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X-ray and Infrared Microanalyses of *Mona Lisa*'s Ground Layer and Significance Regarding Leonardo da Vinci's Palette

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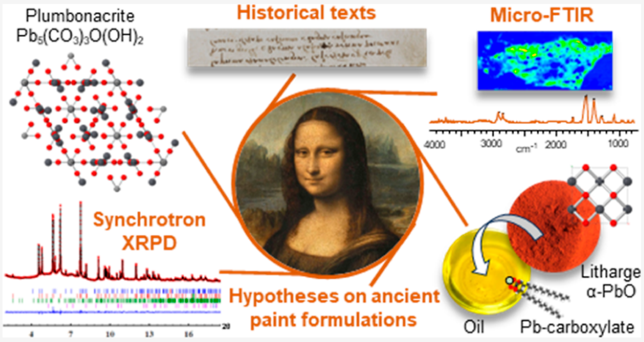
ABSTRACT: An exceptional microsample from the ground layer of Leonardo da Vinci's *Mona Lisa* was analyzed by high-angular resolution synchrotron X-ray diffraction and micro Fourier transform infrared spectroscopy, revealing a singular mixture of strongly saponified oil with high lead content and a cerussite ($PbCO_3$)-depleted lead white pigment. The most remarkable signature in the sample is the presence of plumbonacrite ($Pb_5(CO_3)_3O(OH)_2$), a rare compound that is stable only in an alkaline environment. Leonardo probably endeavored to prepare a thick paint suitable for covering the wooden panel of the *Mona Lisa* by treating the oil with a high load of lead II oxide, PbO. The review of Leonardo's manuscripts (original and latter translation) to track the mention of PbO gives ambiguous information. Conversely, the analysis of fragments from the *Last Supper* confirms that not only PbO was part of Leonardo's palette, through the detection of both litharge (α-PbO) and massicot (β-PbO) but also plumbonacrite and shannonite (Pb_2OCO_3), the latter phase being detected for the first time in a historical painting.



INTRODUCTION

Leonardo da Vinci (1452−1519) is widely considered as one of the most important painters of all time, even if only fewer than 20 of his paintings have survived. Among them, the *Mona Lisa* (Figure 1A), painted c. 1503−1519 and conserved in the *Musée du Louvre* (Paris, France) is undoubtedly the most famous and today considered an archetypal masterpiece of the Italian Renaissance.[1] The materials and techniques adopted by Leonardo, especially those employed in the *Mona Lisa*, constitute an extremely important research topic as his pictorial practice still puzzles experts today. Indeed, while Leonardo wrote numerous manuscripts bearing on his many sources of interest, he left few clues about his painting materials. In addition, recent scientific examination of his paint corpus has revealed that his famous taste for experimentation was strikingly present within his craft: the buildup of each of his paintings is different as are the materials employed. This is especially true for the ground layer(s), i.e., the thick layer(s) applied between the wooden panel and the paint layers as extensively described by Ravaud et al.[2]

In certain cases, such as the *Virgin and Child with St. Anne* (c. 1503−1519, Musée du Louvre), he used a preparatory buildup composed of a *gesso* (a mixture of water-soluble glue with gypsum, $CaSO_4{\cdot}2H_2O$) ground layer, typical in the Italian Renaissance, followed by a priming layer containing lead white (LW, a mixture of two lead carbonates, cerussite, $PbCO_3$, denoted as "Cer" and hydrocerussite, $Pb_3(CO_3)_2(OH)_2$, denoted as "HCer").[3] In other paintings such as the *La Belle Ferronnière* (c. 1495−1497, Musée du Louvre), he applied an orange oil-based ground layer, made of white and red lead (Pb_3O_4) directly on the wooden panel. A hypothesis proposed by Ravaud et al. to explain these different ground layers is related to the size of the different wooden panels:[2] a large panel like the one used for the *St. Anne* would have been difficult for Leonardo to build by himself and might have thus been ordered in a carpenter studio where the wooden support was frequently also covered by *gesso* (or gypsum) as was common in Italy. Conversely, smaller panels such as the ones used in the *Belle Ferronnière* or the *Mona Lisa* did not require carpentry skills, so the wooden planks could have been purchased unpainted, leaving Leonardo more freedom to experiment with mixtures of his own for the ground layers. From 1485 to 1490, each known easel painting of Leonardo presents a different type of ground layer. Their only common features are that they are oil-based and that they contain the

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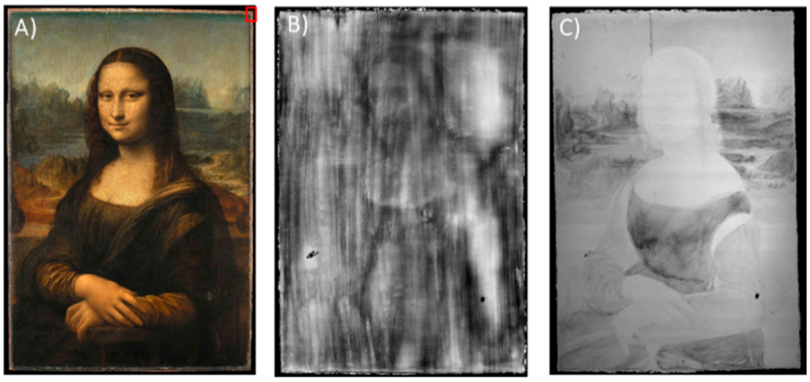

Figure 1. (A) *Mona Lisa*, Leonardo da Vinci, painted c. 1503−1519 (77 × 53 cm), Musée du Louvre, Paris. The area of sampling is indicated by a red rectangle. Copyright E. Lambert − C2RMF. (B) X-ray radiography revealing a radio-opaque, thick absorbing paint layer under the painting surface. Copyright E. Ravaud − C2RMF. (C) Pb-Lα MA-XRF map. Copyright E. Laval, T. Calligaro − C2RMF.

LW pigment, called *biacca* (i.e., "lead white") by Leonardo in his writings. Interestingly, Leonardo experimented with the application of such oil-LW priming layer in the preparation of the ground of the large wall painting of the *Last Supper* (1494−1498), in the convent of Santa Maria delle Grazie, Milan.[4] This has been interpreted as an attempt to unconventionally prepare the wall for an oil-based paint that would have offered more flexibility in color rendering and finishing than the traditional *fresco* technique.

Considering the unique place of the *Mona Lisa* in Western art history, noninvasive analytical techniques have been extensively utilized to gather new insights on Leonardo's materials and techniques. In particular, macro X-ray fluorescence (MA-XRF) analysis at the C2RMF (Paris, France) (Figure 1C) revealed the presence of Pb all over the painting, both in the background and in the *Mona Lisa*. In addition, X-ray radiography (Figure 1B) highlighted the penetration of heavy element(s) within the vessels (max. diameter 70 μm) of the poplar wood, suggesting the use of a lead-based pigment and/or an oil medium treated with a high load of lead in the ground.[5] Moreover, detailed inspection of X-ray images led researchers to postulate that the ground is a single layer of LW without gesso.[5] MA-XRF analysis provided numerous new insights on the paint stratigraphy applied by Leonardo.[2] In addition, a minute paint fragment was sampled in 2007 from the barb of the ground layer in the upper right zone of the artwork hidden by the frame (Figures 1A and S1), giving the opportunity to collect more precise information on the composition of the lead-based ground layer. Most of the sample was embedded in resin for microscopic studies. It contains not only the white ground but also a blue paint layer (left of the fragment in Figure 3A) and a thin yellowish top layer (top surface of the fragment in Figure 3A). A small (<100 μm) fragment from the white ground layer was kept unembedded with the objective of collecting structural information on the pictorial material prepared by Leonardo.

Preliminary scanning electron microscopy with energy-dispersive spectroscopy (SEM−EDS) analysis of the cross section (details in Supporting Information, Section 2.2) highlights the presence of Al, Si, and K in the blue paint layer (ascribed to lazurite $Na_7Ca(Al_6Si_6O_{24})(SO_4)(S_3)\cdot H_2O$), main component of the ultramarine pigment, and the presence of Ca without S in the yellowish upper layer (ascribed to calcite, $CaCO_3$). Pb was found as the main component of the white ground layer (presumably LW) (Figure S5). LW was used from the Egyptian Antiquity until the early 20th century and became ubiquitous in 15−19th century easel painting.[6] Its two constitutive crystalline phases, HCer and Cer, are the result of the historical "stack" process, a corrosion synthesis which consisted in exposing metallic lead to acetic acid vapor (from vinegar), CO_2 (from decaying organic matter), H_2O vapor, and atmospheric O_2 leading to lead oxidation, carbonation, and hydroxylation.[7]

Some of the authors recently performed structural studies on LW pigments used in a large corpus of Old Masters paintings, among them other artworks by Leonardo da Vinci, and demonstrated that the composition and microstructure of the LW pigments constituted a marker of the pigment's historical synthesis and postsynthesis treatments, leading to the production of different LW qualities.[8−12] By implementing synchrotron radiation high-angular resolution X-ray powder diffraction (SR-HR-XRPD) and micro Fourier transform infrared spectroscopy (μ-FTIR) to gather new clues on the *Mona Lisa*'s ground layer, a very uncommon composition was discovered. This led us to question Leonardo's writings and to study additional paint fragments from his *Last Supper*, also based on an LW preparatory layer, that were studied by synchrotron radiation micro X-ray powder diffraction (SR-μ-XRPD) and μ-FTIR. These converging clues lead us to propose a new hypothesis regarding the formulation used by Leonardo in his paintings.

■ RESULTS AND DISCUSSION

Crystalline Phases in Mona Lisa's Ground Layer. The unembedded *Mona Lisa*'s white ground fragment was analyzed by SR-HR-XRPD (ESRF, ID22 beamline, details in Supporting Information, Section 2.1). Unsurprisingly, the main diffraction peaks were assigned to HCer and Cer, confirming the assumptions made from SEM−EDS analyses regarding the use of the LW pigment (Figure 2). More unexpectedly, some additional faint and diffuse lines could be noticed (Figures 2 and S2), revealing the presence of the plumbonacrite $Pb_5(CO_3)_3O(OH)_2$ (PN). The diffraction pattern of this phase consisted in a few faint peaks, all strongly broadened and often overlapped by those of HCer or Cer, but unambiguous. Besides, the unique intense 104 peak of calcite (again in agreement with SEM−EDS results) was observed at 0.6% of the intensity of the main HCer peak. No other crystalline phase was observed, despite mineral extenders such as gypsum

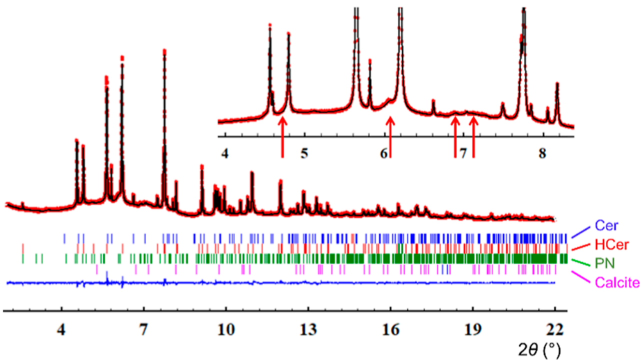

Figure 2. Whole Rietveld plot and low-angle zoom for the SR-HR-XRPD pattern of the *Mona Lisa*'s ground layer sample collected at λ = 0.354693 Å. Red dots: raw data (iobs), black line: calculated data (icalc), blue line: iobs − icalc, and bars: Bragg positions for Cer, HCer, PN, and calcite. Upper right: arrows indicate the diffuse PN peaks.

$CaSO_4 \cdot 2H_2O$ or silica SiO_2 sometimes being used during the Italian Renaissance.

Rietveld analysis allowed the assessment of the ratios of the lead carbonates and the microstructure of the crystallites (Figures S3 and S4). The mineral composition was found to be 11(1) w % Cer, 76(2) w % HCer, and 13(3) w % PN, along with 0.3(1) w % calcite. The presence of PN was all the more unexpected as this rare lead carbonate was never detected during our previous XRPD analyses on Italian Renaissance corpuses.[9] Until now, it had been reported once in a fragment from a painting by Vincent van Gogh and was ascribed to the photodegradation of red lead pigment (minium Pb_3O_4)[13] and more recently in several paintings by Rembrandt, notably in his *impasto* (thick LW-based paint used to confer tridimensional rendering).[14,15]

Another striking similarity between *Mona Lisa*'s ground and Rembrandt's *impasto* is the low level of cerussite in the LW pigment. Concerning the former, the composition (Cer/HCer/PN = 11/76/13 w %) clearly departs from the usual values measured on other Renaissance paintings (in average ∼ 30/70/0 w %), including Leonardo's *Belle Ferronière* (36/64/0 w %) (Louvre, FR) and *The Virgin and Child with Saint Anne* (54/46/0 w % in layer, 35/65/0 w % in priming) (Louvre, FR).[3,9,11] The depletion in Cer together with the presence of PN is also observed in Rembrandt's *impasto* but at an even greater extent [Cer/HCer/PN = 1/60/39, 2/70/28, and 9/70/21 w % as measured in three samples from *the Portrait of*

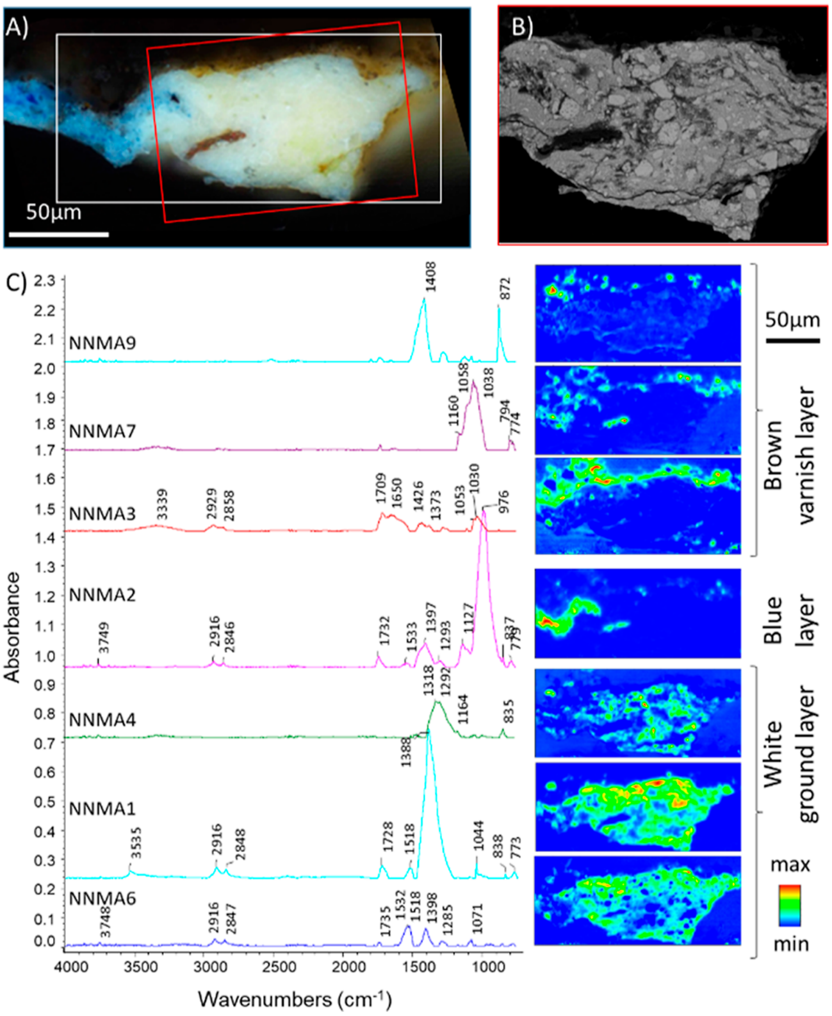

Figure 3. Analysis of the cross section of the embedded fragment taken from the *Mona Lisa* painting. (A) Optical light microscopy. The white rectangle displays the area mapped via micro-FTIR while the red rectangle shows the area mapped by SEM−EDS (elemental maps displayed in Figure S5). (B) SEM-BSE map. (C) μ-FTIR map with NNMA vectors and maps. Components 0, 5, and 8 are shown in Figure S6.

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Marten Soolmans (Rijksmuseum, NL), *Susanna* (Mauritshuis, NL), and *Bathsheba at Her Bath* (Louvre, FR), respectively], while the other colored layers of the same artworks show usual LW compositions, without PN.[14] While the pictorial practices of these two painters cannot be compared, in terms of either materials or techniques, the clear inverse correlation between the concentrations of Cer and PN in paintings by the two artists could be seen as a common signature of the process(es) they used.

The microstructural analysis derived from the peak profiles of the *Mona Lisa* fragment showed that HCer (rhombohedral) and PN (hexagonal), both with related 2D crystal structures, adopt the usual (001) lamellar habitus. The average thickness of the HCer platelets was assessed through a Williamson−Hall analysis based on 11 strong, nonoverlapped diffraction peaks (Figures S3 and S4). Concerning PN, peak 115 was the only one suitable, but its marked Lorentzian broadening also accounted for a predominant size effect; therefore, the mean PN platelet thickness was simply estimated using the Scherrer formula. The obtained L001 values for HCer was 80(10) nm vs ∼100 nm in Rembrandt's *impastos*.[14] Concerning PN, the thickness was found to be identical (∼10 nm) for the two artists, suggesting an *in situ* formation of the crystallites in both cases.

As PN is only stable in an alkaline environment, it is then hypothesized that its growth could have resulted from chemical reactions involving an alkaline lead compound, such as lead oxide $Pb^{II}O$, a Brønsted base commonly used in Renaissance painting as a siccative (or drier) as reported in several treaties of this time.[16−18] For example, Théodore Turquet de Mayerne (1620) explains how to prepare a thick paste and improve oil drying, by dissolving one part of PbO in four parts of heated nut oil.[19] A reconstruction of this recipe led to the oil saponification by PbO, with the formation of lead carboxylates (long chain Pb soaps).[20,21] Upon drying, other crystals were detected in this cooked oil, notably lead formate[15] and PN.[15,17]

Accordingly, it was essential to analyze the molecular composition of *Mona Lisa*'s cross section and track the presence of similar organo-lead compounds. This was achieved using μ-FTIR mapping (details in Supporting Information, Section 2.3) applied to the embedded sample, over the white rectangle as shown in Figure 3A. The μ-FTIR map was processed using statistical non-negative matrix approximation (NNMA) analysis on the basis of 10 components (details in Supporting Information, Section 2.3).[22] The white ground layer encompasses several NNMA components (NNMA1, NNMA4, and NNMA6, Figure 3C). The main one, NNMA1, shows the characteristic peaks of LW [ν(OH) at 3535 cm^{-1}, broad and intense $\nu_3(CO_3)$ at 1388 cm^{-1}, and small and sharp ν_1 and $\nu_2(CO_3)$ at 1044 and 838 cm^{-1}][23] mixed with a partially saponified oil [ν(CH) series at 2916 and 2848 cm^{-1}, ν(CO ester) at 1728 cm^{-1}, and asymmetric ν(CO lead carboxylate) at 1518 cm^{-1}]. While NNMA1 is homogeneously distributed in the ground, NNMA4 rather highlights aggregates (∼5−10 μm) containing only inorganic components (no CH, no organic CO). The NNMA4 spectrum shows similarity to that of LW but with subtle differences: a broader and less intense $\nu_1(CO_3)$ peak at 1045 cm^{-1}, a more intense $\nu_2(CO_3)$ peak red-shifted to 835 cm^{-1}, and a broader and less intense peak at $\nu_3(CO_3)$ red-shifted to 1345 cm^{-1} with an intense and broad shoulder at 1280 cm^{-1}. Comparison with the literature[23,24] has not allowed the identification of this component. In contrast to HR-XRPD, FTIR is not an efficient probe to detect PN when mixed with LW as its main signature peaks overlap with those of HCer and Cer.[23,24] NNMA6 gives a very good match with a strongly saponified oil [ν(CH) series at 2916 and 2847 cm^{-1}, weak ν(CO ester) at 1735 cm^{-1}, strong asymmetric ν(CO lead carboxylate) at 1532−1518 cm^{-1}, and strong symmetric ν(CO lead carboxylate) at 1398 cm^{-1}][18] without LW and is interlaced with NNMA1 in the white layer.

The blue layer is represented by NNMA2 and contains a mixture of ultramarine pigment (confirming SEM−EDS results) and LW with partially saponified oil.

The yellowish varnish at the sample surface contains mainly NNMA3, present as a diffused matrix, and which may contain an alumina-silicate such as montmorillonite (also present in the NNMA7, distributed as some particles) and some organic material that could be a natural resin [ν(CH) series at 2929 and 2858 cm^{-1} and ν(CO) at 1709 cm^{-1}].[25] Calcite ($CaCO_3$) particles are also present in this brown varnish as highlighted in NNMA9 (in agreement with SEM−EDS and HR-XRPD). The NNMA0 and NNMA5 components correspond to the embedding resin. NNMA8 shows CO_2 artifact signals (Figure S6).

The comparison of NNMA1, NNMA6, and NNMA2 (in particular, the soap versus ester ratio) clearly underlines a higher saponification rate in the ground white layer compared to the blue paint layer (Figure S7). This strongly supports the hypothesis that Leonardo used a specific preparation for the ground layer, in particular a highly saponified oil (containing a higher amount of lead soaps). This is also supported by the diffuse presence of Pb in the oil matrix (dark gray in SEM-BSE image in Figure 3B) surrounding the LW pigment particles (5−10 μm, lighter gray) in the white ground layer. The absence of the LW signal in NNMA6 vector supports the fact that the main lead agent responsible for saponification was a drier, such as lead oxide, rather than the LW pigment.

Lead II Oxide: Terminology, Use as a Painting Material, and References in Leonardo's Writings. From the foregoing, the use of a specific, strongly saponified oil for the making of the ground layer of the *Mona Lisa* appears possible and is linked with the presence of PN and the low Cer level insofar as these compounds are respectively the most basic and the most acidic lead carbonates. To evaluate the hypothesis that Leonardo used PbO for the ground layer of the *Mona Lisa*, it was decided to review his manuscripts (original and earliest translations) tracking for the occurrence of terms that could be related to lead oxide. Here, explanations about the chemical nature, historical use, and naming of PbO compounds in historical treatises are necessary.

From the chemical point of view, lead II oxide is a polymorph with two varieties: α-PbO or litharge is the tetragonal, orange-red form stable at room temperature while β-PbO or massicot is the orthorhombic, yellow high-temperature form. The reversibility of the phase transition depends on the cooling rate, so β-PbO can be quenched easily. Both occur naturally as rare minerals. Litharge is also an intermediate product in the formation of minium (also named red lead) Pb_3O_4 (or $Pb^{II}_2Pb^{IV}O_4$), obtained by roasting lead or LW, but excessive heating may lead to the reduction of Pb_3O_4 into β-PbO. As a result, the traditional red lead pigments often contain substantial amounts of residual lead monoxide, in either litharge or massicot crystalline forms.[26,27]

From the art historical standpoint, terminology is much more complex. "*Litharge*" (also spelled *litarge*) was originally

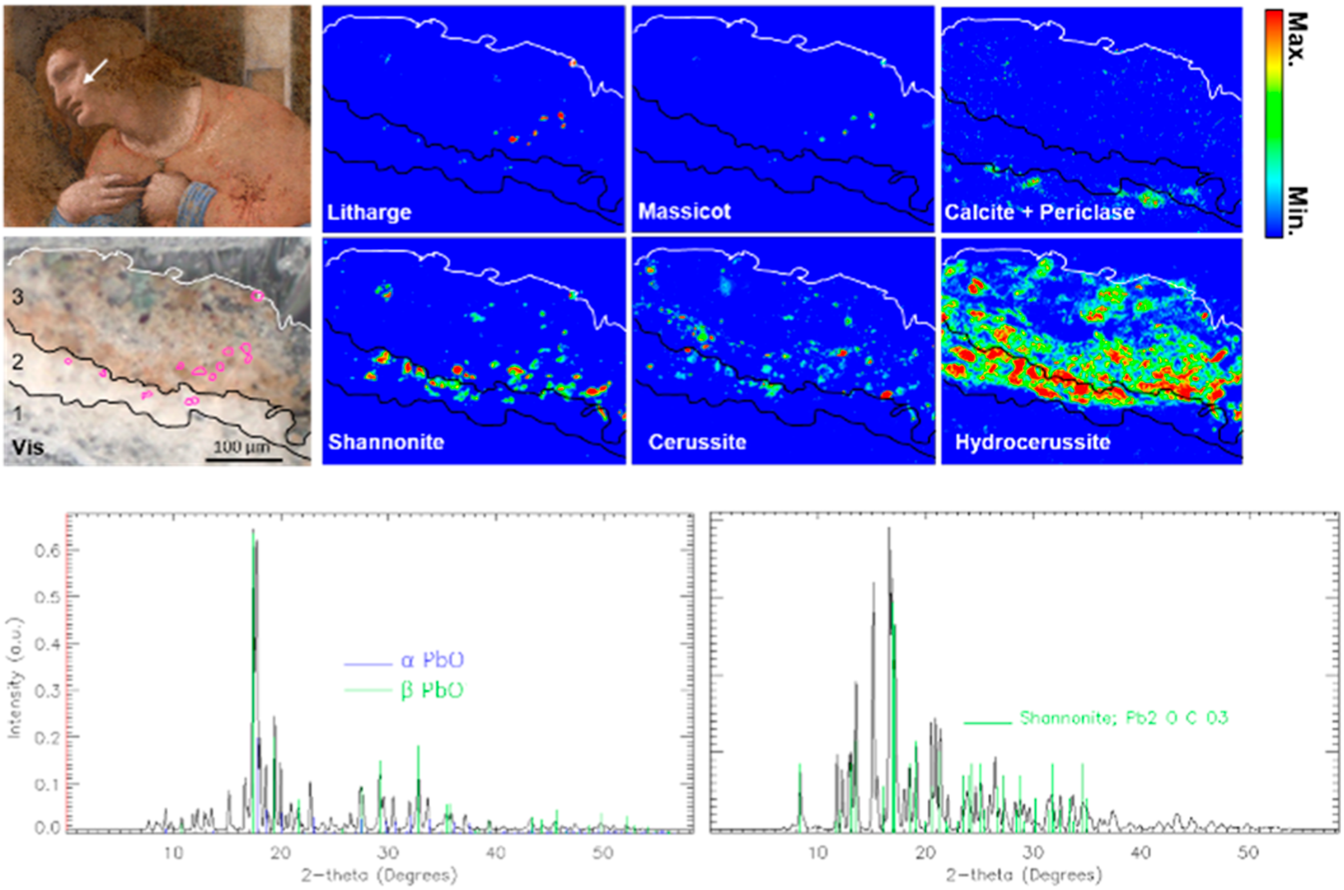

Figure 4. Detail of the *Last Supper* where the fragment (L)A10 was sampled in Philip's face (flesh tone) (white arrow). Visible OM image and SR-μ-XRPD maps of the thin section. Numbers 1, 2, and 3 in the visible image denote: 1—ground layer, 2—priming layer, and 3—colored layers. SR-μ-XRPD (map size: 400 × 300 μm^2, step size: 1 × 1 μm^2) distribution of lead crystalline phases. The average XRPD patterns calculated over hot spots of shannonite and α/β-PbO are presented.

referring to a byproduct of cupellation of precious metals, in particular silver, hence its Greek etymology, from λίθος "*stone*" and άργυρος "*silver*" and its name in Latin pharmacopeia "*spuma argenti*", i.e., *silver foam*. To extract silver from silver−lead ores by cupellation, the ores had to be heated until they melted and oxidized when in contact with air. The so-formed "*litharge*" was then carefully removed to recover pure silver.[28,29] In practice, both α-PbO and β-PbO could be obtained by this process, the exact composition depending on the temperature and cooling during the cupellation process.[29] "*Litharge*" has been extensively mentioned since Antiquity in admixture with fats and oils to prepare pharmaceutical pastes and ointments.[16] In paintings, "*litharge*" is most frequently cited in historical European sources in the context of driers (siccatives) added to oil,[16,17,27,29] with only few occurrences as a pigment.[27] In practice, the product sold by paint manufacturers under the name "*litharge*" is usually a mixture of the two polymorphs.

Regarding "*massicot*", there is more confusion about the terminology in historical paint treatises and about the exact chemical compound(s) designated under this name. The word "*massicot*", also written as *macicot* or *masticot*, comes from *marzachotto* which referred to a glaze on faience.[27] Through history, the Dutch, French, and English term "massicot" could have been used to designate different lead-based yellow pigments, notably a pigment made of lead and tin, but sometimes pigments made of lead only.[27,30] In historical Italian texts, such pigments were rather called under the name *giallolino* (also written *gialolino*, *gialdolino*, or *gialorino*) with a similar confusion about the chemical composition of the referred pigments.[27,30,31] In addition to a synthetic yellow lead oxide analogue of massicot[30,31] and a synthetic lead−tin yellow pigment (of which manufacture is described in 15th century Bolognese manuscript, and which has been identified as Pb_2SnO_4, type I),[27,31,32] "*giallolino*" has been used to designate a natural yellow mineral pigment found in the neighborhood of volcanoes[30] and a synthetic lead antimonate yellow as well[30] (first mentioned at the end of the 17th century, mainly used as a pigment from 1750 to 1850, and usually named in English as "Naples yellow"). In several historical Italian texts (including those written by Leonardo), the name "*giallolino*" has been translated in French and English by "*massicot*".[31] The hypotheses of the nature of the different pigments designated as "*giallolino*" or "*massicot*" are based on the analysis and reproduction of historical recipes as well as on the comparison between the frequency of these names in texts and the occurrences of these pigments in artworks. Some recipes clearly describe the synthesis of *giallolino* or *zallolino* by the association and calcination of tin and lead making clear the meaning of *giallolino* to designate the abovementioned lead−tin yellow pigment.[27,32] However, few other recipes from the late 16th century indicate that *giallolino* is obtained by calcinating lead or LW, leading some authors to associate this name to β-PbO, also yellow.[27,31,33] The pigment named

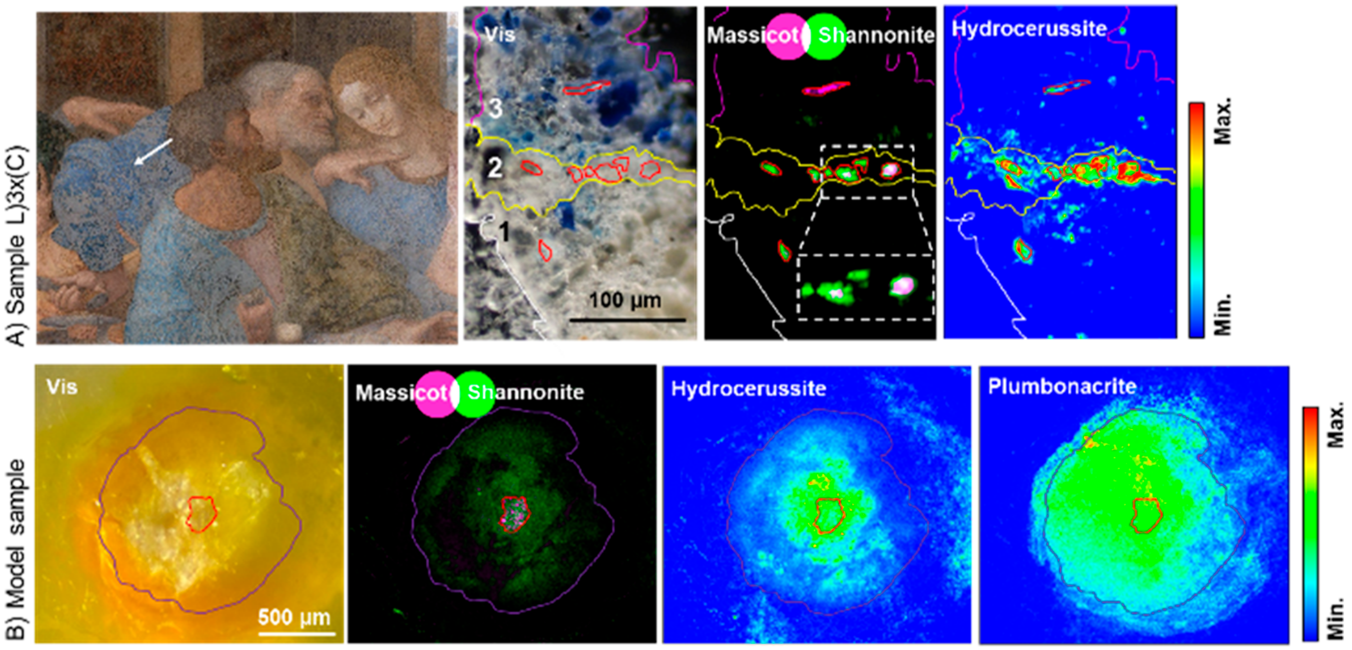

Figure 5. Visible OM images and SR-μ-XRPD maps of samples. (A) Historical sample (L)3×(C) sampled from the *Last Supper*, in Peter's mantle (blue) (white arrow) and (B) model sample containing linseed oil cooked with PbO and water and in which additional PbO particles were added at room temperature (named "PaWetPbO" in our previous work[15]). Numbers 1, 2, and 3 in the visible images denote: 1—ground layer, 2—priming layer, and 3—layers. SR-μ-XRPD distribution of PbO, shannonite, PN, and HCer in these samples is presented by the magenta-green and red-green-blue color models. PN was not detected in this historical sample. A zoomed area (white dotted line) is inserted in part A to show the core–shell like structure formed by shannonite at the surface of PbO particles.

"*giallolino*" became more confusing with a progressive shift of meaning over time. While it is now accepted that from "the 18th or early 19th century the term "massicot" came to be applied to lead monoxide",[27] the almost absence of PbO and the frequent detection of lead–tin yellow pigment in earlier paintings support the hypothesis that until the end of the 16th century, *massicot* and *giallolino* designate mainly lead–tin yellow pigments. Finally, an additional degree of complexity is found in the fact that the lead–tin yellow pigment usually contains traces of β-PbO.

A detailed analysis of the collection of the editions of Leonardo's work (his manuscripts, some transcripts published since 1651 and main historical translations) [https://www.leonardodigitale.com/en/] is presented in the Supporting Information. In brief, the most relevant and conclusive finding is in *Codice Arundel*, a collection of texts written by Leonardo between 1480 and 1518. It contains one mention of the literature, under the spelling of *letargirio di pionbo*, to prepare remedies to treat skin and hair. This recipe proves that this compound was at Leonardo's disposal and reminds us how he was not only interested in arts and paintings but also in sciences and medicine and that pharmaceutical practices might have influenced his painting techniques.

For "*massicot*", observations are less reliable. Despite the fact that several French and English translations mention the word "*macicot*" or "*masticot*", respectively (for example in the recipe on "how to secure a painting from decay and to preserve it always fresh and unfaded"), the original word used by Leonardo in his *Trattato della pittura* ("*gialorino*") may have designated the lead–tin yellow pigment, rather than lead oxide. The detailed study of the occurrences of the word *giallo* and associated terms such as *giallolino* or *giallorino* in Leonardo's writing is given in Table S2. It highlights the difficulty in assessing the actual mention of massicot (i.e., β-PbO) in Leonardo's texts following the successive posterior translations of original painting treatises.

More Experimental Clues on the Use of PbO by Leonardo. Until today, the only reported use of PbO by Leonardo was in microsamples from the *Last Supper* (c. 1495–1498, Convent of *Santa Maria delle Grazie*, Milan, Italy),[34] although the detailed analytical proofs of this finding remained unpublished. The *Last Supper* is a unique artwork for many reasons, one of them being the painting technique explored by Leonardo for its execution. Instead of using a traditional *fresco* approach, he experimented with the application of drying oil typical of easel paintings but on a wall. For this purpose, he prepared the refectory wall of *Santa Maria delle Grazie*, using an unusual buildup made of a plaster layer of calcium and magnesium carbonates, covered with a LW priming offering a white surface for the application of the paint layers. This white layer enhances the luminosity of the above colored layers as indicated by Leonardo da Vinci himself.[4,34]

To fully assess the suspected presence and the in-depth distribution of PbO over the paint stratigraphy, 17 samples from the *Archivio Gallone* (hosted in the Physics Department of the *Politecnico di Milano*) were recently reanalyzed using SR-μ-XRPD (ESRF, ID13 beamline; details in Supporting Information, Section 2.4).[35] Thin sections (10 μm) were prepared from the historical cross sections following a procedure detailed elsewhere.[11] Results on the distribution of crystalline phases in the probed thin sections are summarized in Table S1 and illustrated with one sample [named (L)A10] taken from the flesh tones of the Apostle Philip (Figure 4).

Based on visual observations of the thin sections, three different types of layers can be distinguished: (1) a translucent white ground layer, (2) an opaque, ~50 μm white layer denoted as the priming layer, and (3) one or several colored layers. SR-μ-XRPD maps revealed a clear chemical signature among the three different regions. The ground layer contains mainly calcium and magnesium carbonate-based compounds.[34] Unsurprisingly, high amounts of HCer and some Cer were found in the priming layer, clearly separating the ground layer from the colored paint layers but also spreading throughout the colored layers where they are mixed with various pigments. Cer is usually observed as individual particles while HCer forms a rather homogeneous matrix.

The presence of intact PbO grains, both α-PbO and β-PbO, was indeed confirmed in 12 of the 17 samples, proving that PbO was one of the components of Leonardo's palette. Although the composition of the *Last Supper* samples is complex and heterogeneous, general trends could be drawn on the distribution of PbO and other correlated lead-based compounds (Table S1). In brief, in most cases, both PbO forms (litharge and massicot) were found in the priming layer as well as spread throughout the colored paint layers. Interestingly, they were detected in both blue and orange paint layers. In the priming layer, the PbO particles are usually surrounded by a layer of neo-formed lead carbonate, shannonite (Pb_2OCO_3). PN was also detected in seven samples in the priming layer and further spread throughout the colored paint matrix often as small particles.

The case of the *Last Supper* is particularly interesting as it shows that crystalline PbO can be present in historical paint layers and remain uncarbonated after more than 500 years. In our opinion, shannonite and PN both derive in that case from the carbonation of PbO. Shannonite here might be interpreted as an intermediate form between PbO and PN. According to the literature, this would be the first time that shannonite is detected in an historical painting.[36] By analyzing model samples prepared following historical recipes of oil treated with PbO, we previously reported the formation of lead carboxylates,[20,21] PN, and lead formate.[15] Besides, we have observed in some of these samples, in particular around PbO particles, the *in situ* crystallization of layers of shannonite, PN, and HCer (Figure 5A). This core−shell like structure is also observed in samples from the *Last Supper*, in which shannonite is clearly formed around a nucleus of PbO (Figure 5B). In both historical and model samples, the large size of PbO particles, in particular in the *Last Supper* priming, may explain that both PbO and shannonite are still present and have not fully converted into the less alkaline PN and ultimately HCer. The fact that PbO/shannonite/PN were detected both in orange and in blue paint layers of the *Last Supper* suggests that PbO could have been used for its drying properties rather than for pigmentation. The *Last Supper* fragments were also analyzed by a synchrotron-based FTIR microscope (Figure S9). Maps revealed the presence of lead carboxylates in the priming and colored layers, which can be interpreted as the result of oil saponification by PbO.

■ CONCLUSIONS

At the time Leonardo began painting the *Mona Lisa*, around 1503, the ground layer made of a LW−oil mixture was still a novelty in Italy,[2,37] maybe even an experiment as most artists still used *gesso* for this purpose. A similar oil-based layer also composes the *Last Supper* priming. The detection of PbO, together with shannonite and PN in the *Last Supper*, and the detection of PN in the *Mona Lisa* suggest that in both cases Leonardo aimed at preparing a strongly siccative preparatory layer. In the colored layers of the *Last Supper*, it can be hypothesized that he used a similar oil mixed with PbO. The growth of PN and shannonite crystallites, despite the most visible signature of Leonardo's processes, was probably not the goal but a simple consequence of the strong alkalinity of the medium. Besides, previous studies on the drying effect of metal salts have shown that "*slow-drying paints can be made to dry faster by applying them over a quicker-drying paint or an accelerating substrate*".[38] Perhaps Leonardo achieved this effect in the *Mona Lisa* and *Last Supper*, but in the current state of our knowledge and in the absence of written descriptions of the artist's recipes, this can only be suggested as another hypothesis.

The presence of PN as well as shannonite in the *Last Supper* motivates us to further analyze and track the presence of such unusual lead-based mineral phases in other artworks by Leonardo and his contemporaries. It is quite probable that using highly sensitive probes such as SR-based XRPD combined with careful data analysis, such neo-formed compounds will be discovered in other paint samples. The presence of these phases together with the low cerussite level in the preparatory layers of both the *Mona Lisa* and *Last Supper* is probably the mere consequence of the resulting alkalinity from a PbO-based medium. These features raise questions about the mechanism at stake. In a follow-up article, we will explore through dedicated experiments on model paints the reaction pathways likely to yield such a particular composition by analyzing the interactions between the oil medium, lead oxide, and the LW pigment. Another aspect deserving future investigations is the effect of such a formulation containing PbO on the paint's physical properties, notably in terms of rheological behavior.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c07000.

> Information on the paint microsamples from the *Mona Lisa* and *Last Supper*; details on the analytical methods: SR-HR-XRPD and Rietveld procedure, SR-μ-XRPD, SEM−EDS, μ-FTIR; final Rietveld plots for the *Mona Lisa* ground layer sample; Williamson−Hall analysis of the hydrocerussite crystallites; SEM−EDS elemental maps; complementary μ-FTIR results; complementary SR-μ-XRPD results obtained on fragments from the *Last Supper*; and bibliographic research of the mention of lead oxide in Leonardo's texts (PDF)

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ABBREVIATIONS

LW, lead white; HCer, hydrocerussite; Cer, cerussite; PN, plumbonacrite; SEM, scanning electron microscopy; EDS, energy-dispersive spectroscopy; BSE, backscattered electrons; SR, synchrotron radiation; HR-XRPD, high-angular resolution X-ray powder diffraction; μ-XRPD, micro X-ray powder diffraction; OM, optical microscopy; μ-FTIR, micro Fourier transform infrared spectroscopy; NNMA, non-negative matrix approximation

REFERENCES

(1) Delieuvin, V.; Frank, L. *Léonard de Vinci*; Louvre éditions, 2019.

(2) Ravaud, E.; Eveno, M.; Bastian, G. *L'art de la matière*; L'art et la manière, Léonard de Vinci, 2019; pp 358−369.

(3) Gonzalez, V.; Hageraats, S.; Wallez, G.; Eveno, M.; Ravaud, E.; Réfrégiers, M.; Thoury, M.; Menu, M.; Gourier, D. Microchemical analysis of Leonardo da Vinci's lead white paints reveals knowledge and control over pigment scattering properties. *Sci. Rep.* **2020**, *10* (1), 21715.

(4) Barcilon, P. B.; Marani, P. C. *Leonardo: The Last Supper*; University of Chicago Press, 2001.

(5) Mohen, J. P.; Menu, M.; Mottin, B. *Au cœur de la Joconde*; Louvre éditions, 2006.

(6) Gettens, R. J.; Kühn, H.; Chase, W. T. 3. Lead White. *Stud. Conserv.* **1967**, *12* (4), 125−139.

(7) Gonzalez, V.; Wallez, G.; Calligaro, T.; Gourier, D.; Menu, M. Synthesizing lead white pigments by lead corrosion: New insights into the ancient manufacturing processes. *Corros. Sci.* **2019**, *146*, 10−17.

(8) Gonzalez, V.; Calligaro, T.; Pichon, L.; Wallez, G.; Mottin, B. Leonardo da Vinci's drapery studies: characterization of lead white pigments by μ-XRD and 2D scanning XRF. *Appl. Phys. A: Mater. Sci. Process.* **2015**, *121* (3), 849−856.

(9) Gonzalez, V.; Calligaro, T.; Wallez, G.; Eveno, M.; Toussaint, K.; Menu, M. Composition and microstructure of the lead white pigment in Masters paintings using HR Synchrotron XRD. *Microchem. J.* **2016**, *125*, 43−49.

(10) Gonzalez, V.; Gourier, D.; Calligaro, T.; Toussaint, K.; Wallez, G.; Menu, M. Revealing the origin and history of lead-white pigments by their Photoluminescence properties. *Anal. Chem.* **2017**, *89* (5), 2909−2918.

(11) Gonzalez, V.; Wallez, G.; Calligaro, T.; Cotte, M.; De Nolf, W.; Eveno, M.; Ravaud, E.; Menu, M. Synchrotron-Based High Angle Resolution and High Lateral Resolution X-ray Diffraction: Revealing Lead White Pigment Qualities in Old Masters Paintings. *Anal. Chem.* **2017**, *89* (24), 13203−13211.

(12) De Meyer, S.; Vanmeert, F.; Vertongen, R.; Van Loon, A.; Gonzalez, V.; Delaney, J.; Dooley, K.; Dik, J.; Van der Snickt, G.; Vandivere, A.; Janssens, K. Macroscopic x-ray powder diffraction imaging reveals Vermeer's discriminating use of lead white pigments in Girl with a Pearl Earring. *Sci. Adv.* **2019**, *5* (8), No. eaax1975.

(13) Vanmeert, F.; Van der Snickt, G.; Janssens, K. Plumbonacrite Identified by X-ray Powder Diffraction Tomography as a Missing Link during Degradation of Red Lead in a Van Gogh Painting. *Angew. Chem.* **2015**, *127* (12), 3678−3681.

(14) Gonzalez, V.; Cotte, M.; Wallez, G.; van Loon, A.; de Nolf, W.; Eveno, M.; Keune, K.; Noble, P.; Dik, J. Unraveling the Composition of Rembrandt's Impasto through the Identification of Unusual Plumbonacrite by Multimodal X-ray Diffraction Analysis. *Angew. Chem., Int. Ed.* **2019**, *58* (17), 5619−5622.

(15) Gonzalez, V.; Fazlic, I.; Cotte, M.; Vanmeert, F.; Gestels, A.; De Meyer, S.; Broers, F.; Hermans, J.; van Loon, A.; Janssens, K.; et al. Lead (II) Formate in Rembrandt's Night Watch: Detection and Distribution from the Macro-to the Micro-scale. *Angew. Chem.* **2023**, *135* (16), No. e202216478.

(16) Cotte, M.; De Viguerie, L.; Checroun, E.; Susini, J.; Walter, P. Historical evolutions of lead-fat/oil formula from Antiquity to modern times in a set of European pharmaceutical and painting treatises. In *Metal Soaps in Art*; Springer, 2019; pp 85−106.

(17) Cotte, M.; Checroun, E.; De Nolf, W.; Taniguchi, Y.; De Viguerie, L.; Burghammer, M.; Walter, P.; Rivard, C.; Salomé, M.; Janssens, K.; Susini, J. Lead soaps in paintings: Friends or foes? *Stud. Conserv.* **2017**, *62* (1), 2−23.

(18) de Viguerie, L.; Payard, P. A.; Portero, E.; Walter, P.; Cotte, M. The drying of linseed oil investigated by Fourier transform infrared spectroscopy: Historical recipes and influence of lead compounds. *Prog. Org. Coat.* **2016**, *93*, 46−60.

(19) Mayerne, T. T. D. *Pictoria, Sculptoria, Tinctoria, et quae subalternarum artium (manuscript)*; British Museum London, Ms. Sloane 2052, 1620−1646.

(20) Cotte, M.; Checroun, E.; Susini, J.; Dumas, P.; Tchoreloff, P.; Besnard, M.; Walter, P. Kinetics of oil saponification by lead salts in ancient preparations of pharmaceutical lead plasters and painting lead mediums. *Talanta* **2006**, *70* (5), 1136−1142.

(21) Cotte, M.; Checroun, E.; Susini, J.; Walter, P. Micro-analytical study of interactions between oil and lead compounds in paintings. *Appl. Phys. A: Mater. Sci. Process.* **2007**, *89* (4), 841−848.

(22) Cotte, M.; Fabris, T.; Agostini, G.; Motta Meira, D.; De Viguerie, L.; Solé, V. A. Watching kinetic studies as chemical maps using open-source software. *Anal. Chem.* **2016**, *88*, 6154−6160.

(23) Brooker, M. H.; Sunder, S.; Taylor, P.; Lopata, V. J. Infrared and Raman spectra and X-ray diffraction studies of solid lead(II) carbonates. *Can. J. Chem.* **1983**, *61* (3), 494−502.

(24) Siidra, O.; Nekrasova, D.; Depmeier, W.; Chukanov, N.; Zaitsev, A.; Turner, R. Hydrocerussite-related minerals and materials: structural principles, chemical variations and infrared spectroscopy. *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.* **2018**, *74* (2), 182−195.

(25) Derrick, M.; Stulik, D.; Landry, J. M. *Infrared spectroscopy in conservation science*; The Getty conservation institute ed., 1999; p 235.

(26) Anthony, J.; Bideaux, R.; Bladh, K.; Nichols, M. *Handbook of Mineralogy, 1*; Chantilly, Ed.; Mineralogical Society of America, 2003; p 588.

(27) Eastaugh, N.; Walsh, V.; Chaplin, T.; Siddall, R. *Pigment compendium: a dictionary of historical pigments*; Routledge, 2007.

(28) Schenk, A.; Meisser, N. Un tube de litharge dans le palais de Derrièrre la Tour, und découverte inédite à Avenches. Bulletin de l'Association Pro Aventico 2014, *55*, 209−220.

(29) Zumbühl, S.; Zindel, C. *Historical Siccatives for Oil Paint and Varnishes—the Use of Lead Oxide, Alum, White Vitriol, Pumice, Bone Ash and Venetian Glass as Driers: Historical Written Sources—Production and Raw Material Quality—Technological Significance*, 2022.

(30) Feller, R. L. *Artist's pigments: a handbook of their history and characteristics*; Archetype Publications, 1986; Vol. *1*.

(31) Merrifield, M. M. P. *Medieval and renaissance treatises on the arts of painting: Original texts with English translations*; Courier Dover Publications: Mineola, 1999.

(32) Kühn, H. Lead-tin yellow. *Stud. Conserv.* **1968**, *13* (1), 7−33.

(33) Seccaroni, C. *Giallorino: storia dei pigmenti gialli di natura sintetica: dal vetro giallo per patre nostro o ambre al giallo di Napoli*; De Luca Ed.i d'Arte, 2006.

(34) Newton, H. T. Leonardo da Vinci as mural painter: some observations on his materials and working methods. *Arte Lomb.* **1983**, *66*, 71−88.

(35) Gonzalez, V.; Cotte, M.; Vanmeert, F.; de Nolf, W.; Janssens, K. X-ray Diffraction Mapping for Cultural Heritage Science: a Review of Experimental Configurations and Applications. *Chem.—Eur. J.* **2020**, *26*, 1703−1719.

(36) Gliozzo, E.; Ionescu, C. Pigments—Lead-based whites, reds, yellows and oranges and their alteration phases. *Archaeol. Anthropol. Sci.* **2022**, *14* (1), 17−66.

(37) Dunkerton, J.; Spring, M. The development of painting on coloured surfaces in sixteenth-century Italy. *Stud. Conserv.* **1998**, *43* (sup1), 120−130.

(38) Tumosa, C. S.; Mecklenburg, M. F. The influence of lead ions on the drying of oils. *Stud. Conserv.* **2005**, *50* (sup1), 39−47.