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Characterization of the reconversion products of darkened lead white and development of an innovative approach for its stabilization

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Abstract In wall paintings, the darkening of lead-based pigments is a widespread alteration process due to the oxidation of lead Pb(II) into Pb(IV) in the form of lead dioxide (primarily plattnerite, β-PbO_2). In the case of lead white, it consists of lead carbonate transforming by oxidation into plattnerite. This phenomenon can severely affect the esthetical appearance of a painting and seems related to several factors such as alkaline environment, humidity, light, oxidizing agents, and microorganisms. These elements have been investigated as potential responsible for the darkening, but without firmly establish the causes, mechanisms, and kinetics of the reactions. Nevertheless, the desire of recovering the original colors encouraged conservators to use a chemical redox treatment known as "reconversion", based on the use of hydrogen peroxide and diluted acetic acid. Although never analytically confirmed, this chemical treatment was successfully applied on darkened portions of several wall paintings proving the recovery of the white appearance. Unfortunately, in some cases, particularly those in humid environments, the reconversion was not stable and darkening reoccurred over time. This evidence highlights the need to ensure the stability of the recovered white guaranteeing the long-term efficacy of the reconversion. This study illustrates the results of in vitro laboratory tests, performed on pure powdered plattnerite, to investigate the chemical nature of the reconversion products and to develop an innovative stabilization method based on the use of di-ammonium phosphate (DAP). The attenuated total reflection mode infrared analyses (ATR-FTIR) and the X-ray powder diffraction (XRD) data showed that the addition of DAP leads to the formation of a white compound, namely hydroxypyromorphite [$Pb_5(PO_4)_3OH$], which thanks to its extremely low solubility, could prevent the occurrence of redarkening of the treated painted surface.

1 Introduction

Historically, the use of lead-containing pigments was not recommended in wall paintings due to their instability over time [1–3]. Indeed, several painting treatises describe that lead-based pigments are not suitable pigments for *a fresco* painting technique, thus suggesting their application with *a secco* technique (i.e., on dry plaster with organic paint binders, such as egg, animal glue, and oil) [4–7]. Nevertheless, they have been widely used in wall paintings, and in many occurrences, the original white/yellow/red/orange lead-based pigments have turned to a dark color (violet-gray to brown-black) compromising the visual appearance and, in some cases, the legibility of the artwork itself [8, 9]. Among these chromatic variations, the darkening of lead white is reported as one of the most common alteration processes on wall paintings [10]. An early description of this phenomenon was provided by Baldinucci: "*Lead white, the whitest color, coming from lead with the help of vinegar, which is used for painting in oil and tempera but not in fresco: but when it has been used on walls with tempera in the open air it gets black and spoils the pictures*" [11].

The lead white pigment is a lead carbonate occurring in two mineral forms, namely: hydrocerussite [basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$] and cerussite (neutral lead carbonate, $PbCO_3$) [12]. Generally, in the pre-industrial production of the pigment, the hydrocerussite/cerussite ratio varied with the manufacturing process followed or with the preparation mode adopted by the

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artist [12–16]. On wall paintings, the darkening of lead white is due to the oxidation of Pb(II) in lead carbonates into two different polymorphs Pb(IV) di-oxides, i.e., plattnerite (β-PbO_2) and/or scrutinyite (α-PbO_2), through the following redox reaction [17]:

$$2PbCO_3 \cdot Pb(OH)_2 + 2H_2O \rightarrow 3PbO_2 + 2CO_2 + 6H^+ + 6e^-$$

The oxidation process is not thermodynamically favored because Pb(IV) is significantly less stable than Pb(II); therefore, it requires a high value of redox potential ($E° = -1.455$ V) to take place. Nevertheless, the analysis of electrochemical potential (Eh)-pH diagrams suggests that the oxidation of Pb(II) to Pb(IV) can be promoted in an alkaline environment, where the redox potential is significantly reduced ($Eh > +0.6$ at $pH > 10$) [18]. As a result, the alkaline nature of the lime-based plaster was one of the first possible triggers of the darkening process to be explored [19]. Notable, experimental studies on pigment powders proved that in an alkaline environment lead carbonate does not transform into plattnerite, but rather into other lead oxides, including red lead (Pb_3O_4), massicot (β-PbO), and litharge (α-PbO) [20, 21]. Specifically, Vagnini et al. [21] found that under *a fresco* conditions, hydrocerussite was more reactive than cerussite by forming red lead [Pb_3O_4 with Pb(II)/Pb(IV)], while cerussite simply turned into litharge [α-PbO, Pb(II)] without changing its oxidation number. However, no plattnerite formation was observed, therefore the research focused on the role of strong oxidizing agents, as ozone (O_3) [22], hydrogen peroxide (H_2O_2) [20], and sodium hypochlorite (NaClO) to obtain darkening phenomenon [21, 23]. Among these, NaClO proved to be the most effective agent in promoting the oxidation of Pb(II) to Pb(IV). The contribution of chlorine-containing oxidizers to this reaction emerged from analytical studies performed on a series of fragments from the wall paintings that decorate the Upper Basilica of San Francesco in Assisi (Italy) [18, 24]. In the altered layers of these samples, several chlorine-based compounds were identified in addition to lead dioxide (both plattnerite and scrutyinite were found). In particular, the detection of different Cl-containing compounds, including laurionite (Pb(OH)Cl), suggests the potential role of chlorine species (i.e., disinfecting/cleaning products, biocides, or Cl-containing salts in the mortar) as catalysts of the alteration mechanism of lead white and other pigments, including azurite. However, it is important to note that no chlorine-containing species were found in samples coming from other wall paintings affected by alteration of lead-based pigments [25, 26].

Microbiological activity has been examined as a further potential cause of darkening of lead white. Specifically, some studies explored the metabolic activity of certain bacteria [27–30], while others focused on that of fungi belonging to *Penicillium* and *Cladosporium* species [31, 32]. On the other hand, microbiological analyses of samples from darkened wall paintings, such as those performed for the Castle Strechau in Styria (Austria), ruled out the involvement of microorganisms [33].

These examples proved that no single factor can be considered responsible for all cases of darkening of lead-based pigments, but rather a combination and a synergy of different factors. Consequently, to date, the actual causes, mechanisms, and kinetics of the reaction(s) leading to the darkening process have not been completely elucidated.

Matteini was the first to propose a solution to recover the original white appearance of altered lead white on wall paintings [17, 19, 34]. The method consists of treating the darkened areas with hydrogen peroxide and diluted acetic acid to obtain over time hydrocerussite according to the following reactions:

$$PbO_2 + H_2O_2 + 2CH_3COOH \rightarrow Pb(CH_3COO)_{2(s)} + O_{2(g)} + 2H_2O_{(g)} \quad (1)$$

$$3Pb(CH_3COO)_2 + 2H_2O \rightarrow 2Pb(CH_3COO)_2 \cdot Pb(OH)_{2(s)} + 2CH_3COOH_{(g)} \quad (2)$$

$$2Pb(CH_3COO)_2 \cdot Pb(OH)_2 + 2CO_2 + 2H_2O \rightarrow 2PbCO_3 \cdot Pb(OH)_{2(s)} + 4CH_3COOH_{(g)} \quad (3)$$

This chemical method, commonly known as “reconversion”, was firstly applied on darkened portions of 15th century wall paintings by Alessio Baldovinetti in St. Miniato al Monte church (Firenze, Italy), and on those by Luca Signorelli in the cloister lunettes of Monteoliveto Maggiore Abbey (Siena, Italy) proving the recovery of a white color and confirming, therefore, the visual efficacy of the treatment [17, 19, 34]. The promising results obtained, encouraged conservators to apply the reconversion method on several other darkened wall paintings (Table 1 and Fig. 1 show some examples) [26, 33, 35–40]. However, in some cases, the result of the treatment was not completely successful in terms of esthetics [38] or long-term stability, resulting in the darkening to reoccur (see the cases labeled with an asterisk in Table 1 and those show in Fig. 1) [33, 36, 39, 40]. Similarly to the causes and mechanism of the darkening, the causes of this phenomenon are unknown and have not been investigated. Specifically, only in some cases [33, 39, 40], a chemical and stratigraphical characterization of altered and realtered compounds have been performed confirming the presence of lead dioxide. However, it is not possible to distinguish whether this is a product of the former or the new darkening process.

In addition, it is important to note that although the reconversion was designed to produce a white lead carbonate compound, the treatment was also applied on other darkened lead-based pigments that originally had different colors (see the example shown in Fig. 1c). This shows that the reconversion has often been used in a hazard manner without a complete knowledge or understanding of the reaction mechanisms and the compounds produced but visually following the process. The chemical reactions involved in the treatment (described in Eqs. 1–3 above) were never analytically evaluated to confirm the formation of lead carbonate, which was typically identified through visual observation alone.

To bridge the knowledge gap regarding the long-term efficacy and stability of the reconversion process, the ongoing research combines systematic laboratory studies with in situ testing on wall paintings affected by lead white darkening. The first step of the research aimed at characterizing the chemical process involved in the reconversion through in vitro laboratory tests conducted

Table 1 Reconversion of darkened lead-based pigments on wall paintings

Wall paintings site	Darkened pigment	Reconversion year	References
San Miniato al Monte, Cardinal of Portugal Chapel, Firenze, Italy (15th C wall paintings by Baldovinetti)	Lead white	1976	[19]
Monteoliveto Maggiore Abbey, Lunettes, Siena, Italy (late 15th C wall paintings by Signorelli)	Lead white	1984	[19]
Strechau Castle, Protestant Chapel, Styria, Austria	Lead white	1990*	[33]
Chapel XXVII, Sacro Monte di Varallo, Vercelli, Italy (17th C wall paintings by Tanzio da Varallo)	Lead-based yellow in mixture with lead white (?)	1993*	[36]
St. Paul Church, "Red church", Arbedo, Canton Ticino, Switzerland	Lead white	2000–2002	UBC archives[1]
St. Maria delle Grazie Church, Bellinzona, Canton Ticino, Switzerland (16th C wall painting of the *Crucifixion*, unknown author)	Lead white	2001–2005	[37]
Villa Cattaneo Imperiale di Terralba, Genova, Italy (16th C wall paintings by Cambiaso)	Lead white	2005	[38]
St. Annunciata Church, Sacro Monte di Orselina, Canton Ticino, Switzerland (16th C wall painting of the *Marriage at Cana*, unknown author)	Lead white	2010*	UBC archives[1]
North tower of the Trefogli Castle, Torricella, Canton Ticino, Switzerland (ceiling decoration, unknown author)	Lead white	2010*	[39, 40]
St. Stephen's Chapel, Montani, Val Venosta, Bolzano, Italy (15th C wall paintings, unknown author)	Lead white (?)	2020	[26]

[1] Conservation reports viewed at the archives of the Ufficio dei Beni Culturali (UBC) of Canton Ticino (Switzerland)
*: Re-darkening over time

directly on powdered plattnerite alone. This allowed the analysis of the products formed by reconversion in an environment free of any other substances. In addition, a promising compound like the di-ammonium phosphate [$(NH_4)_2HPO_4$] (DAP) was tested to stabilize the reconversion products obtained. Generally, DAP is used for consolidation treatments of limestones [41–46], but in presence of lead-based compounds, it should form lead phosphate [$Pb_3(PO_4)_2$], a white compound much less soluble than lead carbonate. The formation of lead phosphate should prevent the darkening from occurring again because the solubility of Pb-phosphate ($K_{sp} \approx 10^{-44}$) [47] is much lower than that of basic Pb-carbonate ($K_{sp} \approx 10^{-24}$) [48], and therefore, the lead ions are less available for the oxidation process causing darkening. The products obtained from the in vitro laboratory tests were analyzed by attenuated total reflection mode infrared spectroscopy (ATR-FTIR) and X-ray powder diffraction (XRD), and the results are presented and discussed in this study. These findings provide the basis for developing a targeted method to stabilize the reconversion products over time.

2 Materials and methods

2.1 In vitro laboratory tests

Laboratory experimentations were conducted at room temperature between 20 and 25 °C and RH between 40 and 50% and focused on the process of reconversion and reconversion followed by stabilization:

1. "Traditional" reconversion of lead dioxide into lead carbonate according to Matteini's method (acronym TR) [17, 19, 34];
2. TR followed by the addition of di-ammonium phosphate (acronym TR + DAP).

Plattnerite powder (β-PbO_2), purchased from Sigma-Aldrich (99.998% trace metals basis), was placed inside Petri dishes and made to react with the reconversion solution (pH range between 2 and 3) consisting of:

- 40% of 3% hydrogen peroxide (H_2O_2, 10 vol, provided by Laboratoires Gilbert);
- 1% of 81% acetic acid (CH_3COOH, provided by ECSA Group);
- 59% of distilled water (H_2O).

Fig. 1 Examples of stable (**a**, **b**) and unstable (**c**, **d**) reconversion treatments performed on darkened portions of wall paintings. **a** 15th C wall paintings by Luca Signorelli in the cloister lunettes of Monteoliveto Maggiore Abbey (Siena, Italy), reconversion on the mountains and on the hourglass; **b** 16th C wall painting of the *Crucifixion*, unknown author, in St. Maria delle Grazie Church (Bellinzona, Canton Ticino, Switzerland), reconversion on the lower portion of the sky [37]; **c** detail of 17th C wall paintings by Tanzio da Varallo in the Chapel XXVII, Sacro Monte di Varallo (Vercelli, Italy) reconversion on the coat, pre- (SABAP-TO_SBSAE-PIE_AR973 n.20323) and post-treatment (SABAP-TO_SBSAE-PIE_AR973 n.35838) ©Sabap-TO, tutti i diritti riservati, su concessione del MiC **d**) detail of 16th C wall painting of the *Marriage at Cana*, unknown author, in the St. Annunciata Church, Sacro Monte di Orselina (Orselina, Canton Ticino, Switzerland), reconversion on the face of a figure, ©Archives Ufficio dei Beni Culturali, Bellinzona – pictures P. Bolli

For both TR and TR + DAP tests, 6 mL of the reconversion solution were gradually added to 0.1 g of plattnerite. Then, after the complete drying of the reconversion solution, 6 mL of an aqueous solution containing 0.055 g of DAP [$(NH_4)_2HPO_4$] (pure by Carlo Erba Reagents)[1] was added only for the reconversion and stabilization TR + DAP test. During the tests, pictures by both camera and portable digital microscope were captured [Appendix]. The products of the tests were analyzed by ATR-FTIR spectroscopy and powder XRD after complete drying of the solutions. Both tests and analyses of the products were repeated twice to confirm the reproducibility of the data obtained.

2.2 ATR-FTIR spectroscopy

Infrared measurements of TR and TR + DAP products were carried out using an Alpha II spectrometer (Bruker Optics GmbH, Ettlingen, Germany) equipped with a diamond unit (platinum-ATR) for analyses in ATR mode, a CenterGlow IR-source, a RockSolid interferometer, and a temperature controlled DTGS detector. Generally, the spectra acquired in ATR mode show spectral distortions and shifts in position of the bands when compared to those recorded in transmission [49], therefore, to avoid possible spectral misinterpretation, the spectra of reference substances used in this study were also acquired in ATR mode. The spectra were collected in the 4000–400 cm^{-1} range by setting 128 scans, a resolution of 2 cm^{-1}, and using a spectrum of air previously recorded with the same instrumental conditions as background. Data analysis was operated with OPUS software.

2.3 X-ray powder diffraction (XRD)

X-ray powder diffraction data were acquired in theta-theta reflection geometry on a Bruker D8 Advance diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) equipped with a Lynxeye XE-T position sensitive detector, Cu Kα radiation ($\lambda = 1.5406$ Å) operating at 40 kV and 40 mA, with a step size of 0.017° 2θ, and a step scan of 1 s. The phase identification was performed by using the Bruker DIFFRAC.EVA V5 software with the help of the COD database [50]. Quantitative phase analyses were performed with the Rietveld method using the GSAS-II program [51].

3 Results and discussion

The first objective of the in vitro tests performed in laboratory (TR) was to analytically verify the formation of basic lead carbonate (hydrocerussite) as a result of the chemical reactions involved in the reconversion treatment (see Eqs. 1–3 above). Specifically, the test and the analytical methodology to be followed were implemented based on preliminary analysis performed during previous research [40]. The IR analyses of the reconversion products performed as part of this research, proved that 1 month was not sufficient to complete the carbonation, i.e., the transformation of the intermediate product lead acetate (identified compound) into basic lead carbonate. Accordingly, the TR test was repeated, and the products were periodically analyzed by ATR -FTIR considering a longer time frame. During the test, the reconversion solution gradually reacted with the particles of powdered plattnerite resulting in a semi-transparent whitish solution (Fig. 2a). After 2 days, the deposition of a white compound was noticed (Fig. 2b). The ATR-FTIR spectrum obtained from this compound indicated the formation of lead acetate (see the comparison with a reference spectrum in Fig. 2e, f). A very similar infrared spectrum was obtained 4 days after the test (data not shown), while the spectra recorded after 7 and 20 days, compared with that of the basic lead acetate, revealed the possible loss of OH groups (disappearance of the broad bands at ca. 3270, 1670, and 840 cm^{-1}) [52]. In addition, new bands at ca. 1570 (possible v_{as} of carboxylate anion COO^-) [53], 975 (weak shoulder), 640, 575, and 534 cm^{-1} were noticed. The first weak bands ascribable to basic lead carbonate at ca. 3540 (O–H stretching vibration), 1730 ($v_1 + v_4$ combination mode of CO_3^{2-}), 1390 (v_3 of CO_3^{2-}), 680 (v_4 of CO_3^{2-}), 770 (Pb···O–H bending vibrations), and 853 cm^{-1} (v_2 of CO_3^{2-}) [54] appeared in the spectrum collected 69 days after the test (see the comparison with a reference spectrum in Fig. 2e, f). The intensity of the band at ca. 1730 cm^{-1} of the basic lead carbonate increased in the later recorded spectrum (88 d), and a very weak doublet at 1098 and 1115 cm^{-1}, of more complex attribution, was observed up to 102 days after the test. The data acquired 102 days (included those corresponding at 116 and 123 d) were crucial in determining the disappearance of the lead acetate bands and the enhancement of those related to basic lead carbonate. However, in these last spectra, weak bands at about 575, 534, and 975 cm^{-1}, already detected after 7 and 20 days, were still visible but could not be assigned to any compound.

The formation of basic lead white was also confirmed by powder XRD analysis. Specifically, the XRD pattern obtained from the product of the TR test revealed the exclusive presence of the hydrocerussite mineral phase (COD no. 2012740), as confirmed by the search and match procedure and the Rietveld method (Fig. 3).

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[1] The amount of DAP was determined by stoichiometric calculation considering the number of Pb moles corresponding to 0.1 g of plattnerite.

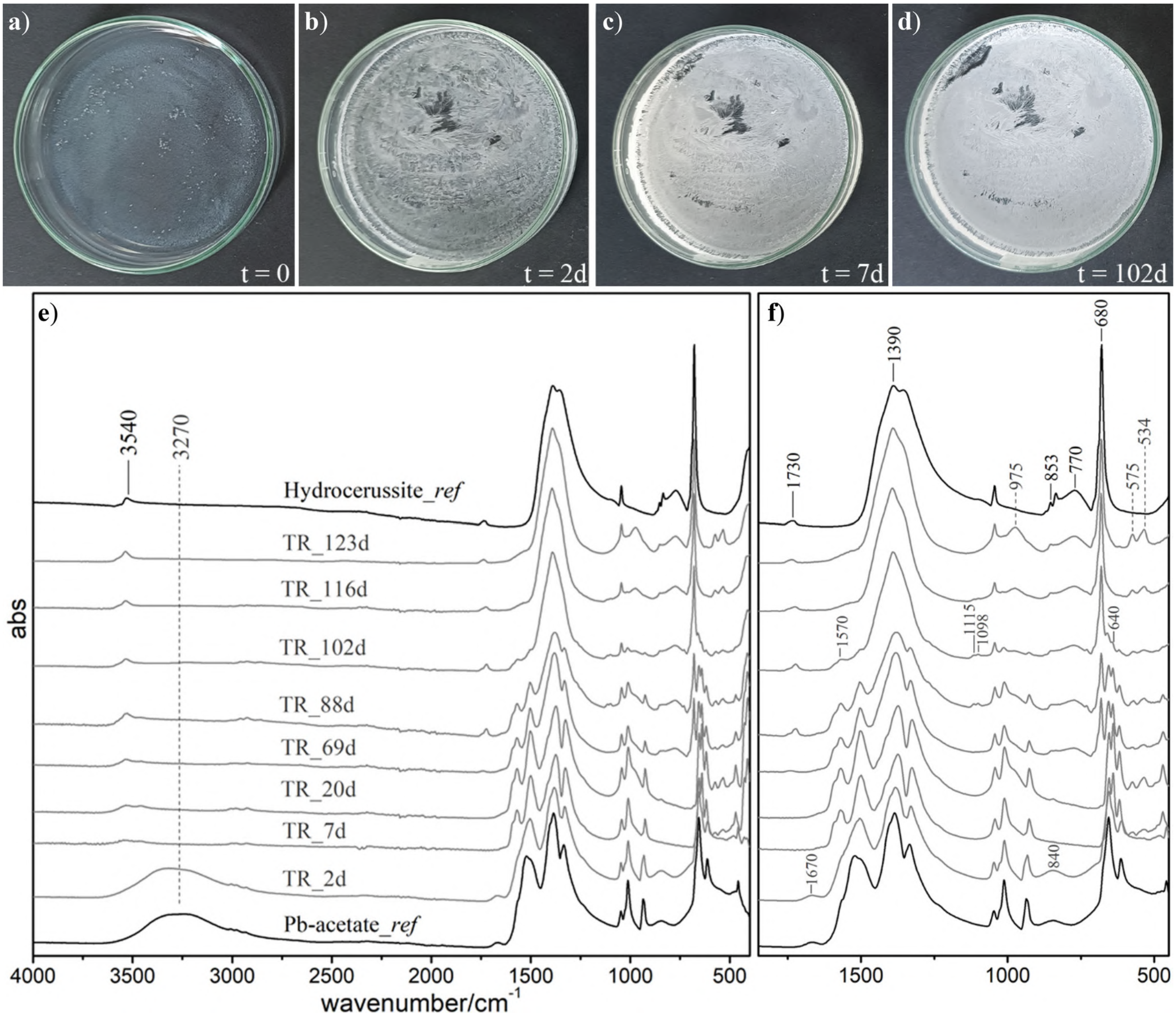

Fig. 2 **a–d** Pictures of the TR test products collected over time and (**e**) corresponding ATR-FTIR spectra (gray) in comparison with the reference IR spectra of basic lead acetate and basic lead carbonate (black). **f** Detail of the spectral region between 1850 and 450 cm^{-1} of the graph shown in (**e**)

For the TR + DAP test, the same reconversion solution adopted for TR test was used following by the addition of an aqueous solution containing DAP (Fig. 4a–d). Specifically, DAP solution was added after the “traditional” reconversion to enable the reaction between DAP and lead acetate, which was quickly formed as reconversion product (see the infrared spectra TR_2d and TR + DAP_4d in Figs. 2 and 4, respectively). Thus, the proposed treatment involves first the reconversion to transform plattnerite reducing it to lead acetate, and later the stabilization with DAP to produce lead phosphate. Visually, DAP-lead acetate reaction immediately produced a rather homogeneous white compound that was analyzed by ATR-FTIR spectroscopy following the complete evaporation of the water (Fig. 4c, d). The infrared profile obtained (Fig. 4e, f) showed the typical phosphate vibration bands, and their shift toward lower wavenumbers suggested the formation of hydroxypyromorphite [$Pb_5(PO_4)_3OH$] [55]. Specifically, the comparison between the spectrum of TR + DAP product and the spectrum of a reference of hydroxypyromorphite (indicated with HPy), proved a full match of the bands at ca. 1030, 960, 570 and 532 cm^{-1}, related to v_3, $v_{1,}$ and v_4 modes of (PO_4^{3-}), respectively, and that of ν(OH) mode at ca. 3560 cm^{-1} (Fig. 4e, f).

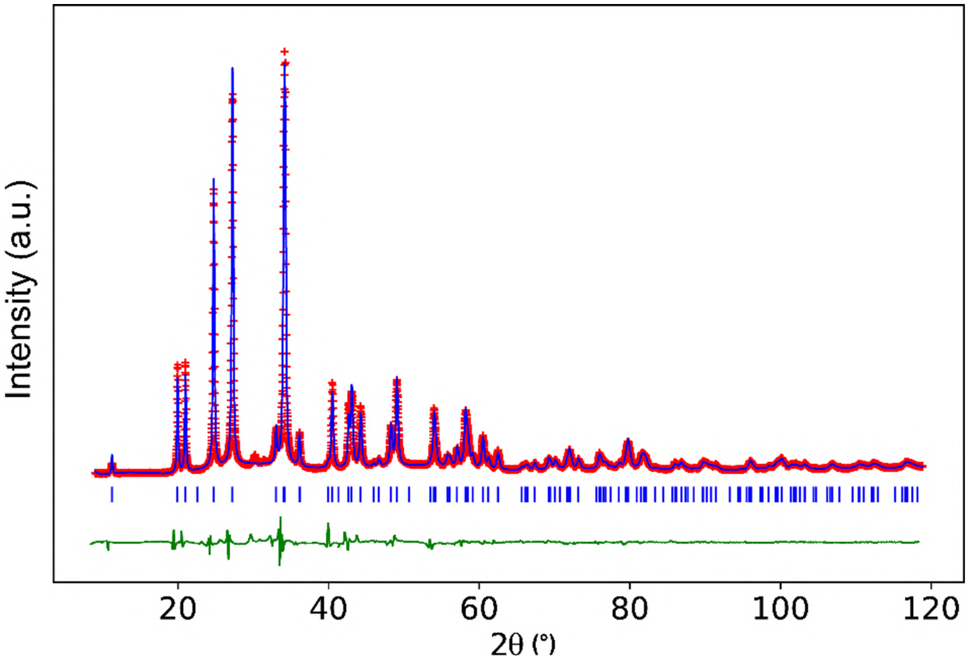

Fig. 3 Final Rietveld plot for TR test, reporting the observed pattern (red symbols), the calculated pattern (blue line), and their difference (green line). Blue markers at the bottom indicate the calculated positions of peaks. Statistical agreement factors: *Rwp* = 0.073; *Rp* = 0.055

The XRD analysis confirmed the formation of hydroxypyromorphite (COD no. 9012631, 82.0% ± 0.2 w/w). In addition, the diffractogram collected from the TR + DAP product (Fig. 5) showed also a lower amount of ammonium dihydrogen phosphate ($NH_4H_2PO_4$, COD no. 9007580, 18.0% ± 0.2 w/w) that could be associated with an excess of DAP used for the test. The presence of ammonium dihydrogen phosphate was also recognized in the infrared spectrum collected for the TR + DAP product (Fig. 4e, f) through the detection of the doublet at ca. 1442 and 1404 cm^{-1} ascribable to the bending modes of the NH_2 group [56].

Thus, the data obtained from this test confirmed that the addition of DAP after the traditional reconversion resulted in the formation of a lead phosphate-based compound, specifically hydroxypyromorphite [$Pb_5(PO_4)_3OH$]. Notable, the solubility product K_{sp} estimated for this compound at 25 °C is $10^{-80.77\pm0.20}$ [57], is much lower than that of lead phosphate ($\approx 10^{-44}$) and that of basic lead carbonate ($\approx 10^{-24}$) produced by reconversion alone. The extremely low solubility of lead phosphate compounds is leveraged for remediating Pb-contaminated sites, where phosphorus compounds are introduced to form insoluble Pb-phosphate precipitates, effectively removing free lead from the environment [58]. Generally, in pH range of 3–7, $H_2PO_4{}^-$ is the predominant phosphate species; therefore, the relevant chemical equations for Pb precipitation by phosphate are the following [59]:

$$5Pb^{2+}_{(aq)} + 3H_2PO^-_{4\ (aq)} + H_2O_{(l)} = Pb_5(PO_4)_3OH_{(s)} + 7H^+_{(aq)} \tag{4}$$

$$3Pb^{2+}_{(aq)} + 2H_2PO^-_{4\ (aq)} = Pb_3(PO_4)_{2(s)} + 4H^+_{(aq)} \tag{5}$$

$$Pb^{2+}_{(aq)} + H_2PO^-_{4\ (aq)} = PbHPO_{4(s)} + H^+_{(aq)} \tag{6}$$

The Gibbs free energy for the solid phases $Pb_5(PO_4)_3OH$, $Pb_3(PO_4)_2$, and $PbHPO_4$ was calculated to be − 902.0, − 565.0, and − 281.8 kcal/mol, respectively [60]. The lowest value obtained for the formation of hydroxypyromorphite (ca. − 907.5 kcal/mol at pH 2.00 and 25 °C from the most recent study by Zhu et al. [57]) proves that the reaction (4) is actually favored in aqueous solution. Indeed, hydroxypyromorphite is often reported as a potential low-solubility mineral to limit solubility and bioavailability of the lead element in both soils and water, including drinking water [61]. Accordingly, the formation of hydroxypyromorphite as product of the reconversion of darkened lead white following by the stabilization with DAP may be of crucial importance for blocking and passivating lead into a highly insoluble and, thus, more stable compound, less prone to oxidation. In this way, no more lead ions should be available for a new darkening process. An additional advantage of using DAP on lime-based wall paintings is that its excess could interact with the calcium ions in the plaster to form calcium phosphate, like hydroxyapatite ($Ca_5(PO_4)_3OH$), which acts as a consolidating agent of the plaster itself. Therefore, in this context, the use of DAP would play a dual role as both stabilizing and consolidating the treated wall painting.

4 Conclusion and future research

The lead white darkening is a pigment alteration phenomenon and a conservation problem that can be found on wall paintings from all epochs and regions of the world. The chemical treatment developed to deal with this problem, commonly called reconversion,

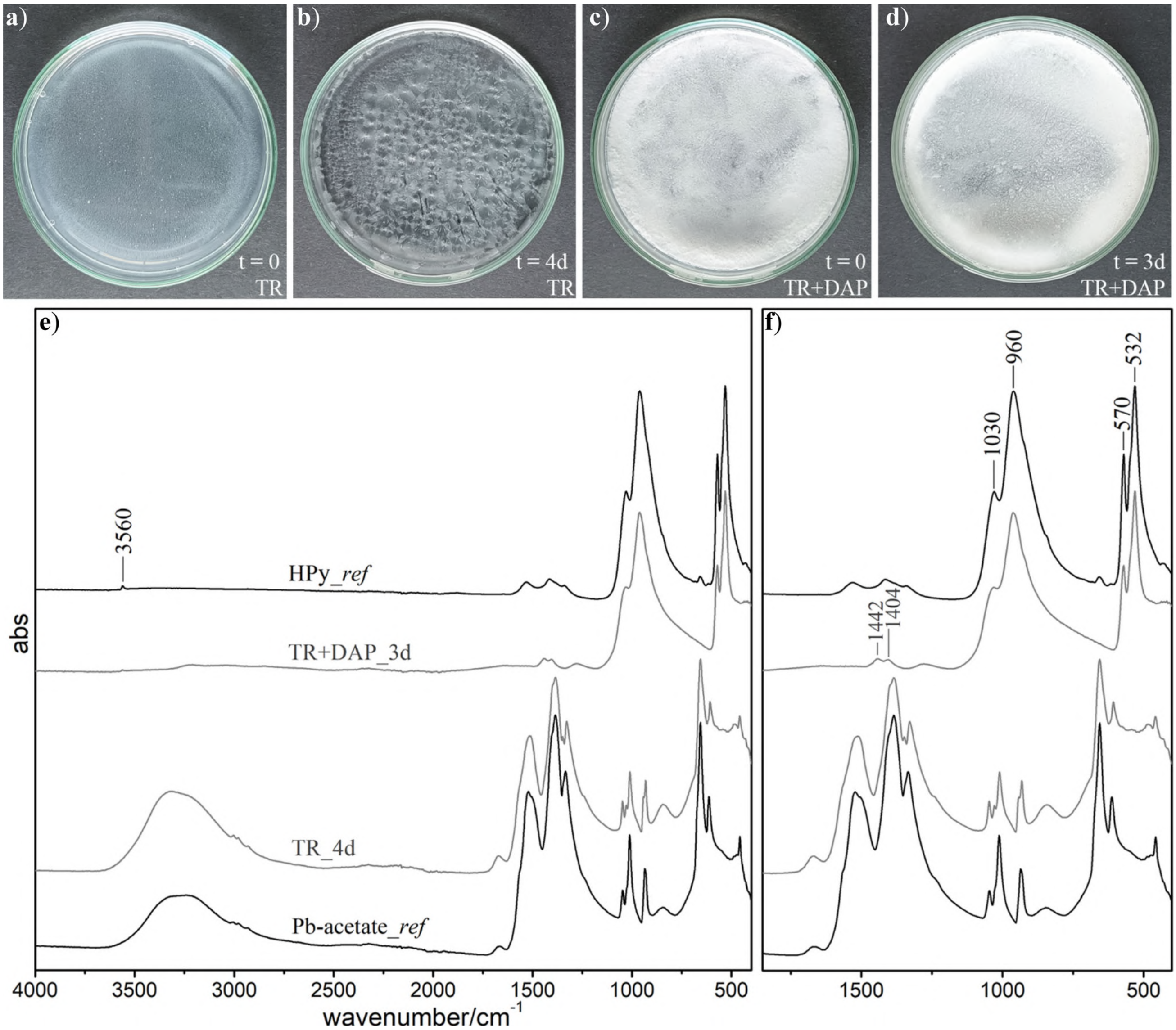

Fig. 4 **a–d** Pictures of the TR + DAP test products collected over time (specifically **b** and **c** were taken before and after DAP addition, respectively) and (**e**) corresponding ATR-FTIR spectra (gray) in comparison with the reference IR spectra of basic lead acetate and hydroxypyromorphite indicated with HPy (black). **f** Detail of the spectral region between 1850 and 450 cm^{-1} of the graph shown in (**e**)

was successfully applied in some cases, while in others did not prove stable over time. The laboratory tests conducted in this study allowed the observation of the effects of the reconversion solution on plattnerite, as well as the analysis of the reaction products and their changes over time.

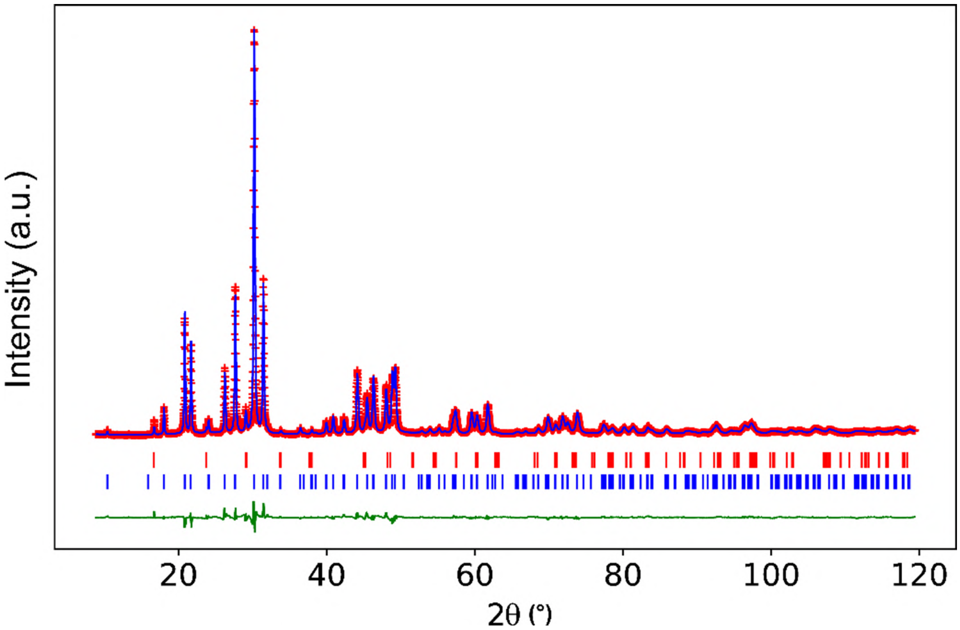

Fig. 5 Final Rietveld plot for TR + DAP, reporting the observed pattern (red symbols), the calculated pattern (blue line), and their difference (green line). Markers at the bottom indicate the calculated positions of the peaks of ammonium dihydrogenphosphate (red) and hydroxypyromorphite (blue). Statistical agreement factors: Rwp = 0.076; Rp = 0.058

The results obtained showed that, in the laboratory environmental conditions, the intermediate reaction product lead acetate persists for a long time, a little over 3 months (detected up to 102 days after treatment), before completely transforming into lead carbonate (hydrocerussite). This transformation begins approximately 2 months after treatment (69 days). At room temperature (20°–25 °C) and RH varying from 40 to 50%, therefore, the carbonation process leading to newly formed lead white can take up to 3 months. Notable, these data confirmed the chemical nature of the compounds supposed to be produced by the reactions involved in the reconversions performed in the past and provided insight into the kinetics of the process itself. Concerning the stabilization of the reconversion products, the reconversion test followed by the addition of di-ammonium phosphate (DAP) provided very promising results. Indeed, only 3 days after the test (time needed for complete evaporation of the solution), a highly insoluble lead phosphate, namely hydroxypyromorphite [$Pb_5(PO_4)_3OH$], was detected. In this form, lead (Pb) is part of a compound that is always white in color but much less soluble and therefore more stable than lead carbonate. As a result, the formation of the hydroxypyromorphite on a painting surface could create a sort of barrier against external agents that cause darkening and, thus, prevent the recurrence of the alteration.

The future foreseen research activities will focus on the implementation of the laboratory tests on wall painting models testing and assessing different application methods and contact times of both reconversion and stabilization treatments. Subsequently, the most effective procedure will be tested in situ on darkened wall paintings selected as case studies and will be periodically monitored by non-invasive techniques. Specifically, chemical-physical proprieties and stability of the new product (i.e., lead phosphate) will be examined and compared with the basic lead carbonate produced by the traditional reconversion.

Overall, the research undertaken intends to provide a solid scientific understanding of the reconversion process and a reliable system to ensure the durability of the retrieved colors over time.

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Author contributions P.M. conceived and wrote the draft article, performed the in vitro laboratory tests, analyzed the products by ATR-FTIR spectroscopy, and interpreted and compared all the data obtained; G.R. performed the in vitro laboratory tests with P.M., prepared all figures, and revised the manuscript; R.V. performed XRD analyses and interpreted the results; L.M., M.M., and F.P. contributed to define the methodology, and integrated, revised, and edited the manuscript. All authors read and approved the final version of the manuscript.

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Data availability The data supporting the findings of this study are available within the article and in the Appendix. All the raw data is archived in digital form in the server of the University of Applied Sciences and Arts of Southern Switzerland (SUPSI). The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request. The manuscript has associated data in a data repository.

Declarations

Conflict of interest There is no conflict of interest to declare.

Appendix

See Figs. 6 and 7.

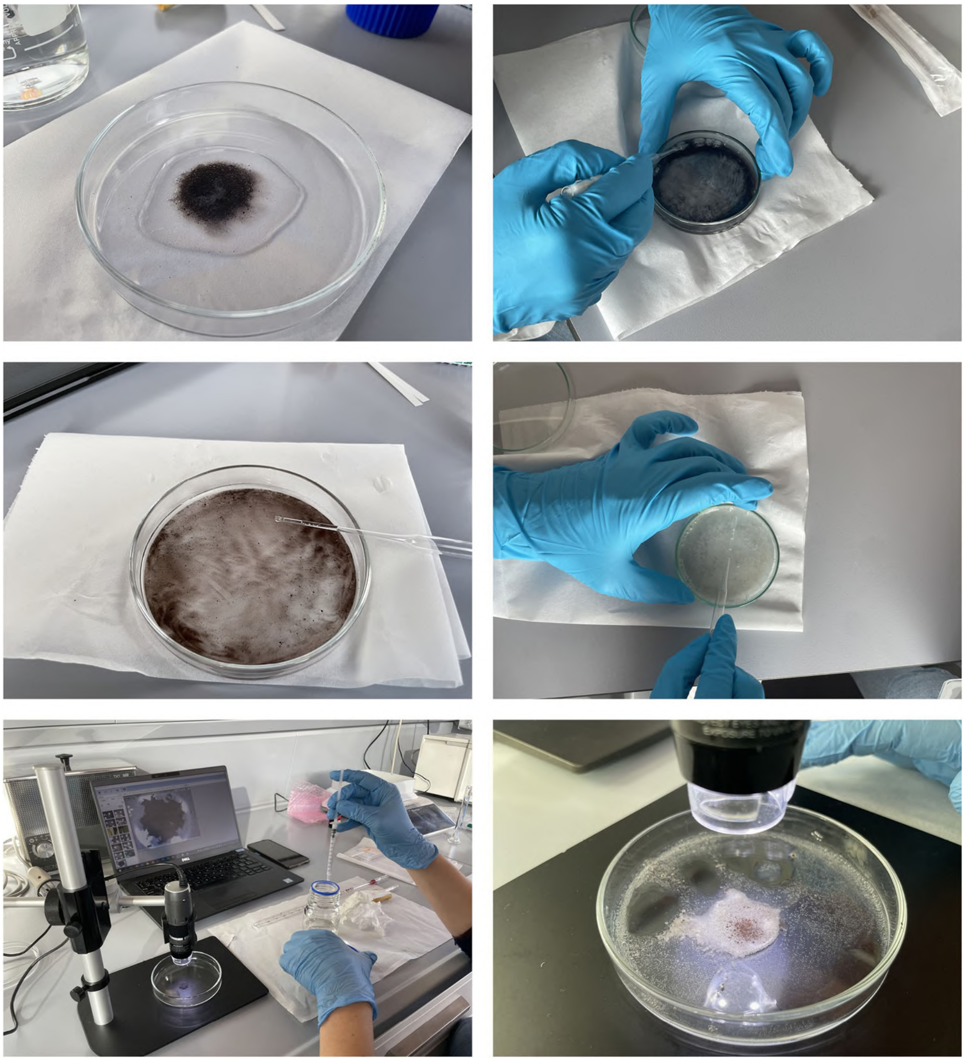

Fig. 6 Set of pictures collected during the in vitro test of reconversion performed on plattnerite powder

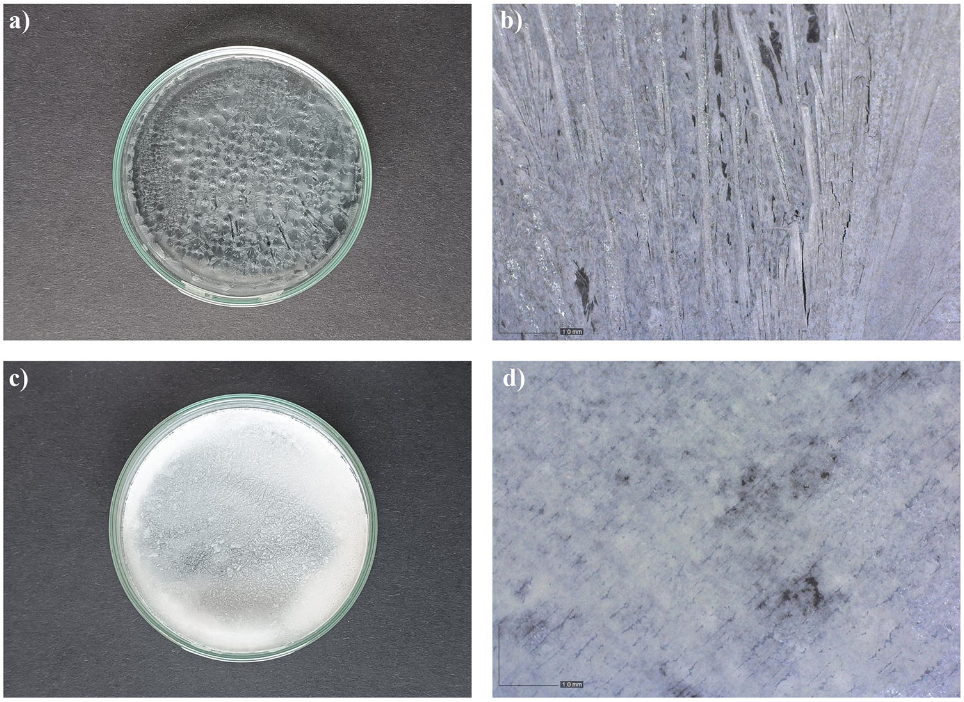

Fig. 7 **a–c** Pictures of the TR + DAP test taken before and after DAP addition, respectively, with the corresponding images (**b–d**) acquired by portable digital microscope (50X magnification)

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