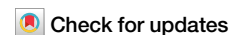


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The fate of neutral verdigris in wall paintings: chromatic, micro-morphological, mineralogical and chemical transformations

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This study fills the gap regarding the behaviour of neutral verdigris pigment ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$) in traditional wall-painting techniques, an area far less studied than its degradation in manuscripts or easel paintings. Verdigris was applied using three historical methods—a secco (egg yolk or rabbit glue), mezzo-fresco (lime water), and fresco (lime paste)—and complementary pigment–binder mixtures were prepared to isolate binder effects. Multimodal analyses (stereomicroscopy, spectrophotometry, OM, SEM, XRD, ATR-FTIR) revealed a striking contrast between acidic and alkaline environments: verdigris remained chemically and microstructurally stable in a secco but underwent rapid and extensive alteration in lime-based techniques. These transformations produced marked colour shifts, micro-textural heterogeneity, and micrometric secondary compounds such as copper and calcium acetates (e.g. paceite), and tenorite. The findings provide new insights into historical wall-painting practices as they re-examine the use of verdigris with certain painting techniques, also with significant implications for conservation strategies involving verdigris-containing artworks.

Verdigris, a term umbrella for copper(II) acetate-based compounds, is one of the earliest known synthetic pigments used in art, with references dating back to the 3rd century BCE^{1,2}. Its manufacturing process was widely described since antiquity, most often involving the exposure of copper or copper alloys to vinegar vapours, subsequently scraping off the resulting corrosion that formed on the surface^{1,3,4}; other organic substances—wine lees, milk, urine, or honey—were also reported to yield mixed compounds^{1,3,4}. These methods yielded various verdigris phases which differ in colour, crystal structure and stability, and can be distinguished by their chemical composition, expressed as the molar ratio $x\text{Cu}(\text{CH}_3\text{COO})_2 \cdot y\text{Cu}(\text{OH})_2 \cdot z\text{H}_2\text{O}$ (the x – y – z phase)⁵. Broadly, verdigris phases can be grouped into two categories: (i) neutral (sometimes distilled or recrystallised) and (ii) basic verdigris⁵. The first group comprises bluish-green copper(II) acetates—both hydrous (1–0–1 phase, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$) and anhydrous (1–0–0 phase, $\text{Cu}(\text{CH}_3\text{COO})_2$)—valued for their relative stability^{5–9}. The second group encompasses copper(II) acetate hydroxide hydrates—up to seven distinct phases—which are more susceptible to alteration^{5–10}.

The use of this pigment was widespread across various substrates during the Middle Ages—including stone, wood, canvas, panel, paper, and

parchment—particularly in 15th- to 17th-century easel painting¹. Its popularity, however, declined in the early 20th century with the advent of alternative green pigments, such as emerald green ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$) or viridian ($\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$)^{11,12}. Despite its extensive historical use in painting, artists and treatises had long acknowledged its instability^{13–16}. Cennino Cennini (14th c.)¹⁷, for instance, recommended its application on paper with egg yolk but cautioned that the colour would not last. Indeed, copper acetates undergo gradual colour changes depending on the binding medium: with resins, they form copper resins; with oils, copper oleates; and with proteins, copper-protein complexes⁴. Other historical sources explicitly discouraged its use in painting due to its high reactivity with atmospheric pollutants such as sulphur dioxide¹⁸ or with other pigments, particularly those sulphur-based^{19,20}. As a result, substantial research has been devoted both to reproducing historical recipes and various forms of verdigris^{6,9,10,21,22}, and to its degradation when combined with organic binders such as gum arabic^{15,16,23–26}, protein-based binders (i.e. egg yolk or rabbit glue)^{25,27–30} and linseed oil^{26,28–33}.

In contrast to its well-documented behaviour in paper, parchment and easel painting, the stability of verdigris—whether neutral or basic—in wall

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paintings remains poorly understood. Verdigris is known to be highly sensitive to alkaline environments, rendering it unsuitable for application on walls due to the inherent alkalinity of mortars²⁰. Nonetheless, verdigris has been identified in Romanesque wall paintings in France³⁴, in several examples of Gothic wall paintings in England³⁵, and in various wall paintings in Italy and Spain that appear to have been executed as a *fresco*^{36–38}. While alternative techniques such as *mezzo-fresco* may also explain these occurrences, no securely documented cases are known. Moreover, the term ‘*fresco*’ has been used loosely in the literature, potentially contributing to misattributions of technique and obscuring the original conditions under which verdigris was originally applied³⁹. Notably, historical authors such as Cennino Cennini (14th c.), Giorgio Vasari (16th c.) or Andrea Pozzo (18th c.) all explicitly warned against using verdigris in *fresco* painting⁴⁰.

This apparent contradiction—clear historical prohibitions vs repeated archaeological identifications—highlights a significant gap in current knowledge. The alteration process of verdigris in wall-painting environments remains insufficiently studied, and its degradation pathways are still a matter of debate. A recent investigation⁴¹ evaluated the stability of several copper-based pigments in *fresco* conditions and found copper acetate to be the most unstable, showing heterogeneous discolouration and morphological changes distinct from the homogeneous blackening observed in copper carbonates and silicates. These findings indicate that verdigris undergoes a more complex, poorly understood alteration trajectory in alkaline media—one that is not satisfactorily explained in existing research.

To address this gap, the present study explicitly aims to evaluate the alteration process of neutral verdigris in alkaline wall-painting environments—from the earliest stages of its degradation to its typical transformation into black copper oxides such as tenorite. Specifically, we investigate how both the binding medium and the painting technique influence its degradation. A bluish-green neutral copper(II) acetate monohydrate with the formula $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was used as pigment. To isolate the pigment-binder interactions, verdigris was mixed in petri dishes with egg yolk, rabbit glue, lime water and lime paste separately. To evaluate the role of the painting technique, the pigment was applied *a secco*, where the pigment is mixed with an organic binder (with egg yolk or with rabbit glue) and applied onto a dry mortar surface and fixed by polymerisation of the binder¹⁹. The pigment was also applied using a *mezzo-fresco* technique, which involves mixing the pigment with lime water and applying it onto a semi-dry mortar, fixed by reactivation of the carbonation process¹⁹. Lastly, the pigment was also applied *a fresco*: the pigment is mixed with water, applied onto a freshly laid lime-based mortar and fixed to the surface by carbonation of the lime¹⁹.

A physical evaluation of the pigment-binder mixtures (petri dishes) and the paintings (on a lime-based mortar substrate) was conducted by digital photography, stereomicroscopy, and colour spectrophotometry, followed by detailed micro-morphological, mineralogical and chemical analyses using optical and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), X-ray diffraction (XRD) and Attenuated Total Reflectance Fourier-transform Infrared Spectroscopy (ATR-FTIR). By combining controlled pigment-binder experiments with systematically prepared wall painting samples, this study provides the first integrated evaluation of how neutral verdigris degrades across traditional wall painting techniques. The finding shed new light on the complex morphological, mineralogical and chemical transformations induced by alkaline environments—transformations that have remained largely uncharacterised until now and that have long hindered the accurate interpretation, conservation and attribution of wall paintings containing verdigris.

Methods

Materials

A calcitic lime paste, stored under water for more than 20 years, was used as a binder in the mortar manufacture. It was mainly composed of portlandite ($\text{Ca}(\text{OH})_2$) and small amounts of calcite (CaCO_3) due to partial carbonation. The lime paste was mixed with three aggregates:

coarse (1–2 mm) and fine silica (0.4–0.8 mm), and marble powder (<0.7 mm). The silica aggregates, composed of quartz (SiO_2), sodium/potassium feldspars and rutile (TiO_2), were supplied by a local hardware store (Granada, Spain). The marble powder, composed of calcite, quartz, and dolomite ($\text{CaMg}(\text{CO}_3)_2$), was supplied by CTS S.L. (Madrid, Spain). The pigment selected for this study was commercialised as a basic copper(II) acetate monohydrate (Ref. 44450), with formula $\text{C}_4\text{H}_6\text{CuO}_4 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot [\text{Cu}(\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$, supplied by Kremer Pigments GmbH & Co. KG (Aichstetten, Germany). The mineralogical characterisation of the raw materials (lime paste, aggregates and pigment) was obtained from ref. 42. As for the binders used for each painting technique, the eggs were purchased at a local supermarket (Pontevedra, Spain), and the rabbit glue (Ref. 63028) and the lime water (Ref. 31808) were supplied by Kremer.

Paint mock-up preparation

To isolate and evaluate the influence of pigment-binder interactions independently from the mortar substrate, an admixture of the pigment mixed in a 1:1 (pigment:binder) ratio in volume with egg yolk (VER-EY hereinafter), rabbit glue (VER-RG hereinafter), lime water (VER-MF hereinafter) and lime paste (VER-F hereinafter) were prepared in petri dishes.

The manufacture of the paint mock-ups, composed of two mortar layers (*arriccio* and *intonaco*), was carried out following the methodology described in ref. 41. The mock-ups took the form of thick, circular discs (≈ 8 cm diameter and ≈ 2.5 cm tall), in which the base structure of historical wall paintings was reproduced⁴³. Four sets of paint mock-ups were prepared (paint mock-ups were identified with a -P after the identifier of the painting technique: EY, RG, MF and F):

- *a secco* with egg-yolk (VER-EY-P hereinafter): the yolk was separated from the white by pouring it back and forth in the half shells. It was then rolled onto a paper towel to remove any remaining egg white. The skin of the yolk was then punctured with a needle, pouring the resulting liquid into a glass jar. The yolk was then mixed with verdigris in a 1:1 (pigment:binder) ratio in volume and applied onto a complete carbonated dry mortar (after 6 months).
- *a secco* with rabbit glue (VER-RG-P hereinafter): 8 g of rabbit glue were soaked in 100 mL of deionised water for 24 h, under periodic stirring. Afterwards, the mixture was heated below 50 °C in a water bath and stirred to obtain a homogeneous mixture. The liquid was then mixed with verdigris in a 1:1 (pigment:binder) ratio in volume and applied onto the lime substrate, as carried out with VER-EY-P.
- *a mezzo-fresco* (VER-MF-P hereinafter): the pigment was mixed with lime water and applied onto the semi-dry mortar (*intonaco*), after 3 days of applying the *intonaco*.
- *a fresco* (VER-F-P hereinafter): verdigris was mixed with water until the right consistency (it flows easily from the brush) was achieved and then applied onto a wet and freshly made lime-based mortar (*intonaco*).

For both *secco* techniques, painting was carried out after 6 months of mortar carbonation, ensuring minimal portlandite content—and therefore low alkalinity. XRD analysis indicated that the *intonaco* contained approximately 8% portlandite, a residual amount consistent with the slow carbonation process, which may remain incomplete even after two years under laboratory conditions⁴⁴. Thus, we can state with confidence that our *a secco* samples were applied to well-carbonated mortars. After paint application, all samples (both pigment-binder mixtures and painted mock-ups) were left to dry for one month under controlled laboratory conditions (22 ± 2 °C and $65 \pm 5\%$ relative humidity).

Analytical techniques

The following analytical protocol was followed:

- The pH of the binders (egg yolk, rabbit glue, lime paste and lime water) was measured using a Crison® PH-25 portable potentiometer (I.C.T., S.L., Madrid, Spain), with a precision of ± 1 mV (± 0.01 pH unit). An

- automatic calibration of the instrument was carried out with buffer solutions at 2.00, 4.01, 7.00, 9.21 and 10.90 pH.
- Digital photographs of the paint samples and the mixtures in the petri dishes were taken with a Nikon D3400 digital camera (Shinagawa, Tokyo, Japan) equipped with a Nikon Nikkor Zoom Lens, DX 18–105 mm.
 - A Nikon SMZ 1000 stereomicroscope (Melville, New York, United States) was used to examine the textural and chromatic features of the raw pigment, the surface of the paint mock-ups, the petri dish samples, and the alteration products.
 - The colour of the alteration products taken from the samples was characterised using CIELAB and CIELCH colour spaces^{45,46}, measuring L^* (lightness), a^* and b^* (colour coordinates) and C^*_{ab} (chroma) values using a Minolta CM-700d spectrophotometer (Tokyo, Japan). L^* represents lightness, varying from 0 (black) to 100 (white). The other two parameters are chromaticity coordinates: a^* goes from red to green (where $+a^*$ is red and $-a^*$ is green) and b^* from yellow to blue ($+b^*$ is yellow and $-b^*$ is blue). C^*_{ab} is calculated according to the following formula: $C^*_{ab} = (a^{*2} + b^{*2})^{1/2}$. The measurements were made in specular component excluded (SCE) mode, for a spot diameter of 8 mm, using illuminant D65 at observer angle 10°. A total of 15 measurements were made for each mock-up, and their average values and standard deviations (STD) were computed. Colour parameters were also measured for the pigment powder, after first flattening it against a glass support to obtain a smooth surface.
 - The paint thin cross sections were studied by polarised light microscopy (PLM) with reflected light (RL) in plane-polarised light (analyser removed) or crossed polarisers (analyser inserted) using a Carl Zeiss Jenapol U microscope (Oberkochen, Germany). For this, the specimens were embedded in epoxy resin (EpoThin 2 Epoxy Resin and EpoThin 2 Epoxy Hardener) and then cut and polished to a mirror shine.
 - The microtexture and elemental composition of the raw pigment, the pigment-binder admixtures, and the paint mock-ups (surface and cross-sections) were evaluated using a FEI Quanta 400 ESEM FEG (Hillsboro, Oregon, USA) with energy-dispersive X-ray spectroscopy (EDS) in both secondary (SE) and backscattered electron (BSE) detection modes. Observation conditions included a working distance of ~10 mm, accelerating potential of 20 kV and specimen current of ~60 mA.
 - The mineralogical composition of the raw pigment and the alteration products obtained from the paint mock-ups was determined using XRD with a XPert PRO (PANalytical B.V., Almelo, The Netherlands), according to the random-powder method. Analyses were performed using Cu-K α radiation, Ni filter, 45 kV voltage, and 40 mA intensity. The exploration range was 3° to 60° 2 θ , and the goniometer speed was 0.05° 2 θ s⁻¹. The mineral phases were identified using X'Pert HighScore software.
 - The molecular composition of the pigment and the alteration products was obtained by Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR), using a Thermo Nicolet 6700 (Thermo Fisher, Massachusetts, United States) at a 2 cm⁻¹ resolution over 100 scans in the mid (4000–400 cm⁻¹) and far (600–200 cm⁻¹) infrared spectral regions. Samples were individually analysed by placing them on a diamond crystal and pressing the plunger against them, exerting the maximum pressure permitted by this instrument so as to ensure the best possible contact with the diamond crystal.

Results

Characterisation of the verdigris pigment and the binders

The bluish-green acetate pigment (VER) corresponds chemically and structurally with the mineral phase hoganite, as confirmed by XRD (Supplementary Fig. 1). Its composition, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, identifies it as a neutral hydrous verdigris (the 1–0–1 phase), considered a pure phase^{5,9}. A small additional peak at $2\theta = 11.53^\circ$ (d

spacing = 7.68 Å) was also detected. Following Bette et al.⁹, this peak can be associated with the anhydrous 1–0–0 phase, $\text{Cu}(\text{CH}_3\text{COO})_2$ (marked with a red arrow in **SI.1**). Interestingly, although the supplier labels the pigment as a basic verdigris and reports a composition that includes both the neutral phase ($\text{C}_4\text{H}_6\text{CuO}_4 \cdot \text{H}_2\text{O}$) and a basic copper acetate hydroxide ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot [\text{Cu}(\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$), our analysis shows that the pigment consists predominantly of the neutral hydrous phase. SEM observations (Supplementary Fig. 2) reveal that the pigment particles are mainly euhedral crystals with prismatic habit, accompanied by a smaller proportion of subhedral crystals. The chemical characterisation by EDS analysis revealed that all particles were composed of variable amounts of carbon (C), oxygen (O) and copper (Cu). Regarding the pH measurements of the binders, egg yolk and rabbit glue were slightly acidic (6.54 and 5.82 pH units, respectively) compared to the high alkalinity detected in lime water (pH = 11.56) and lime paste (pH = 11.92).

Physical evaluation

Figure 1 shows digital photographs and stereomicrographs of the powder pigment, the pigment-binder admixtures (left column) and of the painting mock-ups (right column). It was observed that *a secco* samples, both pigment-binder admixtures (VER-EY and VER-RG) and paint mock-ups (VER-EY-P and VER-RG-P), were homogeneous in terms of colour, though different between them, as observed in Fig. 1b, c, respectively. Egg yolk samples manifested a greenish hue due to the colouration effect of the yolk (orange in colour), whilst rabbit glue ones retained a similar bluish hue to that of the raw pigment. As for mezzo-fresco (VER-MF and VER-MF-P) and fresco (VER-F and VER-F-P) samples, a highly heterogeneous surface was observed due to the presence of different compounds exhibiting various colourations, as shown in Fig. 1d, e, respectively. As opposed to EY and RG samples, MF and F ones showed evident differences between the pigment-binder admixtures and the paint mock-ups. Different coloured compounds were depicted on the surface, ranging from light to dark blues. Greyish-black compounds were also observed, especially in the fresco paint (VER-F-P).

The colour parameters for the pigment-binder admixtures and for the paint mock-ups were obtained (included as Supplementary Table 1). By comparing L^* and C^*_{ab} parameters (Fig. 2a), it was observed that mezzo-fresco (VER-MF and VER-MF-P) and fresco (VER-F and VER-F-P) samples showed higher L^* compared to the *a secco* ones. This was related to the whitening effect of the carbonation process of lime water and lime paste. Moreover, the high STDs observed in MF and F, as opposed to EY and RG, were due to the wide range of different-coloured forms observed (Fig. 1d, e). Figure 2b represents a^* (red-green) and b^* (yellow-blue) coordinates. It was observed that EY-based samples showed higher b^* (yellow) and a^* (red) components, thus orange in appearance, as mentioned before, due to the influence of the binder. The bluest samples were RG-based ones (lower b^*), resembling a similar bluish hue to that of the raw pigment (represented with a black star in Fig. 2b). As for MF and F samples, they generally showed a greenish-blue hue. However, we must consider the heterogeneity in colour observed by stereomicroscopy in MF and F samples; thus, while in *a secco* paint, a^* and b^* parameters showed STDs of c.a. 1 unit, in the case of mezzo-fresco and fresco samples, it was generally c.a. 5 units. Therefore, the latter showed higher colour variations (especially in VER-F-P).

A total of 13 different patterns were collected from the pigment-lime water (VER-MF) and pigment-lime paste (VER-F) admixtures, and from the mezzo-fresco (VER-MF-P) and fresco (VER-F-P) paint mock-ups. The selection criteria was based on colour—bluish-green (VER-MF_1), light blue (VER-MF_2, VER-MF-P_5, VER-MF-P_6, VER-F_9, VER-F_10, VER-F-P_11 and VER-F-P_12), dark blue (VER-MF_3, VER-F-P_4, VER-F_7 and VER-F_8) and greyish-black (VER-F-P_13)—and morphology—globular (VER-MF_1, VER-MF-P_4-6, VER-F_7-8, VER-F_10 and VER-F-P_11), acicular (VER-MF_2-3 and VER-F-P_12) and laminar (VER-F_9). In short, these 13 samples were selected as potential alteration forms to be further characterised. Their appearance under stereomicroscopy is included in Fig. 3.

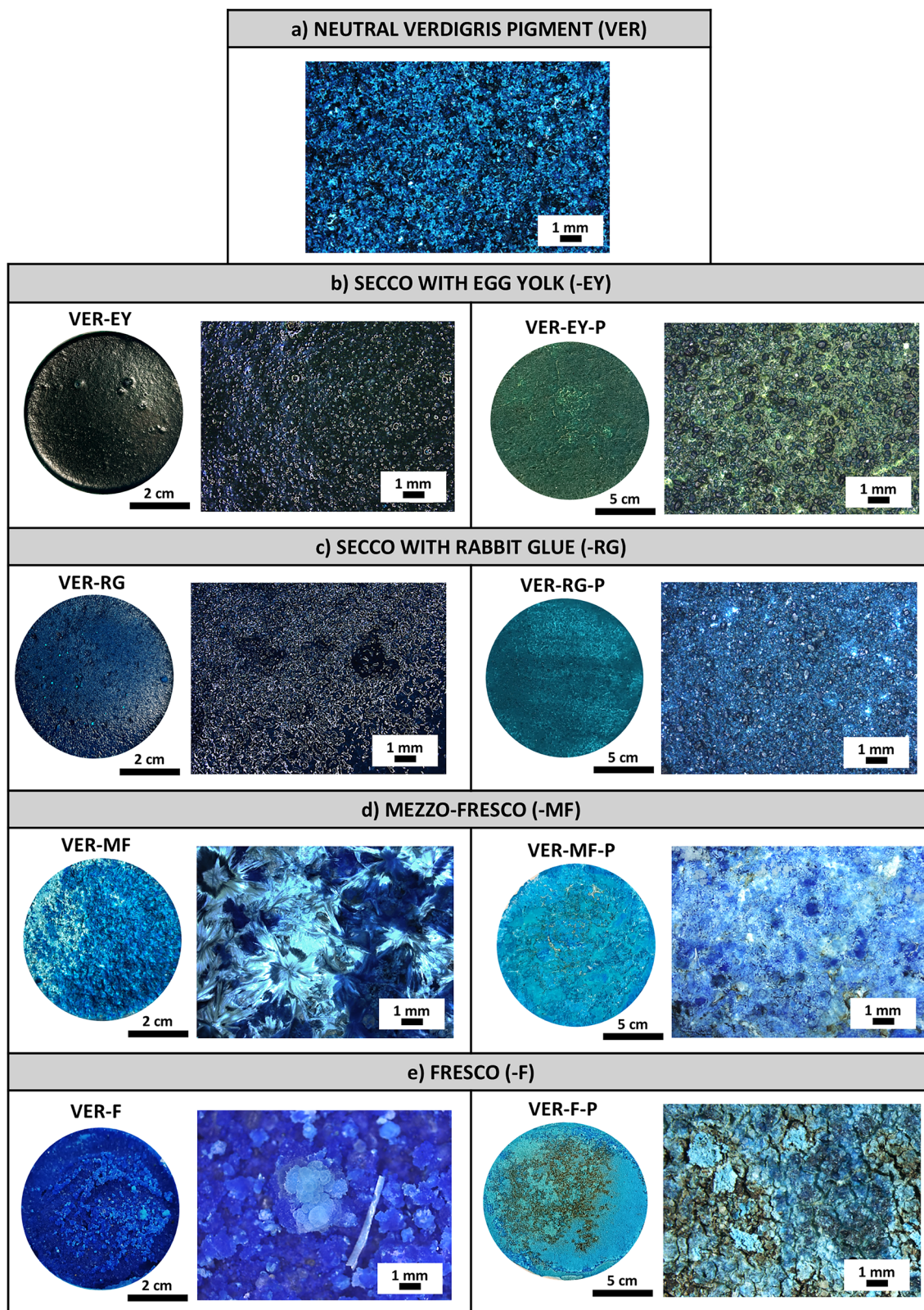


Fig. 1 | Preliminary assesment by stereomicroscopy. a Stereomicrographs of neutral verdigris raw pigment (VER). **b–e** Digital photographs (in the circle) and stereomicrographs (in the rectangle) of the pigment-binder admixtures prepared in

petri dishes (left column) and the paint mock-ups (right column) of **(b)** *a secco* with egg yolk (-EY), **c** *a secco* with rabbit glue (-RG), **d** *a mezzo-fresco* (-MF) and **e** *a fresco* (-F).

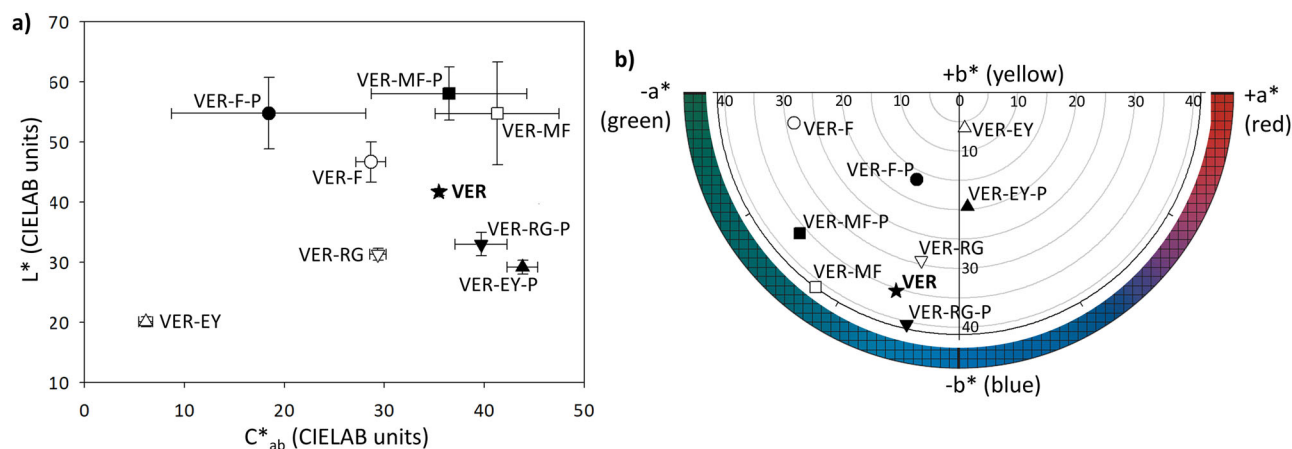


Fig. 2 | Chromatic parameters by spectrophotometry. **a** Scatter plot representing L* (lightness) and C*_ab (chroma) parameters and **b** polar plot representing a* (green to red) and b* (blue to yellow) parameters of neutral verdigris powder pigment

(VER), the pigment-binder admixtures prepared in petri dishes and the paint mock-ups (-P) of a *secco* with egg yolk (-EY), a *secco* with rabbit glue (-RG), a *mezzo-fresco* (-MF) and a *fresco* (-F) samples.

Micro-morphological characterization

SEM-EDS observations enabled the identification of different morphologies and significant micro-textural and micro-morphological changes in *mezzo-fresco* and *fresco* samples as opposed to *secco*. The study of the cross-sections by PLM showed a homogeneous paint layer in both *secco* paints, greener in VER-EY-P and bluer in VER-RG-P (Fig. 4a, c, respectively), as opposed to the heterogeneous paint layer observed in *mezzo-fresco* and *fresco* paints (Fig. 4e g, respectively). Besides different bluish shades, brownish-black areas were observed on both MF and F paints. The evaluation by SEM of the surface of a *secco* paint allowed to identification of the characteristic euhedral prismatic habit of hoganite crystals in both egg yolk (VER-EY-P, Fig. 4b) and rabbit-glue (VER-RG-P, Fig. 4d). No micro-textural nor morphological changes related to a possible degradation of the pigment were observed. By SEM, both the paint cross-section and paint surface in *mezzo-fresco* (VER-MF-P, Fig. 4e, f) and *fresco* paints (VER-MF-P, Fig. 4g, h) were highly irregular and heterogeneous. Both paint layers were composed of varying amounts of C, O, Ca and Cu, as observed by EDS mapping analysis.

The microscopic study of the surface of the pigment-binder admixtures and of the paint mock-ups by SEM-EDS allowed the identification of a great number of neoformed particles with different habits. Figure 5 includes the different micro-morphologies identified in the pigment-binder admixtures (VER-MF and VER-F), and Fig. 6 includes those identified in the paint mock-ups (VER-MF-P and VER-F-P). The micrographs obtained from the samples where the pigment was mixed with lime water (VER-MF) suggested the beginning of an alteration process since the morphology of hoganite was visible albeit with noticeable micro-textural changes in the form of micro-pitting patterns (marked with a white arrow in Fig. 5a). Many subhedral crystals with prismatic habit, not identified previously in the raw pigment characterization, were identified grouped together, as observed in Fig. 5b. EDS analysis showed they were composed of varying amounts of C, O and Cu suggesting they could be related to neoformed hoganite or to other acetates. Bigger agglomerates of particles with similar prismatic habit merged together were also observed (marked with white arrows in Fig. 5c). Other euhedral crystals with similar chemical composition were depicted, some of them with a hexagonal habit (marked with a white arrow in Fig. 5d). Fibrous morphologies could be observed ranging from the surface of some of the particles in VER-MF (marked with red arrows in Fig. 5c–e) suggesting an ongoing transformation. Finally, other ribbon-shaped morphologies conformed by Cu-rich needle-like morphologies were identified (Fig. 5f). The samples where the pigment was mixed with lime paste (VER-F) were predominantly different to those observed in VER-MF. In VER-F, none of the crystals showed the prismatic habits observed in VER-MF (Fig. 5a–e). In turn, the formation of crystals with tabular habit, composed of varying

amounts of C, O, Cu and Ca, and grouped forming rosettes was widespread (Fig. 5g). A laminar corrosion process was clearly visible at higher magnifications in similar particles (Fig. 5h). Lastly, Cu-rich needle-like morphologies, similar to those observed in VER-MF_3 (Fig. 5f) were sporadically seen (Fig. 5i), together with other acicular (Fig. 5j) and laminar morphologies (Fig. 5k).

The study of the surface of *mezzo-fresco* (VER-MF-P) and *fresco* (VER-F-P) paint mock-ups showed completely irregular surfaces, with the presence of numerous neoformed micro-morphologies with heterogeneous micro-texture. The ones presented in Fig. 6 were those more widespread. In the case of MF paint, different Cu-rich acicular morphologies were identified with clear differences in length and thickness (Fig. 6a, c). All micro-morphologies showed varying amounts of C, O, Cu and Ca. Although these acicular shapes were the most widespread, other flower-like morphologies were depicted (Fig. 6d), composed of higher amounts of Ca than the previous particles. Lastly, large areas of the *mezzo-fresco* paint showed fibrous morphologies with a “spider web” appearance (Fig. 6e). As for the *fresco* paint, the morphologies were more different, generally composed of higher contents of Ca than the morphologies identified in the *mezzo-fresco* paint. Still, similar Cu-rich needle-like morphologies were sporadically identified (Fig. 6f). Other acicular (Fig. 6g–i) and spherical (Fig. 6j) morphologies and flake-like agglomerations (Fig. 6k) were also present. Other areas of the *fresco* paint surface were highly cracked and fissured (Fig. 6k, l); no particles with specific morphology were identified.

Mineralogical characterization

The mineralogical characterisation by XRD of the *secco* paintings (VER-EY-P and VER-RG-P), and of the 13 alteration products selected from *mezzo-fresco* (MF) and *fresco* (F) samples, are presented in Table 1. Overall, hoganite ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$)—the main mineral phase of the raw pigment—remains the dominant phase in the *secco* samples (VER-EY-P and VER-RG-P), where no alteration products were detected. Hoganite was also present in all MF-based samples (VER-MF_1, VER-MF_2, VER-MF_3, VER-MF-P_4, VER-MF-P_5 and VER-MF-P_6), accompanied by additional acetate phases associated with the alteration process. The XRD patterns of the verdigris–lime water mixtures (VER-MF_1, VER-MF_2, VER-MF_3, see Supplementary Figs. 3–5) display an additional peak at approximately $2\theta = 9.29^\circ$ (marked with red arrows). Previous studies^{6,10} have attributed this peak to basic verdigris phases 1–3–2 ($\text{Cu}_2(\text{CH}_3\text{COO})(\text{OH})_3 \cdot \text{H}_2\text{O}$) and 2–1–5 ($\text{Cu}_3(\text{CH}_3\text{COO})_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$). Notably, the intensity ratio between the hoganite phase and the $2\theta = 9.29^\circ$ peak varies among the three samples, with the basic phases appearing more prominent in VER-MF_2 and especially in VER-MF_3. Pateite ($\text{CaCu}(\text{CH}_3\text{COO})_4 \cdot 6(\text{H}_2\text{O})$), as well as calcium acetate in its either

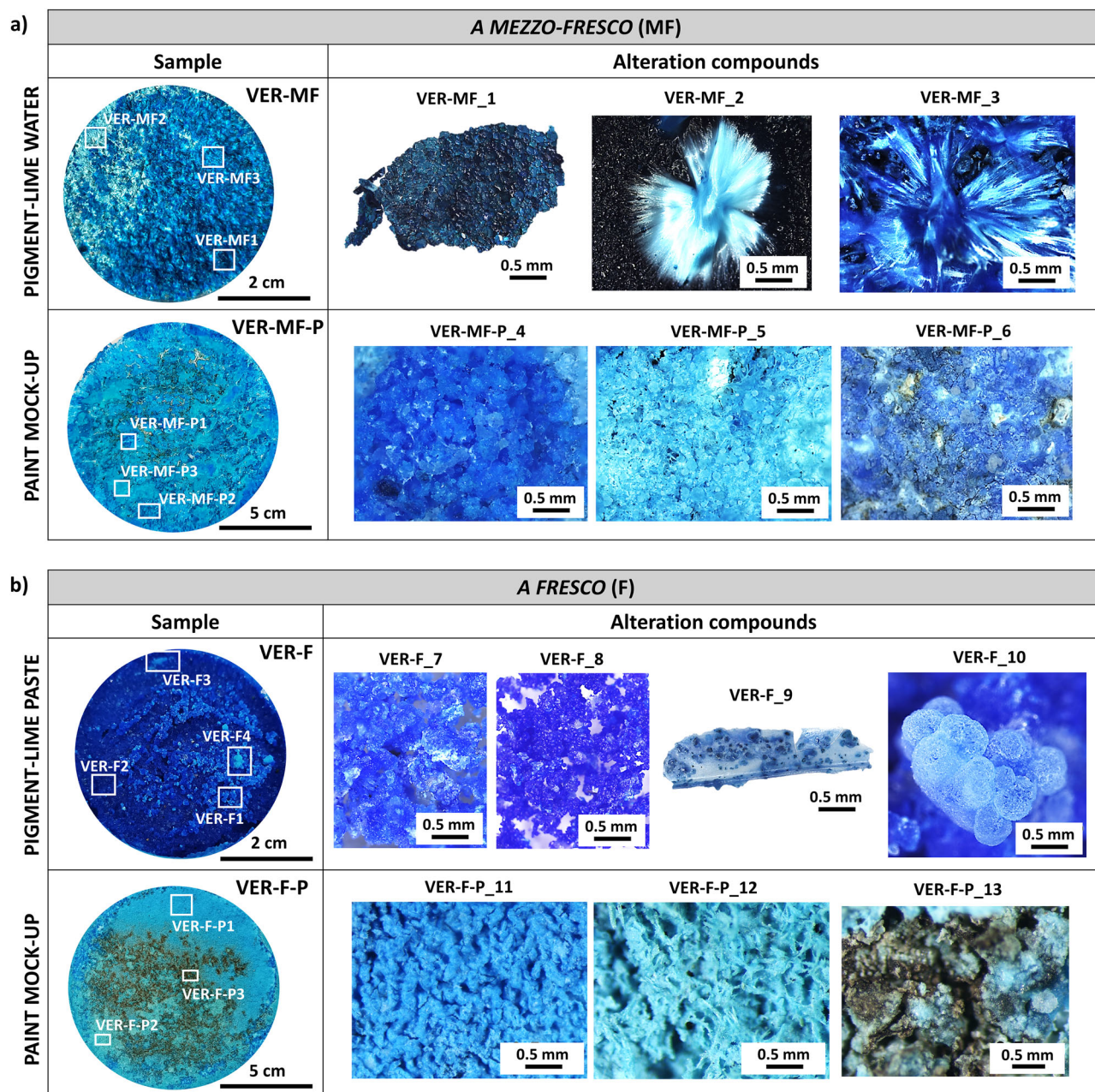


Fig. 3 | Identification of the alteration forms by stereomicroscopy. Identification of the alteration forms by stereomicroscopy. Micrographs of the 13 alteration forms obtained from the pigment-binder admixtures with lime water (VER-MF) and with

lime paste (VER-F), and from the paint mock-ups, **a** mezzo-fresco (VER-MF-P) and **b** fresco (VER-F-P).

monohydrate ($\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$) or hemihydrate ($\text{Ca}(\text{CH}_3\text{COO})_2 \cdot (\text{H}_2\text{O})_{0.5}$) form, was also frequently identified in both MF and F samples. In addition, anhydrous copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$) was detected in several fresco samples. Since this phase was already present in small amounts in the raw pigment, it cannot be considered an alteration product. Copper oxide (tenorite, CuO) was also identified in sample VER-F-P₁₃, which was also the only sample showing distinctly black alteration. Some XRD patterns also revealed a sharp, well-defined unassigned peak that did not correspond to any phase in our database. This peak—listed in Table 1—appeared exclusively in the verdigris–lime paste admixtures (VER-F). Samples VER-F₇, VER-F₈ and VER-F₉ (see red arrows in Supplementary Fig. 9–11) displayed a strong peak at approximately $2\theta = 10.30^\circ$. Finally, calcite (CaCO_3) was present in most samples, occasionally together with portlandite ($\text{Ca}(\text{OH})_2$). Portlandite was exclusively present in verdigris–lime paste samples, consistent with the slow nature of the

carbonation process. Sporadic detection of quartz (SiO_2), illite ($\text{KAl}_4(\text{Si}, \text{Al})_8\text{O}_{10} \cdot 4\text{H}_2\text{O}$) or anorthoclase ($(\text{Na}, \text{K})\text{AlSi}_3\text{O}_8$) is attributed to the siliceous sand used for the mortar preparation.

Chemical characterization

For comparative purposes, the FTIR spectrum of neutral verdigris pigment (sample VER) is shown in Figs. 7 and 8 alongside those of the paints and alteration products. The characteristic IR features of the pigment are highlighted with blue rectangles. The spectrum of the raw pigment—composed mainly of the hydrous 1–0–1 phase ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$), with a minor contribution from the anhydrous 1–0–0 phase ($\text{Cu}(\text{CH}_3\text{COO})_2$)—does not perfectly match either of the spectra reported by Bette et al.⁹. Three large bands at 3450, 3365 and 3270 cm^{-1} , assigned to $-\text{OH}$ stretching vibrations related to the water molecules associated to the acetate ion, confirm the presence of the hydrous phase⁹. Additional bands

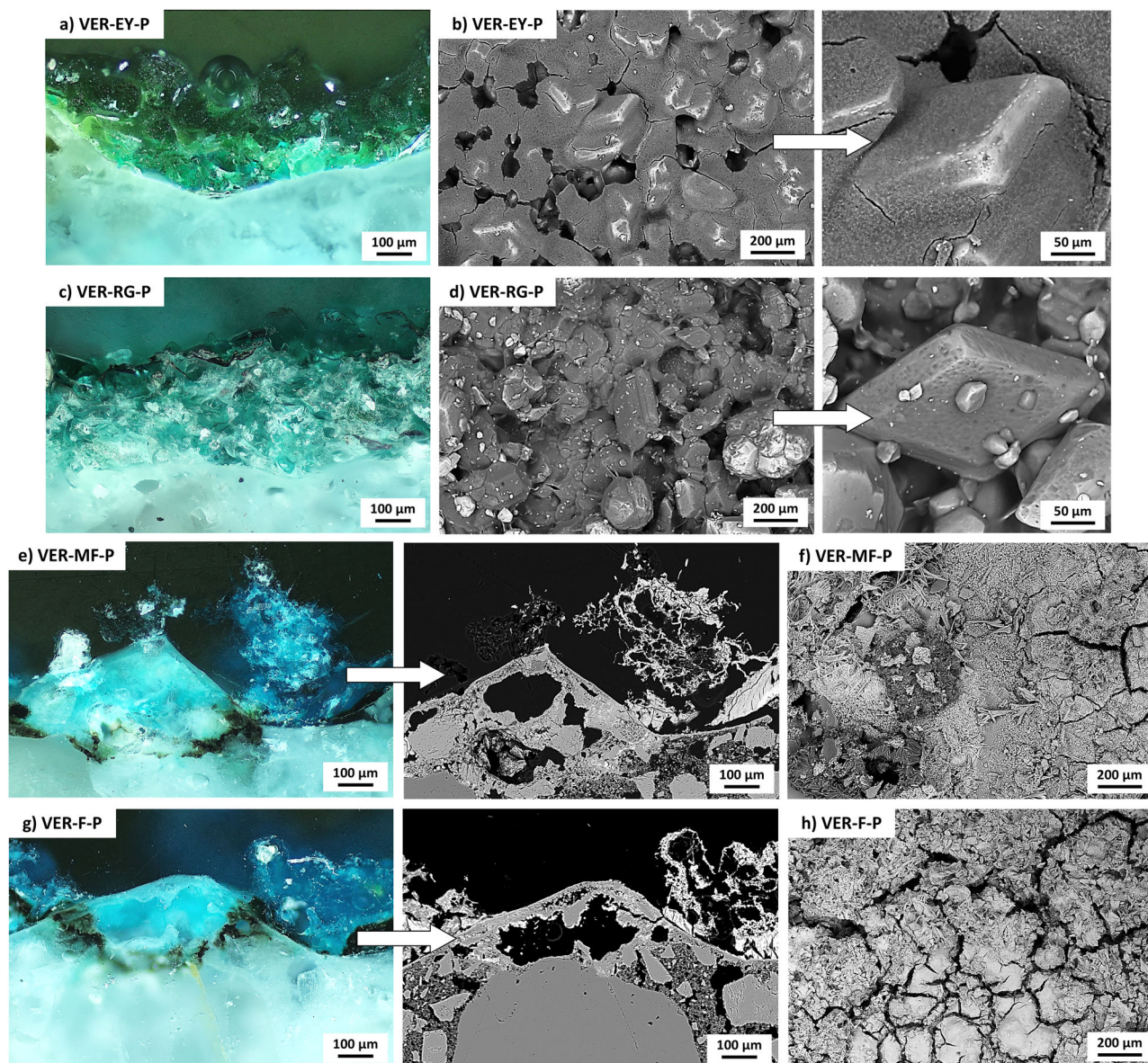


Fig. 4 | Cross-section and surface evaluation of the paint mock-ups by optical and electron microscopies. PLM micrographs of the paint mock-ups: **a** a secco with egg yolk (VER-EY-P), **c** a secco with rabbit glue (VER-RG-P), **e** a mezzo-fresco (VER-

MF-P), and **g** a fresco (VER-F-P). SEM micrographs of the surface of **b** VER-EY-P, **d** VER-RG-P, **e**, **f** VER-MF-P, and **g**, **h** VER-F-P.

characteristic of this phase include a signal at 1355 cm^{-1} (CH_3 rocking vibration) and bands at 1050 and 1035 cm^{-1} (C-H tensions)^{7,9,22,47}. The copper carboxylate (COO^-) functional groups are represented by bands at 1600 and 1420 cm^{-1} (asymmetric and symmetric stretching, respectively), as well as a rocking vibration around 630 cm^{-1} ^{17,9,22,47,48}. The carbonyl group (C=O) was present as a low intensity band at 1260 cm^{-1} (symmetric stretching)^{7,22,47,48}. O-C-O deformation (690 cm^{-1}) and in-plane O-C-O rocking vibrations ($590\text{--}420\text{ cm}^{-1}$) were also present^{7,22,47,48}. However, the raw pigment spectrum also displayed additional low-intensity methyl group (CH_3) bands at 2990 and 2945 cm^{-1} , typical of acetate groups^{7,22,47,48} but not characteristic of either the hydrous or anhydrous phases described in ref. 9. Their presence suggests that minor amounts of other acetate compounds may also be present. Finally, the spectra obtained in the far-IR region ($600\text{--}200\text{ cm}^{-1}$, right spectrum) showed a broad band assigned to O-C-O rocking vibrations around $590\text{--}420\text{ cm}^{-1}$ ^{17,22,47,48}. In addition, high intensity bands at 370 cm^{-1} ($\nu(\text{Cu-C})$), 330 cm^{-1} ($\nu(\text{Cu-OH})$), 270 cm^{-1} ($\delta(\text{Cu-CO})$), 250 and 230 cm^{-1} ($\delta(\text{O-Cu-OH})$) were identified^{7,49}.

On the one hand, in secco paint samples, no significant changes were observed (see Supplementary Figs. 16 and 17). The previously mentioned characteristic bands of verdigris were observed on both egg yolk (VER-EY-P) and rabbit glue (VER-RG-P) paint samples. Slight changes were detected due to the overlap between the CH_3 of verdigris (2990 and 2945 cm^{-1}) and the CH_2 stretching from long-chain fatty acids in egg yolk (at 2920 and 2850 cm^{-1}) and rabbit glue (at 2918 cm^{-1}) paint samples^{50–53}. A shift to lower wavenumbers was observed in the carboxylate group of verdigris (COO^- stretching at 1600 cm^{-1} and 1420 cm^{-1}) due to the overlap with bands assigned to egg yolk—at 1625 cm^{-1} (C=O stretching from amide I) and at 1520 cm^{-1} (C=O bending from amide II)^{50,51}—and to rabbit glue—at 1635 cm^{-1} (C=O stretching from amide I) and around 1533 cm^{-1} (C-N stretching and N-H bending from amide II)^{52,53}. As for the spectra in the far-IR region, VER-EY-P and VER-RG-P showed practically the same shape as that observed in the pigment spectrum (VER). Therefore, no chemical changes were observed.

On the other hand, major differences were observed when comparing the pigment spectrum with that of the 13 samples collected from mezzo-fresco (MF) and fresco (F) samples (Figs. 7 and 8, respectively). VER-MF_1

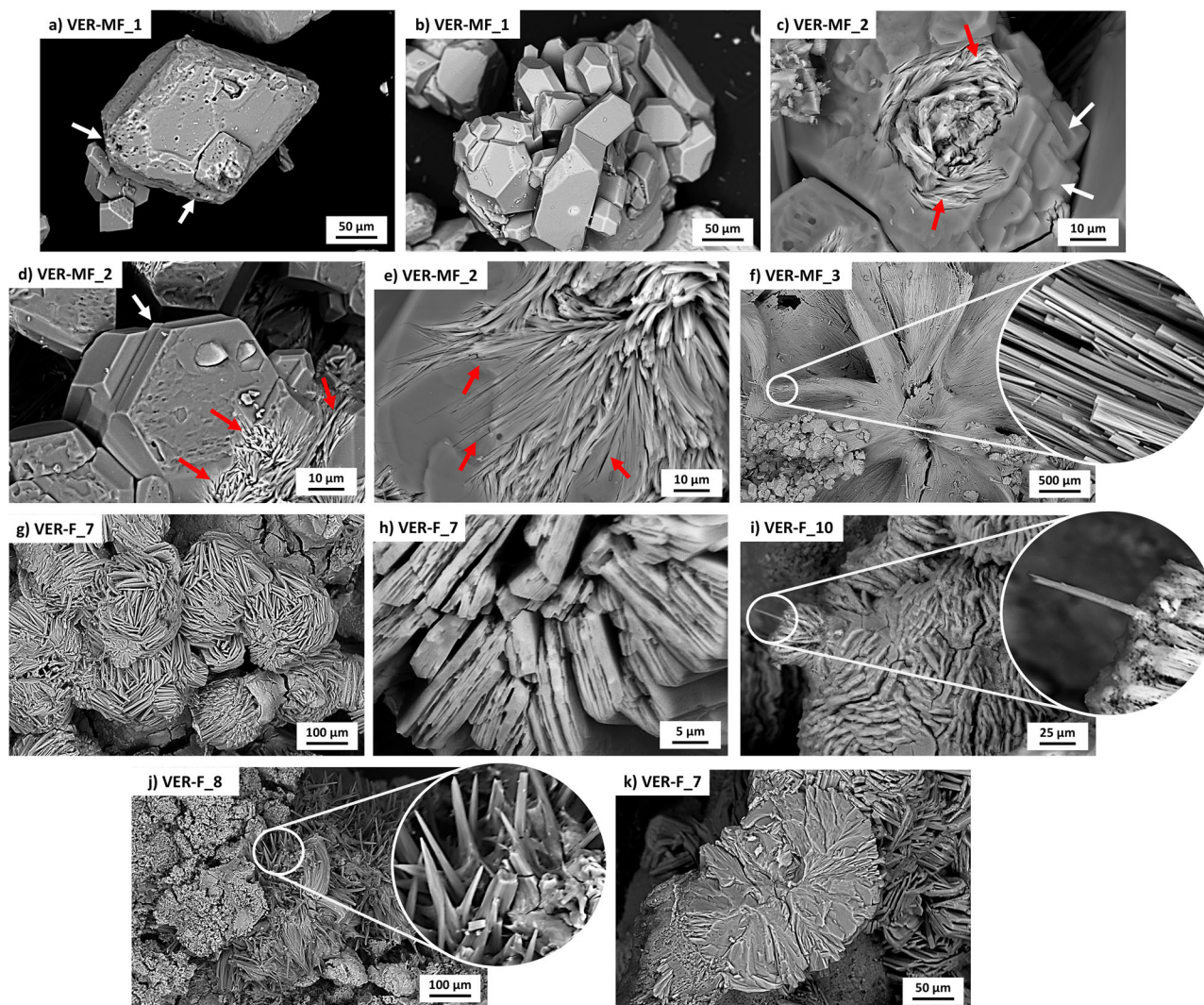


Fig. 5 | SEM micrographs of alteration forms observed in the pigment and binder admixtures with lime water (VER-MF) and lime paste (VER-F). The samples selected are shown in Fig. 3 from the samples in Fig. 2d, e.

and VER-MF_2 showed a similar spectra to that of the pigment—suggesting that hoganite was still present—(highlighted with blue rectangles in Fig. 7). In turn, the acetate characteristic bands assigned to carboxyl (COO^-), methyl (CH_3) and carbonyl (C=O) groups shifted to higher or lower wavenumbers and/or changed their intensity ratios to a greater or lesser extent in the other 11 samples (marked in red in Figs. 7a and 8a, respectively). In fact, Supplementary Table 2 displays the IR vibrational position of each of the characteristic acetate bands present in the 13 samples. It is clear that the results indicate that $-\text{OH}$ and COO^- underwent considerable shifts when compared to those of the raw pigment (sample VER). Also, the characteristic bands assigned to $\nu(\text{Cu}-\text{C})$, $\nu(\text{Cu}-\text{OH})$, $\delta(\text{Cu}-\text{CO})$ and $\delta(\text{O}-\text{Cu}-\text{OH})$ either disappeared—appearing other bands assigned to $\text{Cu}-\text{O}$ and $\text{Cu}-\text{OH}$ bonding (highlighted with pink rectangles in Figs. 7b and 8b)—or changed in shape. All these changes were more prominent in F samples (Fig. 8). Moreover, all samples (except VER-MF_1 and VER-MF_2) presented broad bands assigned to hydroxyl groups ($-\text{OH}$) in the region $3600\text{--}2800\text{ cm}^{-1}$ (Figs. 7a and 8a). A low intensity band at 3740 cm^{-1} was exclusively present in the spectra of fresco-based samples (marked with a black arrow in Fig. 8a). This band is related to $-\text{OH}$ groups associated with metals ($\nu(\text{M}-\text{OH})$)⁵⁴. For that band to be assigned to $\text{M}-\text{OH}$, a band around 1500 cm^{-1} ($\text{H}-\text{O}-\text{H}$ scissoring mode of H_2O molecules) should also be present⁵⁵. However, this band was not visible since it was probably hidden by the bands assigned to $\nu(\text{COO}^-)$. Calcium carbonate (CaCO_3) characteristic bands were occasionally present,

especially in F samples. A black dotted rectangle in Fig. 7 and Fig. 8 highlights the vibrational modes of CaCO_3 : at 1795 cm^{-1} (C=O), 1390 cm^{-1} $\nu(\text{CO}_3^{2-})$, 875 cm^{-1} $\delta_{\text{asym}}(\text{CO}_3^{2-})$, 710 cm^{-1} $\delta_{\text{sym}}(\text{CO}_3^{2-})$ and at $330\text{--}250$, 216 and 215 cm^{-1} (lattice modes of Ca^{2+} and/or CO_3^{2-})^{51,56–58}.

Discussion

Results demonstrate that wall painting techniques, through the properties of their binders and associated pH conditions, strongly influenced the micro-morphological and chemical features of the pigment. A neutral verdigris pigment was employed, primarily composed of the hydrous 1–0–1 phase ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$), with minor presence of the anhydrous phase 1–0–0 ($\text{Cu}(\text{CH}_3\text{COO})_2$). Our results did not align with the supplier's reported composition, which stated that the pigment was composed of both neutral ($\text{C}_4\text{H}_6\text{CuO}_4 \cdot \text{H}_2\text{O}$) and basic phases ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot [\text{Cu}(\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$). Graženaite⁸ likewise identified the hydrous neutral phase—contradictory to the manufacturer's claim—together with other additional unassigned peaks ($2\theta = 19.76^\circ$ and $2\theta = 43.12^\circ$), suggesting the pigment was not entirely pure. Still, the phases reported by the manufacturer may be present in low proportion and therefore below the detection limit of the XRD technique (3 wt %). In fact, the ATR-FTIR spectrum of the powder pigment showed bands (2990 and 2945 cm^{-1}) which are ascribable to the presence of other acetate compounds^{7,22,47,48}; thus, the presence of other phases in minor amounts cannot be excluded.

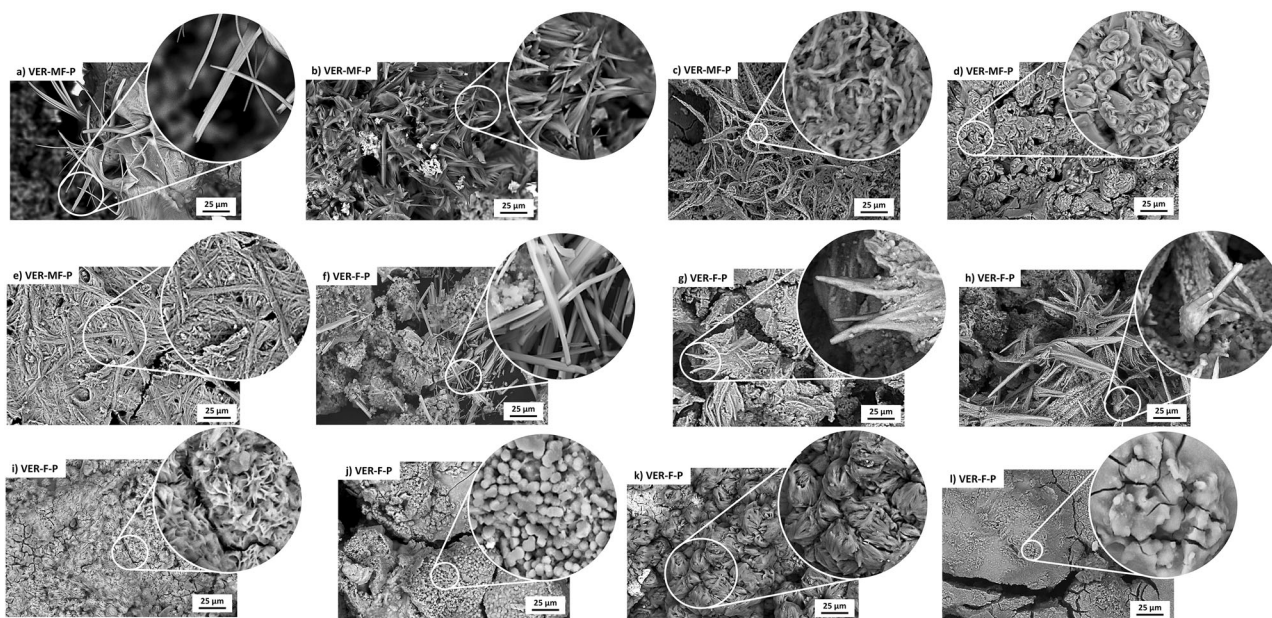


Fig. 6 | SEM micrographs of the alteration forms observed on the surface of the paint mock-ups when applying a *mezzo-fresco* (VER-MF-P) and a *fresco* (VER-F-P). The paint mock-ups are shown in Fig. 2d, e.

Table 1 | XRD mineralogical characterisation of a *secco* with egg yolk (VER-EY-P) and a *secco* with rabbit glue (VER-RG-P) paint mock-ups, and of the 13 alteration forms obtained from the pigment-binder admixtures with lime water (VER-MF) and with lime paste (VER-F), and from the *mezzo-fresco* (VER-MF-P) and *fresco* (VER-F-P) paint mock-ups

Samples	Mineralogical characterisation by XRD			
	Assigned to the raw pigment	Assigned to the mortar	Assigned to alteration products	Unassigned phases ^a
VER-EY-P	Hoganite, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	Calcite, CaCO_3 Quartz, SiO_2	-	-
VER-RG-P	Hoganite, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	Calcite, CaCO_3 Quartz, SiO_2	-	-
VER-MF_1	Hoganite, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	Calcite, CaCO_3 Quartz, SiO_2	$\text{Cu}_2(\text{CH}_3\text{COO})(\text{OH})_3 \cdot \text{H}_2\text{O} / \text{Cu}_3(\text{CH}_3\text{COO})_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$	-
VER-MF_2	Hoganite, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	Quartz, SiO_2	$\text{Cu}_2(\text{CH}_3\text{COO})(\text{OH})_3 \cdot \text{H}_2\text{O} / \text{Cu}_3(\text{CH}_3\text{COO})_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$	-
VER-MF_3	Hoganite, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	Calcite, CaCO_3 Quartz, SiO_2	$\text{Cu}_2(\text{CH}_3\text{COO})(\text{OH})_3 \cdot \text{H}_2\text{O} / \text{Cu}_3(\text{CH}_3\text{COO})_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ Pacheite, $\text{CaCu}(\text{CH}_3\text{COO})_4 \cdot 6(\text{H}_2\text{O})$	-
VER-MF-P_4	Hoganite, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	-	Pacheite, $\text{CaCu}(\text{CH}_3\text{COO})_4 \cdot 6(\text{H}_2\text{O})$ $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot (\text{H}_2\text{O})_{0.5} / \text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	-
VER-MF-P_5	Hoganite, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	Calcite, CaCO_3 Quartz, SiO_2	-	-
VER-MF-P_6	Hoganite, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	Calcite, CaCO_3 Quartz, SiO_2 Illite, $\text{KAl}_2(\text{Si,Al})_4\text{O}_{10} \cdot 4\text{H}_2\text{O}$	$\text{Ca}(\text{CH}_3\text{COO})_2 \cdot (\text{H}_2\text{O})_{0.5} / \text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	-
VER-F_7	$\text{Cu}(\text{CH}_3\text{COO})_2$	Portlandite, $\text{Ca}(\text{OH})_2$ Quartz, SiO_2	$\text{Ca}(\text{CH}_3\text{COO})_2 \cdot (\text{H}_2\text{O})_{0.5} / \text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	$2\theta = 10.30^\circ$
VER-F_8	$\text{Cu}(\text{CH}_3\text{COO})_2$	Portlandite, $\text{Ca}(\text{OH})_2$ Quartz, SiO_2 Anorthoclase, $(\text{Na,K})\text{AlSi}_3\text{O}_8$	Pacheite, $\text{CaCu}(\text{CH}_3\text{COO})_4 \cdot 6(\text{H}_2\text{O})$ $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot (\text{H}_2\text{O})_{0.5} /$ $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	$2\theta = 10.30^\circ$
VER-F_9	$\text{Cu}(\text{CH}_3\text{COO})_2$	Portlandite, $\text{Ca}(\text{OH})_2$ Quartz, SiO_2	$\text{Ca}(\text{CH}_3\text{COO})_2 \cdot (\text{H}_2\text{O})_{0.5} / \text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	$2\theta = 10.30^\circ$
VER-F_10	$\text{Cu}(\text{CH}_3\text{COO})_2$	-	$\text{Ca}(\text{CH}_3\text{COO})_2 \cdot (\text{H}_2\text{O})_{0.5} / \text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	-
VER-F-P_11	$\text{Cu}(\text{CH}_3\text{COO})_2$	Calcite, CaCO_3	-	-
VER-F-P_12	-	Calcite, CaCO_3 Quartz, SiO_2	Pacheite, $\text{CaCu}(\text{CH}_3\text{COO})_4 \cdot 6(\text{H}_2\text{O})$ $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot (\text{H}_2\text{O})_{0.5} /$ $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	-
VER-F-P_13	-	Calcite, CaCO_3 Quartz, SiO_2	Tenorite, CuO	-

The alteration forms selected are shown in Fig. 3.

^aThe XRD patterns (included in Supplementary Figs. 3–15) showed additional unassigned mineral phases. The 2-theta (2θ) position for the main intensity peaks unassigned are included.

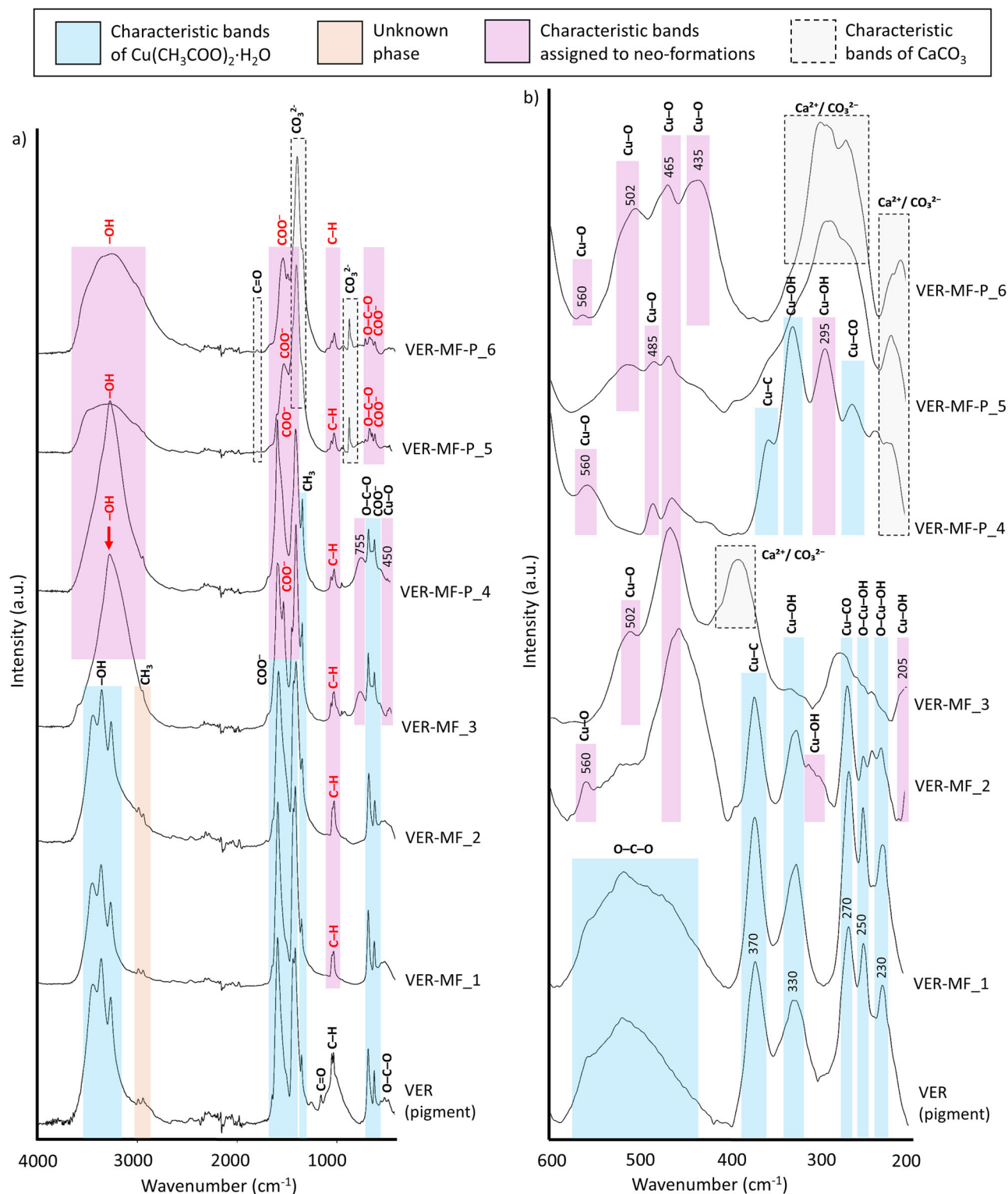


Fig. 7 | FTIR spectra of neutral verdigris raw pigment (VER) and the alteration products identified in the pigment-binder admixtures with lime water (VER-MF) and from the a mezzo-fresco (VER-MF-P) paint mock-ups. Spectra obtained in

the (a) mid-IR (4000–400 cm^{-1}) and (b) far-IR (600–200 cm^{-1}) regions. The samples selected are shown in Fig. 3. Marked in red are the characteristic bands assigned to acetate, which underwent great changes compared to the ones in sample VER.

In a *secco* painting, where egg yolk and rabbit glue were used as binders (6.54 and 5.82 pH units, respectively), the pigment remained physically, mineralogically and chemically stable. However, it is well established that verdigris can react with the fatty acids present in the binder—such as stearic, palmitic, oleic or linoleic acids—to form carboxylates (metal soaps) through a saponification process⁵⁹. In fact, soap formation is part of the natural

drying process of this type of paint and is therefore always expected to form⁶⁰. They play a significant role in degradation processes with an undesirable impact on appearance (darkening) and stability (cracking)^{25,59,61}. Still, our analysis found no evidence of such compounds. The characteristic FTIR band around 1600–1500 cm^{-1} , associated with asymmetric COO^- stretching in free fatty acids, which would suggest soap formation^{60–63}, was

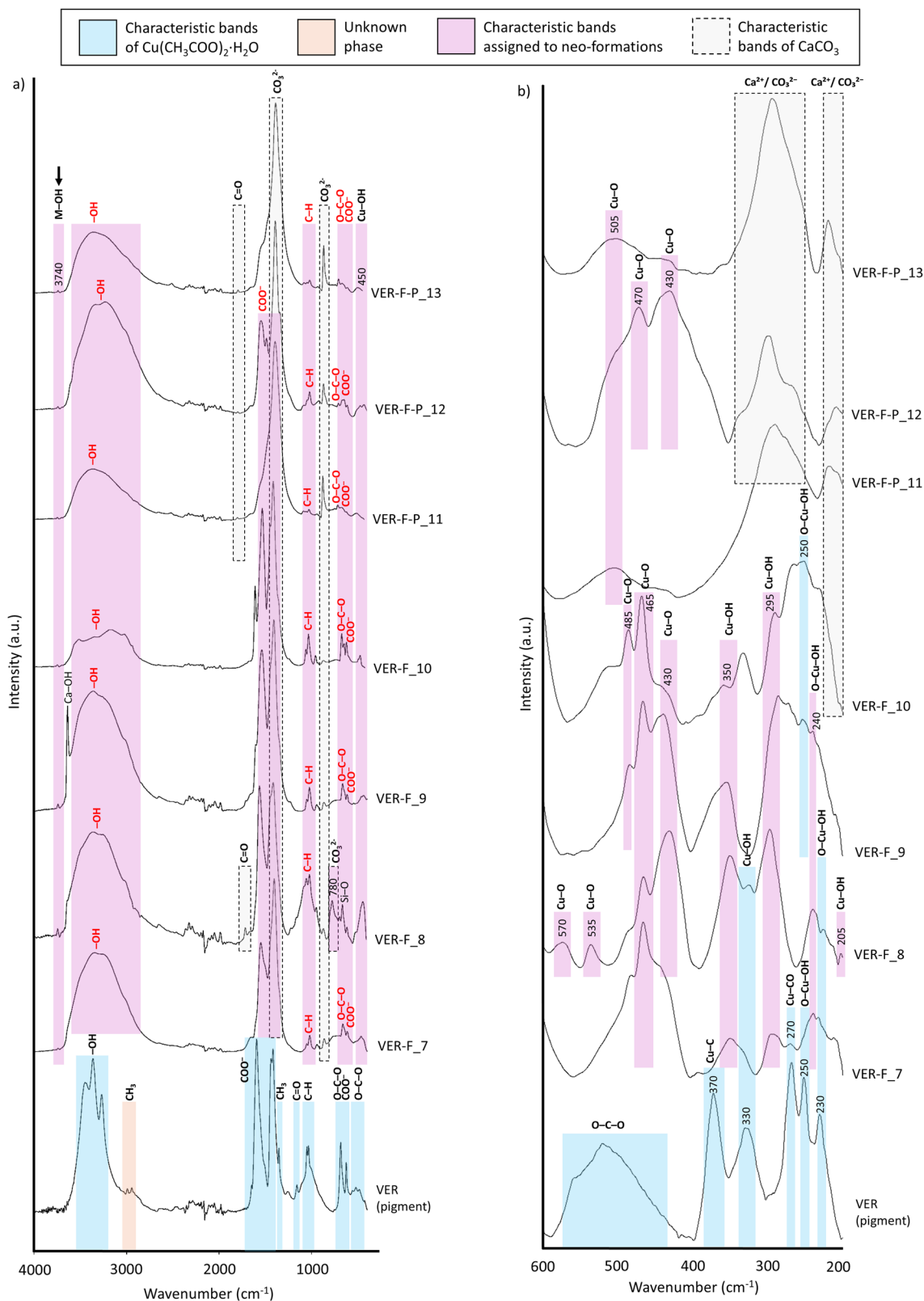


Fig. 8 | FTIR spectra of neutral verdigris raw pigment (VER) and the alteration products identified in the pigment-binder admixtures with lime paste (VER-F) and from the fresco (VER-F-P) paint mock-ups. Spectra obtained in the (a) mid-IR

(4000–400 cm⁻¹) and (b) far-IR (600–200 cm⁻¹) regions. The samples selected are shown in Fig. 3. Marked in red are the characteristic bands assigned to acetate, which underwent great changes compared to the ones in sample VER.

absent from the spectrum. Nonetheless, the absence of soaps in our secco paints may indicate that saponification has not yet occurred—given that it is a long-term process in paintings⁶¹—or that the soaps are present only in trace amounts, insufficient to cause immediate colour changes. Still, the chemistry behind metal soaps is a complicated issue as they can adopt structures ranging from amorphous to crystalline⁶⁴.

Quite so, the alkaline environment of mezzo-fresco and fresco techniques (lime water and lime paste showed 11.56 and 11.92 pH units, respectively) promoted the conversion of bluish-green neutral verdigris into a range of secondary compounds. In the verdigris–lime water mixtures, copper acetates previously described as basic forms of verdigris—specifically phases 1–3–2 ($\text{Cu}_2(\text{CH}_3\text{COO})(\text{OH})_3\cdot\text{H}_2\text{O}$) or 2–1–5 ($\text{Cu}_3(\text{CH}_3\text{COO})_4(\text{OH})_2\cdot 5\text{H}_2\text{O}$)^{6,10}—were identified. Although these phases have very similar XRD patterns, they can be distinguished by their morphology: Bette et al.¹⁰ reported a layer-like morphology for phase 1–3–2 and a needle-like morphology for phase 2–1–5. Our observation by stereo-microscopy (Fig. 3a) and SEM (Figs. 5f and 6a) of samples VER-MF_2 and VER-MF_3 revealed a needle-like morphology consistent with that reported for phase 2–1–5¹⁰. Furthermore, because phase 1–3–2 is metastable under conditions of high hydroxide supersaturation—such as the ones created by lime water ($\text{Ca}(\text{OH})_2$)—it may also form as an intermediate phase before transforming into the 2–1–5 phase⁶. Taken together, these observations suggest that $\text{Cu}_3(\text{CH}_3\text{COO})_4(\text{OH})_2\cdot 5\text{H}_2\text{O}$ (the 2–1–5 phase) likely forms as an alteration product of neutral verdigris in strongly alkaline environments. Indeed, it has been previously reported that neutral verdigris can transform into basic verdigris phases^{15,16}. A dark-blue calcium-copper acetate hexahydrate known as paceite ($\text{CaCu}(\text{CH}_3\text{COO})_4\cdot 6(\text{H}_2\text{O})$) was also identified in some mezzo-fresco samples. This compound has been reported as an alteration product of neutral verdigris in fresco painting, forming through the reaction with calcium hydroxide⁴². In support of this mechanism, Li et al.⁶⁵ successfully synthesised paceite by reacting calcium hydroxide or calcium carbonate with copper acetate (hoganite) in the presence of acetic acid.

Calcium acetate—either monohydrate ($\text{Ca}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$) or hemihydrate ($\text{Ca}(\text{CH}_3\text{COO})_2\cdot(\text{H}_2\text{O})_{0.5}$)—was identified in both MF and F samples. Although no studies have directly described the hemihydrate phase, related work has demonstrated that the monohydrate ($\text{Ca}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$) can be synthesised from mussel shells and acetic acid⁶⁶. These exhibited thin, needle-like crystals similar to those identified in our samples (e.g. Figs. 5f and 6e). This suggests that the phase present in our samples may correspond to the monohydrate phase; however, calcium acetates are known to adopt diverse hydrated forms with comparable morphologies⁶⁷. While we cannot determine the exact hydration state of the calcium acetate in our samples, its identification represents, to our knowledge, the first report of this compound as an alteration product of verdigris.

In contrast, only the fresco samples (F) showed the presence of anhydrous verdigris ($\text{Cu}(\text{CH}_3\text{COO})_2$), a phase already present in trace amounts in the raw pigment. As it is known that temperatures exceeding 90 °C are required for its formation, it cannot be considered as an alteration of neutral verdigris⁹. Tenorite (CuO)—long recognised as a final blackening product in copper-based paintings⁴¹—was also identified and is known to form through decomposition of neutral verdigris ($\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$)⁶⁸. Tenorite particles display morphologies comparable to fibrous nano-ribbons⁶⁹, micro-tubes⁷⁰ and micro-spheres⁷¹ morphologies, similar to those observed in Figs. 5f and 6f, j, respectively. Finally, some XRD patterns of the F samples showed an unassigned XRD peak at $2\theta = 10.30^\circ$, which likely corresponds to an unidentified metal carboxylate. This suggests the presence of additional copper-, calcium-, or mixed copper-calcium acetate phases of yet undetermined composition. The ATR-FTIR results support this interpretation. The presence in the FTIR spectra of broad hydroxyl (–OH) bands, different in each spectrum, confirms an ongoing modification and the presence of hydrated compounds. This could be related to the aforementioned compounds (various hydrated acetates and/or copper hydroxides) as suggested by the widespread presence of acicular and ribbon-like morphologies. Moreover, the shift of COO^- asymmetric stretching to lower wavenumbers, as observed in our spectra (shifts of up to -70 cm^{-1}),

suggests a mixture of compounds is formed⁴⁷. This was further supported by the changes observed related to Cu–O and Cu–OH bonding.

Regarding morphological transformations, the results obtained in this study point to a diverse and complex set of alteration products. The needle-like morphologies (Figs. 5i and 6a, f–h) are most plausibly associated with the following compounds identified in this study: $\text{Cu}_3(\text{CH}_3\text{COO})_4(\text{OH})_2\cdot 5\text{H}_2\text{O}$, diverse hydrated forms of calcium acetates ($\text{CaH}_6\text{CaO}_4\cdot n\text{H}_2\text{O}$), or copper oxides such as tenorite (CuO). Nevertheless, needle-like forms were diverse, and the presence of other compounds not detected by XRD cannot be excluded. For instance, it is well-known that verdigris pigments can transform into blue copper hydroxides, such as spertiniite ($\text{Cu}(\text{OH})_2$), in the presence of alkalis as an intermediate step in copper oxide formation^{1,55}. This compound can also form with a needle-like (or acicular) morphology^{72–74}. Moreover, nano-ribbon morphologies have also been reported for $\text{Cu}(\text{OH})_2$, which highly resembles the morphology observed in Fig. 5f^{72–74}. Finally, the tabular, rosette-like habits observed (Fig. 5g, h) are most likely linked to other forms of copper acetate since similar morphologies to ours have been reported by Raza et al.⁷⁵ who synthesised Cu(II) carboxylates with monoclinic symmetry.

In summary, this study highlights the pronounced instability of neutral verdigris when applied *a mezzo-fresco* and *a fresco*, leading to the formation of a wide variety of secondary compounds. These findings contrast with its documented presence in historical works, raising important questions. It is likely that this discrepancy arises from misattributions to the original painting technique. Even so, future research should investigate whether verdigris can be stabilised in such alkaline environments to enable its practical use in painting. Moreover, unresolved XRD peaks and infrared spectral shifts suggest the presence of additional carboxylates or copper oxides/hydroxides, indicating a more complex alteration pathway than previously recognised. The need for advanced micro-analytical methods, such as synchrotron radiation micro-X-ray powder diffraction (SR- μ PXRD), to fully resolve the complex formation of secondary phases arising from verdigris alteration, is highlighted.

Data availability

All data needed to evaluate the conclusions are present in this paper.

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Author contributions

D.J.-D.: writing—original draft. J.S.P.-A. and A.A.: writing—review and editing. D.J.-D.: data curation and investigation. D.J.-D., J.S.P.-A., and A.A.: formal analysis. J.S.P.-A. and A.A.: funding acquisition, project administration and supervision. All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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