of the motifs detected in the *nucleus 2* from Negrar can be made with the ceilings found on the Pincio

in Rome (Eristov 2009) or, more specifically, with the ceiling found in Via Diaz in Naples (Bragantini 2009).

Narrowing the frame to the ancient Cisalpina region (nowadays roughly corresponding to Northern-Italy), the adoption of the repeated module system develops during the Imperial Age, with several pieces of evidence primarily clustered within the 1<sup>st</sup> and 2<sup>nd</sup> c. CE, with later attestations in the 3<sup>rd</sup> and 4<sup>th</sup> c. CE (Didonè 2020). As far as ceilings are concerned, a general predilection for geometric ornamentation is attested. In an early phase (3<sup>rd</sup> Pompeian style), the decorative solutions strictly recall to styles adopted in the Central Italy and in the Vesuvian area, while, during the Late Imperial Age, more complex and articulated schemes are experimented. In this period, the decorative intents are preferred over perspective, as detected in the wall-paintings from Aquileia, Montegrotto and the Villa of Isera (Didonè 2020), showcasing sophisticated chromatic effects, which are also evident in the case of the ceiling of the *villa* of Negrar. However, in this latter case, illusionism turns towards a pure ornamentation, akin to the late examples found in the *Domus di Via Antiche Mura* in Sirmione (Didonè 2020), strictly recalling the coeval flooring repertoires, as indicated by the analysis of the *villa*'s mosaics (Rinaldi 2005).



**Fig. 5** Portion of the decoration where chromatic alteration of yellow hues is particularly evident. In the highlighted boxes, two high-magnification details of the decoration are reported, where chromatic conversion of the yellow listel is particularly evident

## Analytical approach and methods

The archaeometric analysis of the collapsed paint-plastered ceiling of the Roman *villa* of Negrar allowed to investigate and describe the raw materials and making method adopted for the realization of this decoration. In detail, the research aimed at defining the following research questions.

- **Determination of the compositional and textural features of the preparatory mortars (*tectorium*).** This aspect was investigated via Transmitted-Light Polarized Optical Microscopy (TL-OM) of 30  $\mu\text{m}$  thin sections. The petrographic study was done using a LEICA DM 750 P microscope equipped with an integrated digital camera

FLEXACAM C1. The description of the materials was done in agreement with the norms of the UNI 11176: 2006 standard "Cultural heritage: petrographic description of a mortar" (Pecchioni et al. 2014). The proportions of the aggregates, the overall porosity and the binder to aggregate ratio (L:A) were estimated using visual estimation diagrams (Bacelle and Bosellini 1965).

The mortars of the *tectorium* were investigated also from a mineralogical point of view via Quantitative Phase Analysis - X-Ray Powder Diffraction (QPA-XRPD). For this analysis, each mortar layer has been mechanically separated with chisels and individually analyzed. XRPD profiles were collected using a Bragg-Brentano  $\theta$ - $\theta$  diffractometer (PANalytical X'Pert PRO, Cu K $\alpha$  radiation, 40 kV and 40 mA) equipped with a real-time multiple strip (RTMS) detector (PIXcel by Panalytical). Data acquisition was performed by operating a continuous scan in the 3–85 [ $^{\circ}2\theta$ ] range, with a virtual step scan of 0.02 [ $^{\circ}2\theta$ ]. Diffraction patterns were interpreted with X'Pert HighScore Plus 3.0 software by PANalytical, qualitatively reconstructing mineral profiles of the compounds by comparison with PDF databases from the International Centre for Diffraction Data (ICDD).

The quantification of mineral phases (Quantitative Phase Analysis - QPA) was obtained adopting the Rietveld method (Rietveld 1967). The quantification of both crystalline and amorphous content was obtained through the addition of 20 wt% of zincite to the powders as internal standard. Refinements were carried out with TOPAS software (version 4.1) by Bruker. The observed Bragg peaks in the powder patterns have been modeled through a pseudo-Voigt function, fitting the background with a 12 coefficient Chebyshev polynomial. For each mineral phase, lattice parameters, Lorentzian crystal sizes and scale factors have been refined. Although samples were prepared with the backloading technique to minimize *a priori* the preferred orientation of crystallites, any residual preferred orientation effect was modeled during the refinement with the March Dollase algorithm (Dollase 1986). The starting structural models for the refinements were taken from the International Crystal Structure Database (ICSD).

Finally, a detailed microstructural and microchemical characterization of the binders was performed by Scanning Electron Microscopy coupled with Energy-Dispersive Microanalysis (SEM-EDS). The analysis was carried out using a COXEM EM 30AX scanning electron microscope, equipped with an EDAX Element - C2B energy dispersive X-Ray detector. Standardless semiquantitative analyses were acquired through the Team EDAX software. Prior to analysis, the sections were polished and graphite-coated.

- **Reconstruction of the decorative motif's preparatory drawing and application technique of pigments.** The preparatory drawing, realized with incisions in the mortar substrate, was recognized and studied following the reassembly of the decorative framework. This was accomplished through meticulous grazing-light analyses of the surfaces of the wall-painting. Then, the application technique of the pictorial micro-layers was investigated by analyzing the micro-stratigraphy of the pigment layers under Reflected Light Optical Microscopy (RL-OM), using a Nikon Eclipse Me 600 microscope, equipped with a Canon EOS 600D camera for image acquisition. Cumulative profiles were acquired by merging multiple sets of high-resolution micrographs of the pigment micro-stratigraphy through the built-in tools of Adobe Photoshop CS5 software.
- **Determination of the mineralogical and chemical composition of pigments.** Pigment types were characterized through punctual XRPD analyses for the definition of the inorganic mineral phases, coupled with Micro-Raman spectroscopy for the carbon-based compounds. In this phase, the pigments were mechanically scraped for analyses from the plaster support using a micro-razor blade. The sampling of pigments was microinvasive and limited to the lowest possible concentration for reliable analysis (around 10 mg of material).

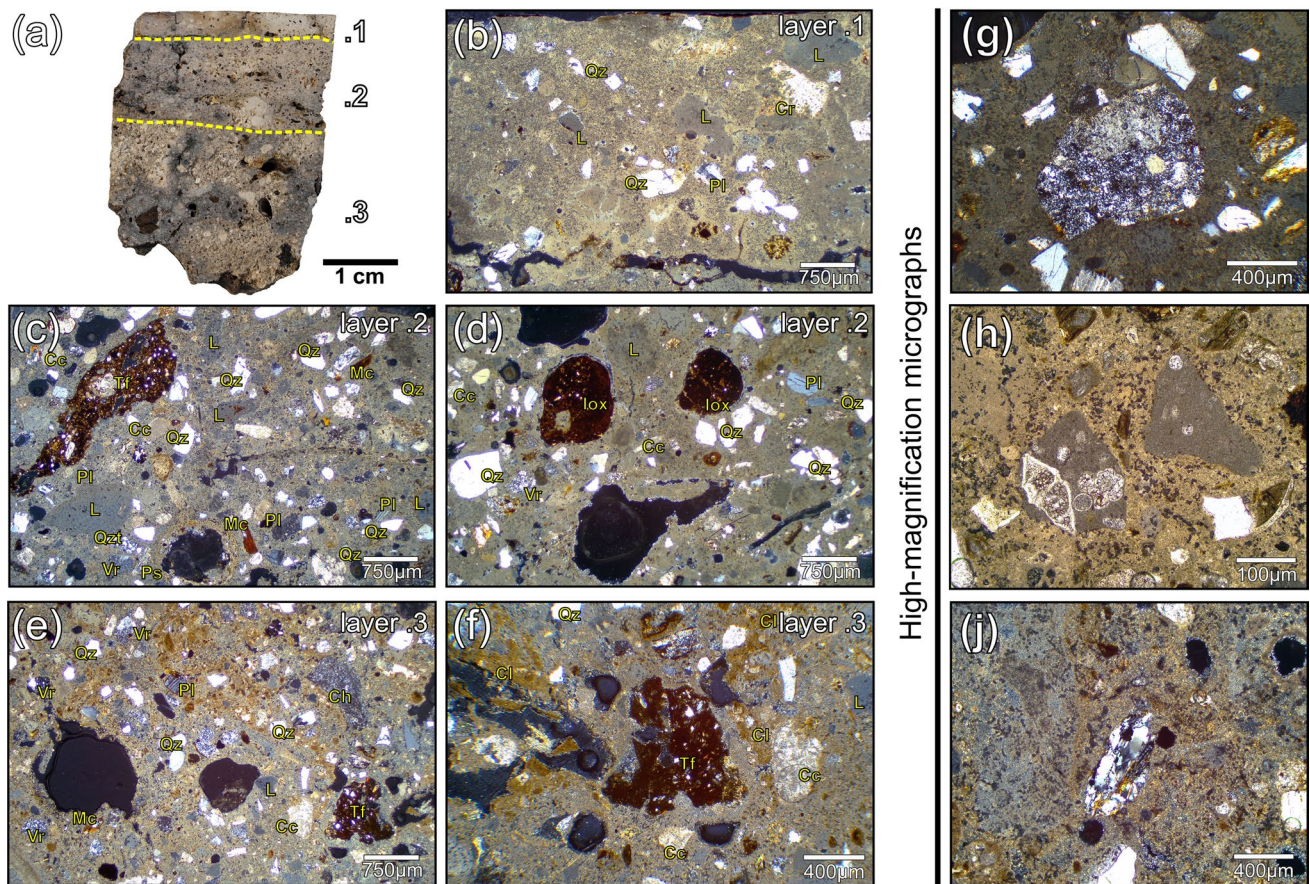
The mineralogical analysis of the pigments was done by qualitative XRPD, loading the samples on silicon zero-background sample holders, using the same instrumentation and software previously described.

Micro-Raman analyses were carried out using a WITec Alpha 300R Raman system (WITec GmbH) equipped with a Zeiss microscope and a 532 nm laser operating at a power of 2mW, with a spot size of 1.1  $\mu\text{m}$ . Spectra were acquired with Control Five program (@WITec) in the range 70–3800  $\text{cm}^{-1}$ , with a resolution of 2  $\text{cm}^{-1}$  and using 1 second of integration time and 30 accumulations and with 300g/mm of grating. The acquired spectra were later processed using Project Five program (@ WITec).

## Results

### The mortars of the *tectorium*

Based on the analysis of the preparation layers' stratigraphy, the *tectorium* of the ceiling exhibits an overall thickness of approximately 2.5–3.0 cm, divided into three macroscopically detectable layers (Fig. 6a). These were labelled, according to Nimmo (2001), from the outermost to the innermost as it follows: a) *intonachino* (.1), about 0.2–0.3 cm thick, serving as the topmost preparatory layer, set immediately beneath the pictorial micro-layers; b) *arriccio* (.2), about 1.3 cm thick,



**Fig. 6** The *tectorium* of the paint-plastered ceiling. (a) Cuttings of a sample from the ceiling plaster (consolidated in epoxy resin) with indication of the stratigraphy of the preparatory mortar layers; (b–j) Micrographs in transmitted-light optical microscopy, crossed nicols, of the plaster layers; (b) *intonachino* layer (.1), characterized by an abundant concentration of micritic lime binder with diffused lumps and remnants of limestone and an aggregate mainly consisting of quartz sand; (c) *arriccio* layer (.2). In comparison with the previous layer, a greater concentration of aggregate is detected, comprising silicate sand (quartz and plagioclases), clasts of carbonate rocks (limestones and dolostones), volcanic rock fragments showing a porphyritic structure, ceramic fragments and, occasionally, micas

and chlorites; (d) an area of the *arriccio* layer (.2), with scattered iron oxides concentrations (probably leftovers of red ochre from the pigment); (e) the *rinzafo* layer (.3). This layer can be distinguished from the previous one for the greater concentration of earthen compounds (i.e. clay); (f) an area of the *rinzafo* layer enriched in clay fraction; (g) volcanic rock fragment showing a porphyritic structure with probable rhyolitic composition; (h) clasts of wakestone with planktonic foraminifera (sp. *globotruncana* and Globigerinoides); (j) granitoid/gneiss clast. Legend: Qz = quartz; Qzt = quartzites; Pl = plagioclases; Vr = volcanic rocks; Tf = ceramic fragments; Mc = micas; Iox = Iron oxides; Cc = carbonate rock clasts (limestones and dolostones); L = lime lumps; Cl = clay minerals

layered below the *intonachino*; c) *rinzafo* (.3), the lowermost preparatory mortar, having a varying thickness up to 1.8 cm. On its reverse side, the ceiling still retains the negative traces of the fiber canes that were originally attached to it.

Through TL-OM analyses, we observed that all the preparatory layers consist of extremely fat air lime-based mortars, with binder to aggregate (B:A) proportions ranging around 3:1 (Table 1). Lime lumps are also very common (Fig. 6b). The aggregate comprises fairly sorted river sands falling within the grain-size distribution of the fine to (rarely) medium sands, according to the Wentworth scale (Wentworth 1922). The porosity mainly consists of planar voids, formed as a consequence of mortars shrinkage after setting, attributed to the low concentration of the

aggregate fraction. From a compositional point of view, the *intonachino* mortar does not significantly differ from the *arriccio* and *rinzafo* ones, with the exception of a greater presence of coarse (0.4–0.5 mm) unmixed lime lumps and an higher concentration of sandy aggregate, especially in the *rinzafo*, having B:A ratio of about 1:1 (Table 1). The chemical composition of the binder, investigated by SEM-EDS, revealed a dominant concentration of calcium (Ca), both in the lumps observed in the *arriccio* (Fig. 7a and b, b1) and *rinzafo* (Fig. 7c, d, d1) layers. This indicates the utilization of Ca-rich limestones for lime production.

The aggregate fraction (Fig. 6c) of both *arriccio* and *rinzafo* layers consists mainly of quartz clasts, quartzites and occasionally flint, with subordinated feldspars, mainly

**Table 1** Composition of the preparatory mortars in the plasters' tectorium of nucleus 2, estimated from TL-OM analyses. Legend: n.d. = not detected; - = slight occurrence (< 10%); • = moderate occurrence (ca 10-25%); ● = sustained occurrence (25-40%); ●● = abundant occurrence (> 40%)

Mortar Layer	Binder		Pores		Aggregate							Binder / Aggregate ratio		
	Composition	Lime lumps	Vesicles	Planar voids	Quartz and quartzite fragments	acid volcanic fragment	Carbonate rock fragments	Feldspar minerals	Flint fragments	Ceramic fragments	Granitoids / Gneiss		Mica and other phyllosilicates	Clay minerals
<i>Intonachino</i> (.1)	calcic lime	•	-	•	•	n.d.	-	-	n.d.	n.d.	n.d.	n.d.	-	3:1
<i>arriccio</i> (.2)	calcic lime	●●	•	n.d.	●●●	•	•	-	-	-	-	-	-	1.5:1
<i>rinzafo</i> (.3)	calcic lime	●●	●●	-	●●	•	•	-	-	-	-	-	•	1:1

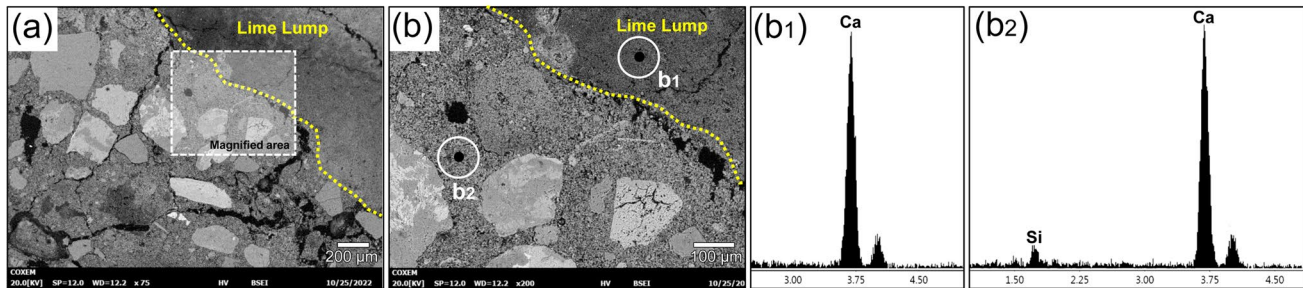
plagioclases. Volcanic rock fragments (Fig. 6g) showing a porphyritic structure are also present, as well as and carbonate clasts of micritic and fossiliferous limestones, among which some wakestones with planktonic foraminifera (*globotruncana* and *Globigerinoides*) (Fig. 6h), relatable to the local *Scaglia Rossa* limestone formation (Massari and Medizza 1973). Dolostones, ceramic fragments and clasts of phyllosilicates (mainly mica) and, occasionally, granitoids/gneiss fragments (Fig. 6j), were observed in lower concentrations. In the upper layer (*intonachino*), the aggregate fraction is mainly represented by quartz and quartzite clasts, with subordinate inclusions of volcanic rocks with porphyritic structure and clasts of carbonate rocks (limestones and dolostones). The petro-mineralogical assemblage of the sand fraction is compositionally compatible with that of the sediments of the Adige river (Jobstraibizer and Malesani 1973; Schiavon and Mazzocchin 2009), which flows just 5-6 km southeast of the Negrar site. This suggests that either the riverbed or the alluvial deposits of the Adige were likely the source of the aggregates used in the preparatory mortars.

In the two lower layers, scattered traces of iron oxides were detected, which probably represent leftovers of red ochre (Fig. 6d) from the pigments (see paragraph 4.3), accidentally included in the preparatory mortars.

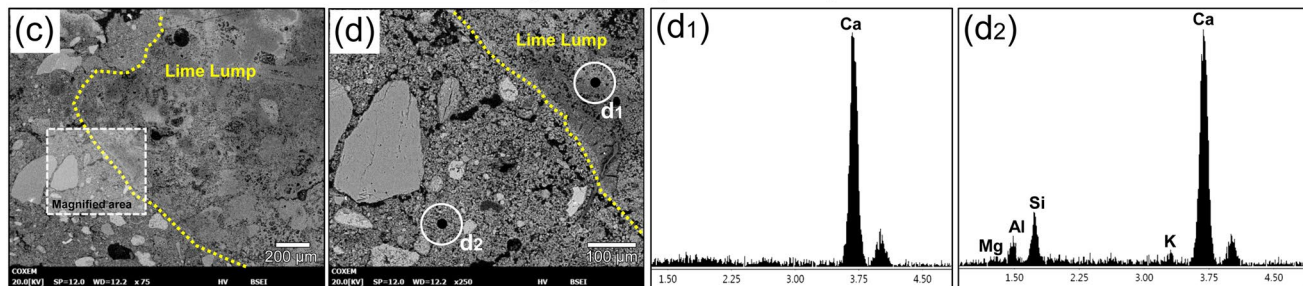
Furthermore, the mortar of the bottommost layer (*rinzafo*) slightly differs from the *arriccio* due to the sustained concentration of a fine clay component, homogeneously blended within the lime binder (Fig. 6e-f). By SEM-EDS microanalysis, the presence of this earthen component within the binder matrix of the *rinzafo* layer is highlighted by relevant amounts of Si and Al, followed by Mg and K (Fig. 7c-d2). These chemical elements, that can be related to clay minerals included in the mortars (Crisci et al. 2004; Carò et al. 2008), were not detected in the analysis of the upper layer that, on the other hand, appears eminently calcic (Fig. 7a-b2). Therefore, the high concentration of the amorphous phase (18.6 wt%), quantified via QPA-XRPD analysis of layer .3, could be related to the crypto-crystalline clay component included in the mortar or to other mineralogical phases not parameterizable with this technique. This assumption is eventually confirmed by the result of the QPA-XRPD analysis of the upper *arriccio* layer (.2) where the amorphous content is extremely low (1.7 wt%), testifying to the minor presence of clay fraction (Table 2). Other relevant clay minerals identified by XRPD in layer .3 are mica of the muscovite type and chlorite with the characteristic low-angle peaks at d-spacing [ $\text{\AA}$ ] = 14.12, 7.14  $^{\circ}2\theta$  (2.7 wt%) and 9.96, 10.32  $^{\circ}2\theta$  (1.3 wt%), respectively (Fig. 8a-c). Most of the other phases defined via XRPD mainly relate to the aggregate fraction of the mortars, while only calcite is primarily relatable to the binder. In fact, its concentration varies in agreement with the amount of binder in the layers detected by TL-OM, with a progressive decrease from



## Layer .2 (arriccio)



## Layer .3 (rinzafo)



**Fig. 7** SEM-EDS investigation of the preparatory mortars (*rinzafo*, *arriccio* and *intonachino* layers) of the paint-plastered ceiling decorations. (a) SEM back-scattered electrons (BSE) image of an area of the *arriccio* layer (.2), reporting a portion of a lime lump and the matrix; (b) BSE magnified image of the area reported at Fig. 7a; (b1) EDS microanalysis of the lime lump; (b2) EDS microanalysis of the binder

in the matrix of the layer; (c) BSE image of an area of the *rinzafo* layer (.3), reporting a portion of a lime lump and the matrix; (d) BSE magnified image of the area reported at Fig. 7c; (d1) EDS microanalysis of the lime lump; (d2) EDS microanalysis of the binder in the matrix of the layer

**Table 2** Results of QPA-XRPD investigations on the *intonachino*, *arriccio* and *rinzafo* layers of the plasters of the *nucleus 2*. Values expressed as %wt; - = below detection limit

Layer	Calcite	Quartz	Dolomite	Plagioclase	K-feldspar	Mica	Ilmenite	Kaolinite	Chlorite	Diopside	Amorphous
Intonachino (.1)	76.2	10.9	3.8	5.0	-	1.4	0.7	-	0.4	-	0.3
Arriccio (.2)	59.6	17.3	7.1	5.7	3.9	2.5	0.4	0.8	1.0	-	1.7
Rinzafo (.3)	48.3	15.1	4.9	4.9	2.7	2.7	0.4	0.3	1.3	0.6	18.7

the *intonachino* (76.2 wt%), to the *arriccio* (59.6 wt%) and *rinzafo* (48.3 wt%) layers.

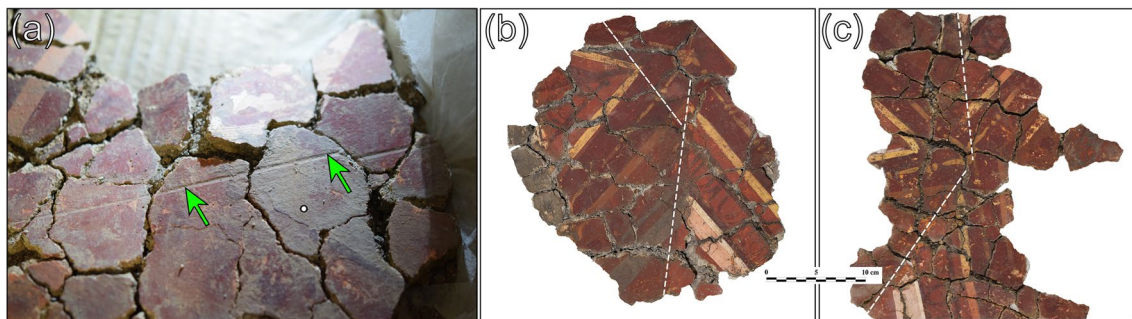
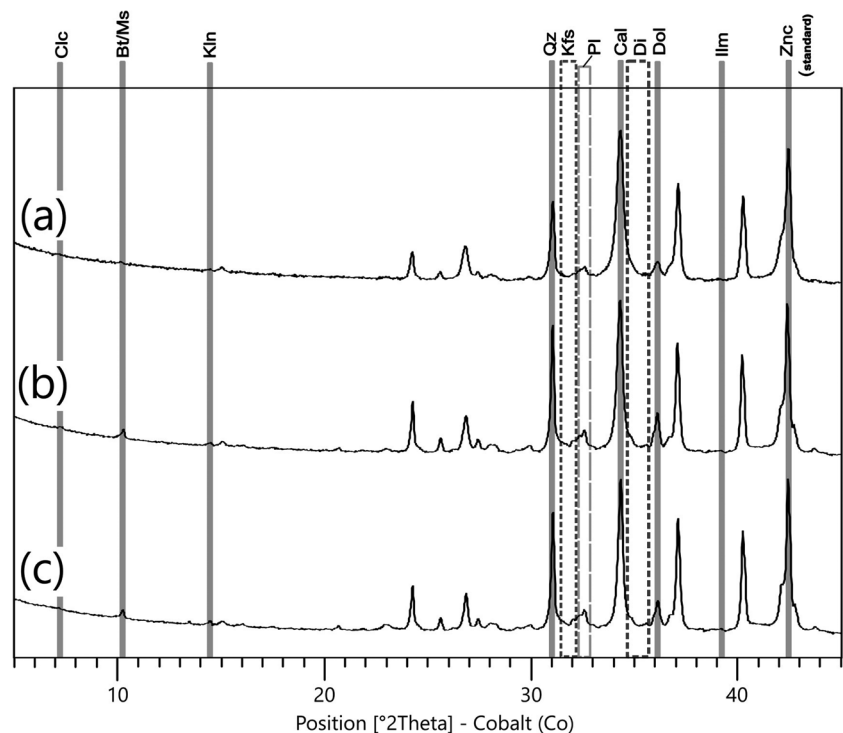
### Painting microstratigraphy

The observation of the painted surface under grazing light (Fig. 9a) has revealed incisions that run obliquely at about 45° degrees within the squares and intersecting approximately at the junction points, marking the basic grid of the composition (Bragantini 2009) (Fig. 9b-c). On the other hand, no traces of chalk-line (Salvadori et al. 2015) or “sinopia” (Salvadori and Sbrolli 2021) are visible, either because they are absent or, more likely, because they are covered by the pigment microlayers.

Regarding the application method of the painted microlayers, the analysis of RL-OM photomosaics of the pigmented profiles (Fig. 10a) revealed that the background of the decoration was applied adopting the dry technique (*a secco*) on the underlying *intonachino* layer (.1). This application method can be perceived in the sharp demarcation interface between the pigment and the substrate, indicating the low-diffusion (usually < 100 μm) of the color within the binder, as the painted coating was applied when the preparatory mortar was already dry.

The background consists of two superimposed colors, encompassing a lower wash of yellow pigment, less than 10 μm thick and spatially poorly distributed, overlaid by a layer of red pigment, up to 50-70 μm thick (Fig. 10b).

**Fig. 8** XRPD patterns of the analyzed mortar layers of the *tectorium*. **(a)** *intonachino* (.1); **(b)** *arriccio* (.2); **(c)** *rinza*ffo (.3). Mineral phases labeled according to Whitney and Evans 2010. Legend: Clc = chlorite; Bt/Ms = biotite/muscovite (mica); Kln = kaolinite; Qz = quartz; Kfs = K-feldspar; Pl = plagioclase; Cal = calcite; Di = diopside; Dol = dolomite; Ilm = ilmenite, Znc = zincite (standard)



**Fig. 9** Preparatory drawings of the decoration of the *nucleus* 2; **(a)** the incisions recognized through grazing-light analysis; **(b-c)** reconstruction of the orientation of the preparatory incisions

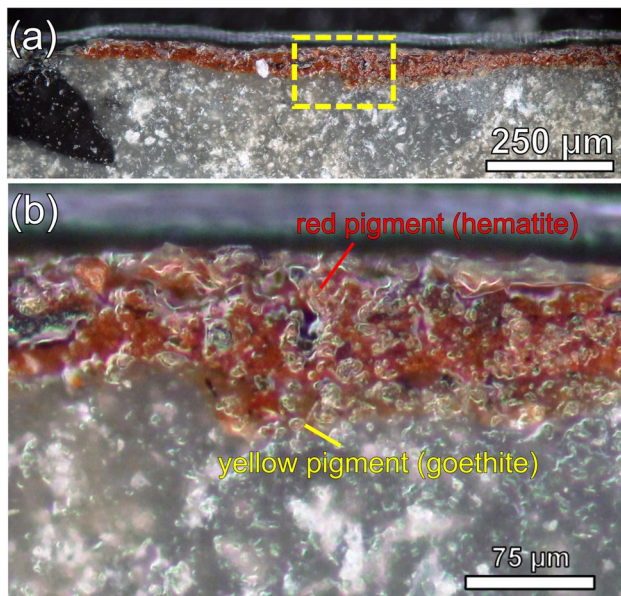
The decorative motifs were applied as over-paintings above this background, presenting a meaningful application sequence, skillfully designed. For example, the bands that mark the corners of the squares and lozenges are clearly overpainted on the background, sometimes with color smudges and dense brushstrokes, as perceivable in Fig. 11a. Similarly, in the center within the squares and lozenges, the palmettes are realized through over-paintings, firstly applying the layer of the light red color, on the left side of Fig. 11b. Then, the right half, depicted in dusky red in Fig. 11b, has been applied over the lighter hue, thus taking advantage of the superior covering properties of darker pigments. The overlapping of colors with varying hues, achieved through broad brushstrokes at

various points in the decoration, follows the same principle observed in the adjacent edges of the same color.

### The color palette of pigments

The types of pigments exploited for the making of the painted decorations were determined by XRPD and Micro-Raman investigations, by analyzing one-by-one the full variation of color shades used in the decoration of the painted ceiling (Fig. 12 and Table 3). Chromatic features of each hue were labelled according to the Munsell Soil Color chart (Munsell 1975).

In general terms, the standard palette of pigments commonly used in Roman times was detected (Siddall 2006,

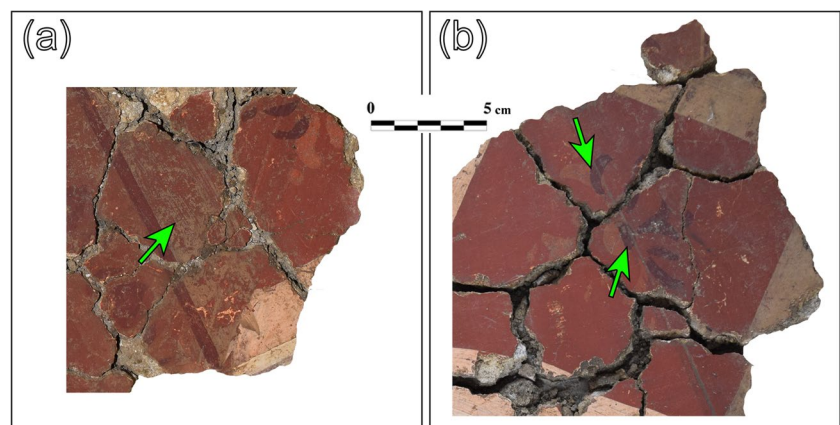


**Fig. 10** Pigment microstratigraphy observed by reflected-light optical microscopy; **(a)** pigment layer profiles acquired by automatized stitching method of multiple high-resolution micrographs; **(b)** in detail micrograph, reporting the magnification of the dashed area in sub-figure **(a)**, where the two superimposed microlayers of pigments are clearly detectable.

2018; Becker 2022). However, the analyses also revealed the utilization of unusual mixes of two or more pigments.

The background, which displays a *red* color (10R - 4/6), consists of hematite (red ochre), relatable to the upper micro-layer, clearly detected in most of the XRPD spectra at  $d\text{-spacing} = 2.70, 38.69 \text{ } ^\circ 2\theta$ . On the other hand, goethite (yellow ochre), with indicative peaks at  $d\text{-spacing} [\text{Å}] = 2.45, 42.84 \text{ } ^\circ 2\theta$  (Fig. 13a), and secondary discriminant peaks at  $d\text{-spacing} [\text{Å}] = 2.69, 38.80 \text{ } ^\circ 2\theta$  and  $4.18, 24.7 \text{ } ^\circ 2\theta$ , relates to the lower layer of the background. The application of the red color (often consisting of red ochre) on top of goethite-based backgrounds is likely a technical expedient taken to enhance and unify the color of the outer coating.

**Fig. 11** **(a)** Details of the dense overpainted brushstrokes; **(b)** Detail of the over-painting application of the palmettes within the squares



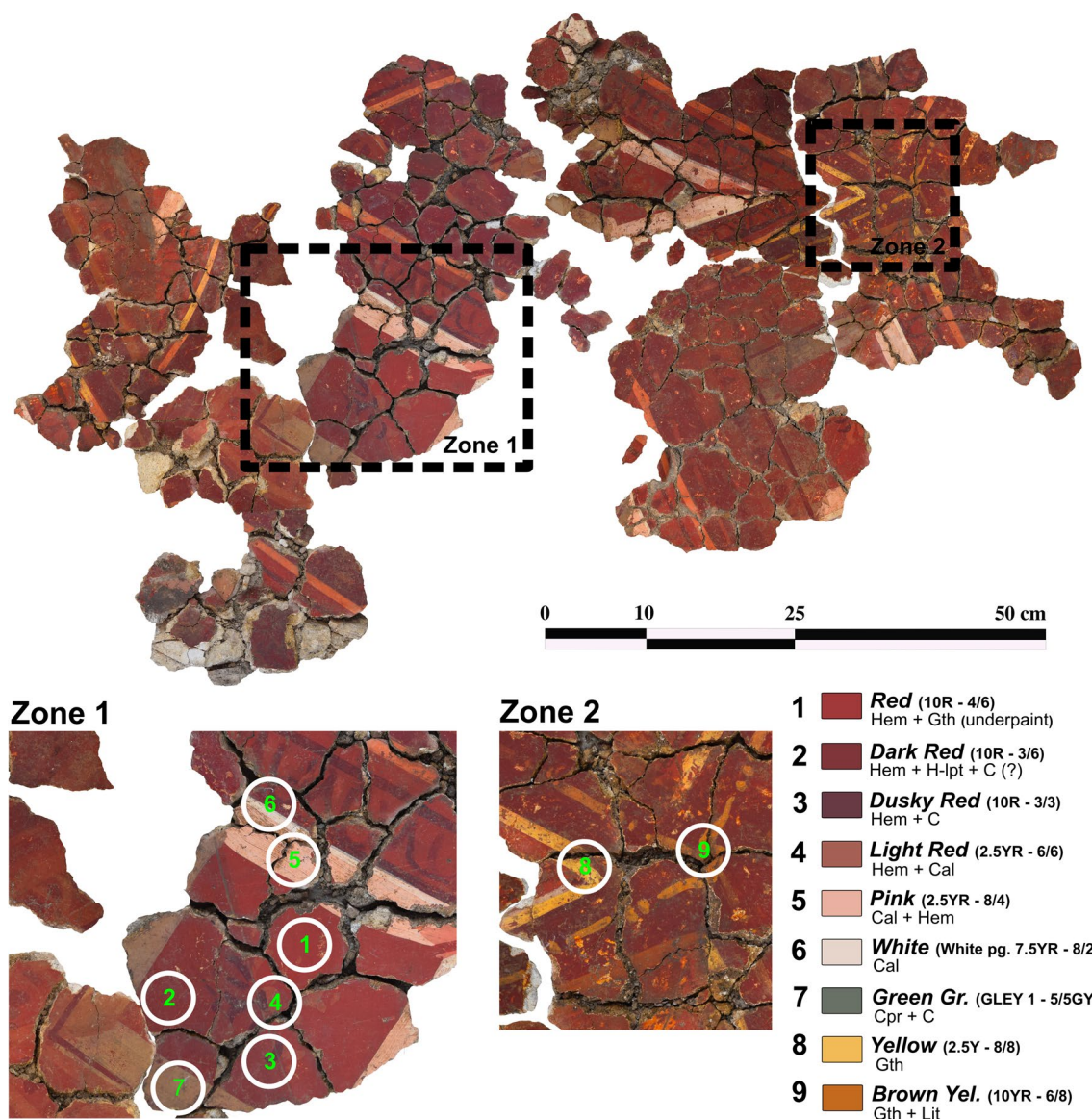
However, the presence of hematite is not common (Dilaria et al. 2021), as yellow ochre is more frequently applied under cinnabar overcoats (Prisco 2005; Gutman et al. 2016; Dilaria 2023).

*Dark red* brushstrokes (10R - 3/6) are applied for the making of certain shades in the background. This hue was obtained by adding to the base of red-ochre (hematite) a small amount of bone black, detected via XRPD in the secondary peak of hydroxyapatite at  $d\text{-spacing} [\text{Å}] = 2.80, 37.12 \text{ } ^\circ 2\theta$  (Fig. 13b). Apatite is, in fact, the inorganic residue of bone tissue. The presence of carbon (C), detected by micro-Raman (Fig. 14a) through the broad peaks around  $1330 \text{ cm}^{-1}$  and  $1580 \text{ cm}^{-1}$  Raman shift, could be related to charcoal (carbon black), added together with bone black to darken the hue of this portion of the decoration. However, considering the broad angle and low intensity of the peaks, the possible attribution of carbon to an accessory component of the red ochre cannot be excluded *a priori*.

Other phases, related mainly to the ochre-based pigments, can be linked to secondary and polluting components of the colors used in the decoration (Eastaugh et al. 2007). In particular, kaolinite, identified in the low peak at  $d\text{-spacing} [\text{Å}] = 7.15, 14.35 \text{ } ^\circ 2\theta$ , and mica of the muscovite type, with the characteristic low-angle peak at  $d\text{-spacing} [\text{Å}] = 9.96, 10.32 \text{ } ^\circ 2\theta$ , represent accessory phases of earthen-based pigments, commonly documented in literature (Eastaugh et al. 2007; Secco et al. 2021).

Above the background, a palette of pigments was adopted to obtain specific hues.

The *dusky red* hue (10R - 3/3), employed for the dark sides of the two-tone palmettes, was obtained by mixing together red ochre (hematite), detected through XRPD (Fig. 13c), with abundant charcoal (carbon black), detected through micro-Raman (Fig. 14b) by the peaks at  $1330 \text{ cm}^{-1}$  and  $1580 \text{ cm}^{-1}$  Raman shift. These are identifiable as the D band related to the vibrational modes of the  $sp^3$  C–C covalent bonds and the G band related to the vibrational modes of the  $sp^2$  C–C covalent bonds of the carbon-based compound, respectively.



**Fig. 12** The sampling points of the analyzed pigments from *nucleus 2*, with indication of the Munsell color (Munsell 1975) and composition according to the results of XRPD and Micro-Raman investi-

gations. Mineral abbreviations labelled according to (Whitney and Evans 2010): Hem = hematite; Gth = goethite; H-lpt = hydroxyapatite; C = carbon; Cal = calcite; Cpr = cuprorivaite; Lit = Litharge

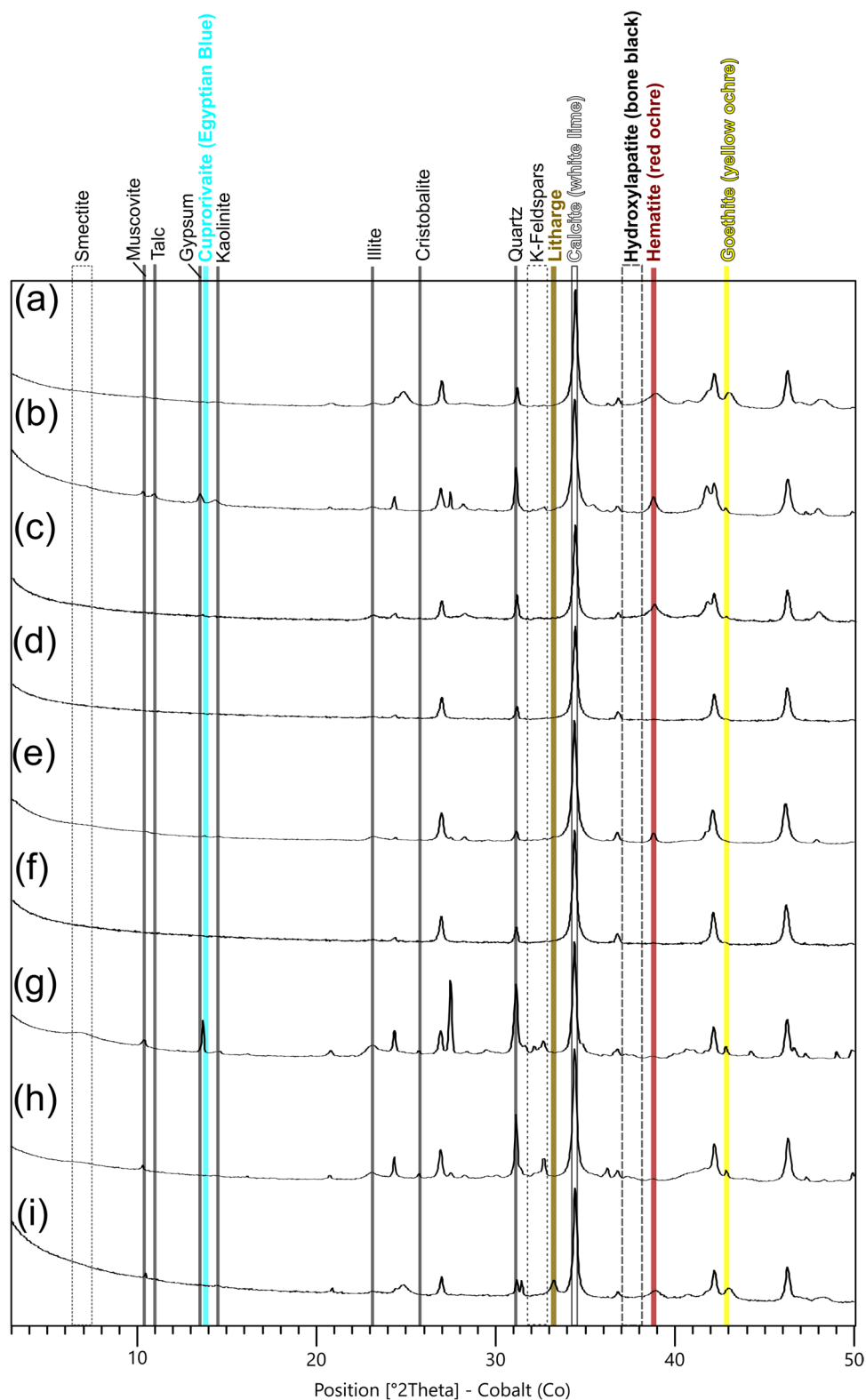
Moreover, a small addition of litharge is also present. Litharge is a Pb-based pigment (PbO) that has been detected also in other colors of the painted decorations and in particular in the *brown yellow* hue. On the other hand, the *light red* (2.5YR - 6/6) overpaint, employed for the light portion of the two-tone palmettes, is composed of hematite possibly mixed with a small amount of lime white. However, calcite, identified by the clear peak at d-spacing [ $\text{\AA}$ ] = 3.03, 34.3  $^{\circ}2\theta$ , has been consistently identified in XRPD patterns of the examined pigments (Fig. 13d). In the majority of cases, this phase corresponds to the binder used in the *intonachino*, accidentally collected during the micro-sampling of the

pictorial micro-layers. Its utilization as chromophore compound in the *light red* hue – as well as in the *pink* and *white* pigments – was esteemed by observing the intensity of the peaks of the XRPD spectra. As a matter of fact, the peak of calcite is extremely pronounced in the *pink* color (2.5YR - 8/4), applied for the making of certain bands of the lozenges and squares, as this hue was obtained by mixing red-ochre with a prevalent lime white component (Fig. 13e). The *white* color (White pg. 7.5YR - 8/2), used for the making of a thin listel over the pink band, is the diffractogram where the calcite peak is at its highest, confirming this superficial film as constituted of almost pure lime white (Fig. 13f).

**Table 3** Mineralogical composition and quantification of the analyzed pigments, estimated from XRPD and micro-Raman analyses. Legend: n.d. = not detected; - = slight occurrence (< 10%); ● = moderate occurrence (ca 10-25%); ●● = sustained occurrence (25-40%); ●●● = abundant occurrence (> 40%). Mineral abbreviations labelled according to (Whitney and Evans 2010)

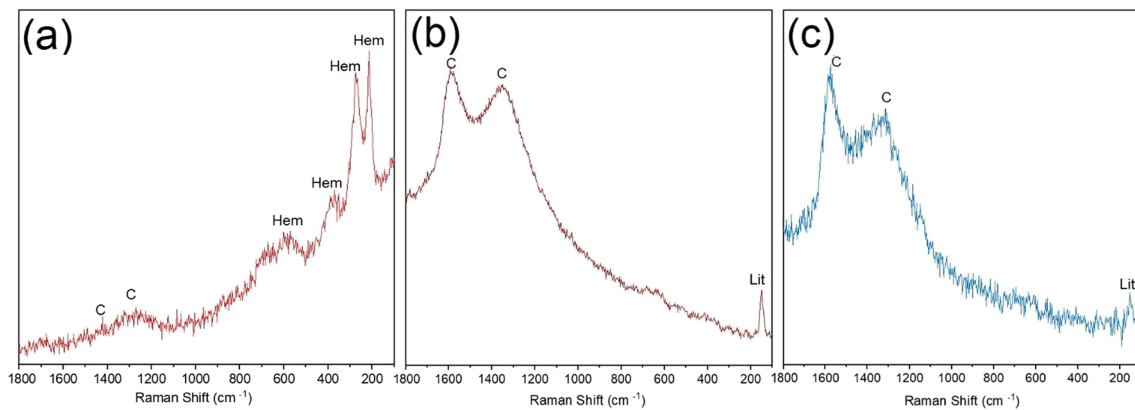
Area	Background			Over-paintings					
	Main color	Shades	Palmettes(dark half)	Palmettes (light-half)	Band of the squares	Listel of squares	Band of the squares	Listel of the lozenges	Frame
Colors	1	2	3	4	5	6	7	8	9
	Red	Dark red	Dusky red	Light red	Pink	White	Greenish grey	Yellow	Brown yellow
	10R - 4/6	10R - 3/6	10R - 3/3	2.5YR - 6/6	2.5YR - 8/4	White pg 7.5YR - 8/2	GLE Y 1 - 5/5GY	2.5Y - 8/8	10YR - 6/8
Analytical Method	XRPD	XRPD, Raman	XRPD, Raman	XRPD	XRPD	XRPD	XRPD, Raman	XRPD	XRPD
Pigment Chromophores	Hem ● Gih ● Carbon ? Cpr ● H-lpt ● Cal ● Lit -	●	●	●	-	●●	●	●	●
Pigment accessory	-	●	-	-	-	-	-	●	●
	Kln -	●	●	-	-	-	-	-	-
	Illt -	-	●	-	-	-	-	-	-
	Sime -	-	-	-	-	-	●	-	-
	Crs -	-	-	-	-	-	●	?	-
	Qz -	●	-	-	-	-	●	-	-
	Kfs -	-	-	-	-	-	●	-	-
Mortar	●●●	●●	●●	●●	●●	●●	●●	●●	●●
	●	●	●	●	-	●●	●	●●	●
	Dol -	-	-	-	-	-	-	-	-
Other phases	Gps ●	●	-	-	-	-	-	-	-
	Tlc ●	●	-	-	-	-	-	-	-

**Fig. 13** XRPD patterns of the analyzed pigments, comprising the background and over-paintings. (a) red (background, spot n.1); (b) dark red (spot n.2); (c) dusky red (spot n.3); (d) light red (spot n.4); (e) pink (spot n.5); (f) white (spot n.6); (g) greenish grey (spot n.7); (h) yellow (spot n.8); (i) brown yellow (spot n. 9)



The *greenish grey* color (GLE Y 1 - 5/5GY), employed in some bands of the lozenges and squares counterposed to the *pink* ones, is peculiar as it was obtained from an Egyptian blue-based mix, presenting the classic assemblage of cuprorivaite,

at d-spacing [ $\text{\AA}$ ] = 7.56, 13.6  $^{\circ}2\theta$  (chromophore mineral), with accessory phases constituted by quartz at d-spacing [ $\text{\AA}$ ] = 3.34, 31.0  $^{\circ}2\theta$ , pertaining to remnants of the sand source used for the production of the pigments, and cristobalite, an



**Fig. 14** Representative Raman spectra of a selection of pigments and relative peaks identifications (compounds abbreviations: Hem = hematite, C = carbon; Lit = litharge). **(a)** dark red; **(b)** dusky red; **(c)** greenish grey

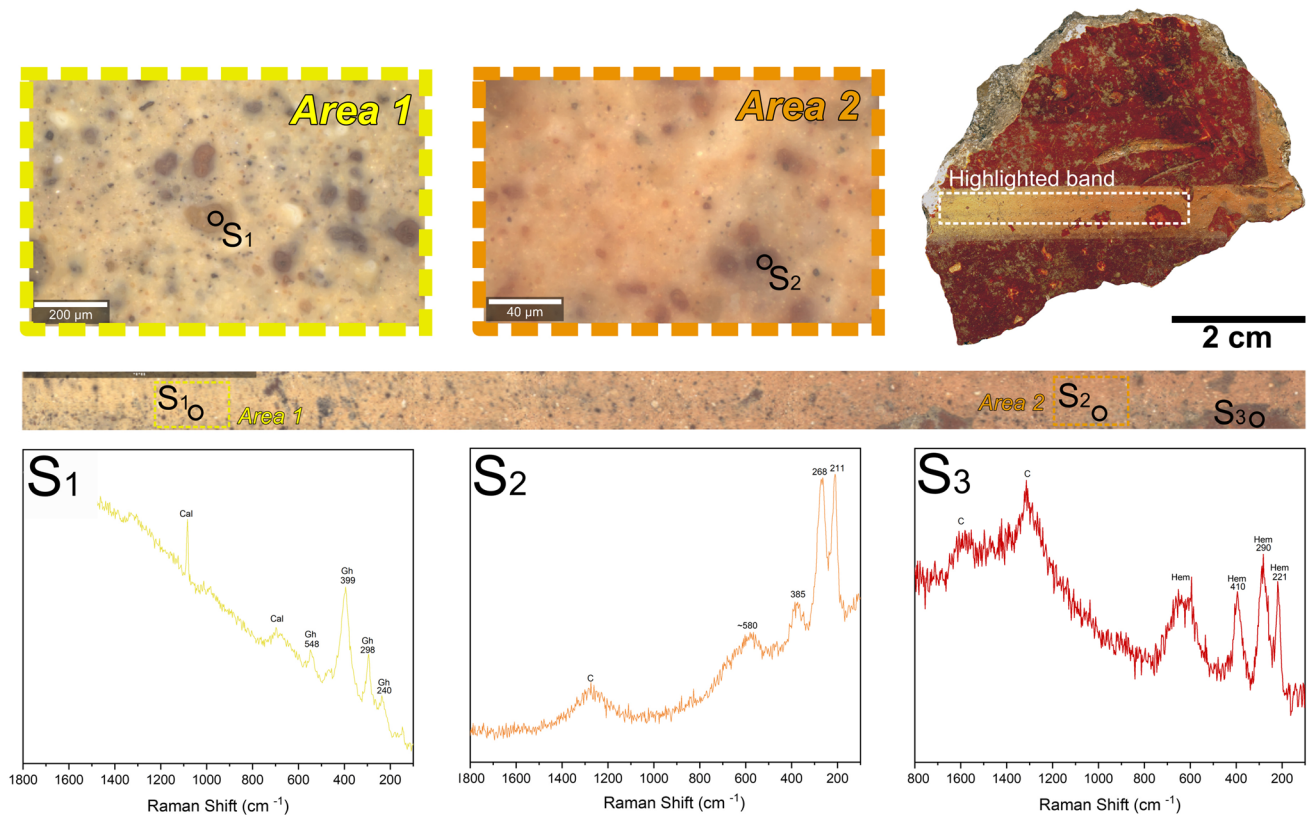
high-temperature polymorphs of  $\text{SiO}_2$ , detected in the low-peak at d-spacing [ $\text{\AA}$ ] = 4.03,  $25.6^\circ 2\theta$ , to be considered as a newformed phase of the production process (Dariz and Schmid 2021). To this base, small amounts of bone black, attested by the low peak of hydroxyapatite at d-spacing [ $\text{\AA}$ ] = 2.80,  $37.12^\circ 2\theta$  (Fig. 13g), combined with charcoal (carbon black), detected though micro-Raman (Fig. 14c), contributed to imparting the grayish tone that denotes the peculiar hue of the microlayer. Additionally, the mixture was enriched with litharge, detected via micro-Raman by the peak at  $147\text{ cm}^{-1}$  Raman shift (Guglielmi et al. 2022).

The yellow hue (2.5Y - 8/8), used to craft the listel of the lozenges/squares, was achieved using goethite (Fig. 13h). The analysis of the ornamental pattern shows a clear alteration of the yellow ochre, indicating exposure to fire when the villa's ceiling was still connected to the roof before collapsing. This color alteration, caused by heat, is evident in the chromatic transition of certain sections of the yellow listels mentioned earlier (see paragraph 2.2). Through micro-Raman analysis, the chemical shift of the altered areas, where the color moves to reddish yellow tones (7.5 YR 6/6), was accurately mapped. In fact, the characteristic peaks of goethite at Raman shift 240, 298, 399,  $548\text{ cm}^{-1}$  were detected in the unaltered sections of the listel (Fig. 15, area 1, S1). Moving toward the reddish yellow portion, sharp Raman peaks at 211, 268,  $385/388\text{ cm}^{-1}$  (Fig. 15, area 2, S2) indicates goethite-transformation into hematite due to heat exposure, according to a well-known dehydroxylation topotactic process of heated-goethite starting from temperatures below  $300^\circ\text{C}$ , thoroughly studied in literature (Pomiès et al. 1998; Gualtieri and Venturelli 1999; Gialanella et al. 2010), also through Raman-based techniques (Burgina et al. 2000; De Faria and Lopes 2007; Marcaida et al. 2019; Krzemnicki et al. 2023). The chemical processes leading to chromatic conversion of goethite into hematite have been extensively attested in the Vesuvian sites and, particularly, in Pompeii and Herculaneum. These were due

to the high temperatures the painted walls were exposed to during the Somma-Vesuvius 79 CE pyroclastic flows and surges (Gurioli et al. 2005; Gialanella et al. 2010; Marcaida et al. 2017, 2019; Secco et al. 2021). The formation of a non-stoichiometrically structured hematite (i.e. proto-hematite, as defined by Gualtieri and Venturelli 1999) is detectable in the low broad-angle peaks recorded at  $385$  and  $\sim 580\text{ cm}^{-1}$  Raman shifts. The characteristic peaks of natural red ochre were detected at Raman shift 221, 290,  $410\text{ cm}^{-1}$  by analyzing a hole in the yellow listel, thus revealing the underlying original red color of the background (Fig. 15, S3).

Finally, the brown yellow (10YR - 6/8) color, used for the frame, was made on a yellow ochre base, mixed with a small amount of red ochre and litharge, identified with the peak at d-spacing [ $\text{\AA}$ ] = 3.14,  $33.1^\circ 2\theta$  (Fig. 13i). The use of this Pb-based chromophore element, whose characteristic peaks in this case are clearly detectable in the XRPD pattern, was likely intended as a hue corrector. It was probably added to the lower-quality earthen-based pigments to provide chromatic homogeneity to the painted layers (Secco et al. 2021). As already stated, traces of this pigment were detected by Raman also in the dusky red and greenish grey pigments, where litharge was possibly added for similar reasons. Alternative hypotheses regard its possible use as a siccative (drying agent), as suggested by (Toniolo et al. 1998). The extensive use of litharge in the painted decoration contrasts with Vitruvius (7.3.5; 6.11), who remarks the pernicious effects of lead and its effect on the body. However, evidence of this pigment has been found in the analyses of ancient pigments from the Hellenistic period onward (Pella, Herculaneum, Monte d'Oro near Rome, Secco et al. 2021; Guglielmi et al. 2022; Brecolouki et al. 2023).

Among the non-chromophore elements, some accessory silicate minerals, such as microcline, muscovite and clay minerals (kaolinite, chlorite and smectite) were identified by XRPD in most of the spectra. Moreover, as already stated, the ubiquitous peaks of calcite can be primarily related to



**Fig. 15** The results of the micro-Raman analyses of the altered portion of yellow listel due to heat exposure. Legend: S1 = goethite; S2 = heated-goethite transformed into hematite; S3 = original hematite (red ochre) pigment from the background

the carbonated lime from the plaster, while quartz and feldspars, when detected, in most cases are likely related to the aggregate fraction of the *intonachino* substrate.

Finally, some mineral phases acting as additives for pigment processing were also identified by XRPD. In particular, talc, documented in the *Dark Red* hue at d-spacing [ $\text{\AA}$ ] = 9.35, 11.98  $^{\circ}2\theta$ , was probably added during the application of the pigment as a surface treatment to improve some of its color physical characteristics and brightness, as discussed in (Angelini et al. 2019) and (Secco et al. 2021).

Secondly, gypsum, attested in the *Dark Red* hue at d-spacing [ $\text{\AA}$ ] = 7.6, 13.52  $^{\circ}2\theta$ , could constitute an accessory component for the processing of the pigment mixture (Aceto 2021). Alternatively, it could be regarded as a secondary phase resulting from sulfation of the carbonate binder (Secco et al. 2021). However, traces of this mineral were identified by XRPD also in the *tectorium* layers, strengthening the reliability of the first hypothesis (see Table 1).

## Discussion

The detailed analysis of the making process of the collapsed paint-plastered ceiling of the Late Roman *villa* of Negrar

provides valuable insights into the materials and painting techniques adopted during Late Antiquity in Northern Italy.

The use of fat mortars for the *tectorium* is a distinctive feature of the analyzed wall-paintings. The lime-aggregate proportions (around 2:1 or even 3:1 in the *intonachino* layer) is, in fact, higher compared to the proportions of the traditional Roman lime mortars reported in the treaties of Vitruvius (2.5.1) and Pliny (36.174-175). Indeed, they both proposed lime-to-fluvial sand aggregate ratios around 1:2. This change in proportions may be related to the increased availability of lime binder during the Late Antique period, due to the recycling and calcination of limestone elements (Plommer 1973), a phenomenon also noted in Late Antique structural mortars in the region (Dilaria; Secco et al. 2018; Dilaria et al. 2019, 2022). Other important distinctive elements are related to the making technique of the *intonachino*. This layer is characterized by the most clear compositional difference compared to the written tradition. Instead of the three-layer system with clasts of sparry calcite or marble (Vitr. 7.6.1, Daniele and Gratzu 1996), having a decreasing grain-size distribution from the inner layer to the outer one (Vitr. 7.3.5-6), the artisans at Negrar opted for a simpler, single thin layer of mortar made of lime mixed with fluvial sand, having the same lithological features of the aggregates reported in the lower strata.



This clearly shows that the aggregates for this layer were not carefully selected by the artisans, as river sand certainly does not impart the same level of vibrancy to the painted surface as the bright marble or sparry calcite grains do.

Finally, the analysis of the microstratigraphy of painting layers revealed for both the backgrounds and over-paintings an extensive adoption of the *secco* over the traditional “*buon fresco*” painting method. Again, even if this application technique was strongly discouraged in ancient treaties due to the risk of pigment detachment from a dry plaster surface (Vitr. 7.3.7-9), this technique allows for the creation of more intricate patterns, but they tend to be less durable over time. Therefore, the overall pieces of evidence here reported describe a substantial qualitative change in the making methods of the wall-paintings of the *villa* of Negrar, that do not match with the standards reported in the ancient literary tradition. Such standards were quite faithfully observed in the pictorial production of Northern Italy during the Late Republican and High Imperial ages, although some necessary simplifications were implemented (Dilaria 2023). However, the unconventional characters detected in Negrar cannot be considered as unique: in fact, similar conclusions were drawn after meticulous archaeometric investigations of Late Antique wall-paintings from Aquileia (Friuli Venezia Giulia, Northern Italy) (Dilaria 2024; Dilaria et al. 2019, 2021; Sebastiani et al. 2019). The methods employed for preparing the mortars and applying pigments to the support of the paint-plastered ceiling of the Negrar’s *villa*, in fact, closely resemble those used to create the paint-plastered ceiling of the South Theodorian Hall of Aquileia, discovered in a state of primary collapse debris during excavations of the building (Salvadori and Tiussi 2010). This evidence suggests that changes in technique and materials outlined for the Late Roman *villa* of Negrar were not isolated occurrences, but they may be part of a larger evolution of the regional practices along time.

Despite changes in the plaster-making process, the characteristics and color choices adopted in the *villa* showcase carefully considered color selection, achieved by skillfully blending a limited range of pigments, typically two or three, to create various hues. This demonstrates the skill and creativity of the artisans in achieving a complex array of shades through the artful mixing of the available pigments. Unconventional materials like litharge were employed in the artwork to lower the chromatic tone of the yellow color, despite their use being discouraged by several ancient authors due to the toxicity of lead (Hodge 1981).

These findings collectively suggest that the artisans of the late Roman *villa* of Negrar had to adapt to the materials and techniques available at the time. Their choices represented a unique blend of high-experienced craftsmanship that may not have strictly adhered to established norms and guidelines suggested by ancient sources, as commonly observed in recent literature. This information enhances our comprehension of

the complexities involved in wall painting production during Late Antiquity in Northern Italy, shedding new light into the influence of accessible resources and the changing preferences of the era.

## Conclusions

The findings of this research offer valuable insights into the production techniques and materials used in the paint-plastered ceiling of the Late Antique *villa* of Negrar. These insights can be summarized into two main points:

- **Methodology:** The primary objective of this study was to establish a multi-analytical protocol for reconstructing wall paintings and other paint-plastered fragments from secondary reworked deposits, as well as investigating comprehensively their constituting materials (mortars and pigments) and production methods. The application of a multidisciplinary methodology has facilitated the achievement of these results, establishing a workflow sequence that can be replicated in similar circumstances.
- **Raw materials and their utilization:** The comprehensive evidence indicates a qualitative shift in the wall painting techniques employed at the *villa* of Negrar compared to the ancient literary prescriptions and productive standards of the Late Republican and High Imperial periods. This departure from established norms has been observed in Northern Italy also in other circumstances, with close terms of comparison recently investigated in Aquileia. This suggests that the changes in technique and materials observed in Negrar may be part of a broader regional evolution over time. Despite alterations in plaster-making methodologies, the *villa* exhibits vibrancy and discerningly chosen colour palettes through the intelligent blending of a restricted array of pigments, highlighting the skill and creativity of the artisans involved. This contributes to a deeper understanding of the complexities involved in wall painting production during Late Antiquity in Northern Italy, a topic that has been marginally considered within the realm of the Greek and Roman wall painting tradition so far.

**Acknowledgements** We kindly thank Dr. Gianni De Zuccato (Soprintendenza Archeologia, Belle Arti e Paesaggio per le province di Verona, Rovigo e Vicenza) and Prof. Patrizia Basso (University of Verona, Department of Cultures and Civilization) for authorizations and permissions to the sampling activities and for the useful suggestion in the interpretation of the results.

**Author contributions** Conceptualization: Simone Dilaria, Monica Salvadori; Supervision: Monica Salvadori; Methodology: Simone Dilaria, Federica Stella Mosimann, Clelia Sbrolli, Michele Secco; Formal analysis and investigation: Simone Dilaria, Federica Stella Mosimann, Clelia Sbrolli, Michele Secco, Lisa Santello, Anna Favero; Visualisation: Simone Dilaria, Federica Stella Mosimann, Clelia Sbrolli; Writing:

Simone Dilaria (paragraphs 3, 4.1, 4.3, 5), Federica Stella Mosimann (paragraph 2.1, 4.2, 5), Clelia Sbrolli (paragraphs 2.2, 5), Anna Favero (paragraph 5, 6, 7), Monica Salvadori (paragraph 1); Funding: Simone Dilaria, Clelia Sbrolli; Review and Editing: all the authors contributed in the review and editing of the manuscript.

**Funding** Open access funding provided by Università degli Studi di Padova within the CRUI-CARE Agreement.

**Data Availability** The datasets generated during the current work are available from the author on reasonable request.

## Declarations

**Competing interests** The authors declare no competing interests.

**Additional information** The OM, XRPD and Raman analyses as well as the preparation of the samples were entirely performed at the laboratories of the Department of Geosciences of the University of Padova. The SEM-EDS investigations were conducted in the laboratories of the CEASC (Analysis Center and Certification Services) laboratory of the University of Padova, in the framework of the Ciba bilateral agreements (Interdepartmental Research Center for the Study and conservation of archaeological, architectural and historical-artistic heritage), in the framework of the World Class Research Infrastructure (WCRI) Sycuri of the University of Padova. The research got a partial financing from the project “Trade and use of volcanic pozzolans in the Roman world. A natural material for the production of eco-sustainable concrete of antiquity” (Principal investigator: Simone Dilaria, BIRD 2023 of the Department of Cultural Heritage of the University of Padova, project code BIRD230232/23).

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