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Citation for published version (APA):

Gonzalez, V., Cotte, M., Wallez, G., van Loon, A., de Nolf, W., Eveno, M., Keune, K., Noble, P., & Dik, J. (2019). Unraveling the Composition of Rembrandt's Impasto through the Identification of Unusual Plumbonacrite by Multimodal X-ray Diffraction Analysis. *Angewandte Chemie*, *131*(17), 5675-5678. https://doi.org/10.1002/ange.201813105, https://doi.org/10.1002/anie.201813105

Unraveling the Composition of Rembrandt's Impasto through the Identification of Unusual Plumbonacrite by Multimodal X-ray Diffraction Analysis

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Abstract: *Rembrandt (1606–1669) is renowned for his impasto technique, involving his use of lead white paint with outstanding rheological properties. This paint was obtained by combining lead white pigment (a mixture of cerussite $PbCO_3$ and hydrocerussite $Pb_3(CO_3)_2(OH)_2$) with an organic binding medium, but the exact formulation used by Rembrandt remains a mystery. A powerful combination of high-angle and high-lateral resolution x-ray diffraction was used to investigate several microscopic paint samples from four Rembrandt masterpieces. A rare lead compound, plumbonacrite ($Pb_5(CO_3)_3O(OH)_2$), was detected in areas of impasto. This can be considered a fingerprint of Rembrandt's recipe and is evidence of the use of an alkaline binding medium, which sheds a new light on Rembrandt's pictorial technique.*

Rembrandt van Rijn (1606–1669), probably the most famous painter of the Dutch Golden Age, is renowned for his constant search for novelty in his painting materials and techniques. Among his many innovative contributions, he revolutionized painting by adding a third dimension with his impasto, a technique whereby thick paint is laid on the canvas in an amount that makes it protrude from the surface.[1] The topography increases the perceptibility of the paint by enhancing its light-reflecting textural properties. For this achievement, Rembrandt may have been influenced by an earlier Venetian painter, Titian (ca. 1488–1576)[2] but owing to temporal and spatial distances between the two painters, they may have used different techniques. For what concerns Dutch Golden Age paintings, Rembrandt used materials tradition-ally available on the 17th century Dutch color market, namely the lead white pigment (a mixture of hydrocerussite $Pb_3(CO_3)_2(OH)_2$ (HC) and cerussite $PbCO_3$ (C) obtained by corrosion of metallic lead in acetic acid vapor- and CO_2-rich conditions[3]) and small amounts of organic media (mainly linseed oil).[1,4] However, the precise recipe that Rembrandt used to obtain his characteristic impastos from those constituents still remains unknown.

Owing to the lack of historical sources reporting Rembrandt's secrets,[4] it was essential to perform chemical characterization of lead white impasto samples to elucidate his unique recipe. In this work, we combined synchrotron high-angular resolution x-ray diffraction (HR-XRD) and micro-x-ray diffraction (μ-XRD) of microscopic fragments sampled from several Rembrandt masterpieces conserved in European museums (Rijksmuseum, Amsterdam; Louvre, Paris; and Mauritshuis, the Hague; Figure 1). The advantage of this combined approach for the analysis of historical paint micro-samples was recently demonstrated with the study of lead-white-based paints.[5] Since the main components of the impasto (lead white pigment and oil) are ubiquitous in easel paintings, whether in the paint layers or in the ground layer, we expected subtle differences in the composition of these different layers. Accordingly, six samples were collected from impasto areas and two from non-impasto paint layers, all containing lead white, for comparison.

The first step of the analysis consisted in HR-XRD bulk analysis of five small paint fragments (one from a ground layer, one from an underlayer paint layer, and three from

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/anie.201813105.

Figure 1. Some of the Rembrandt paintings sampled for this study:
a) *Portrait of Marten Soolmans*, 1634 (210×135 cm), Rijksmuseum.
b,c) Detail of the character rosette showing impasto. d) *Susanna*, 1636
(47.4×38.6 cm), Mauritshuis. e) *Bathsheba*, 1654 (142×142 cm),
Louvre.
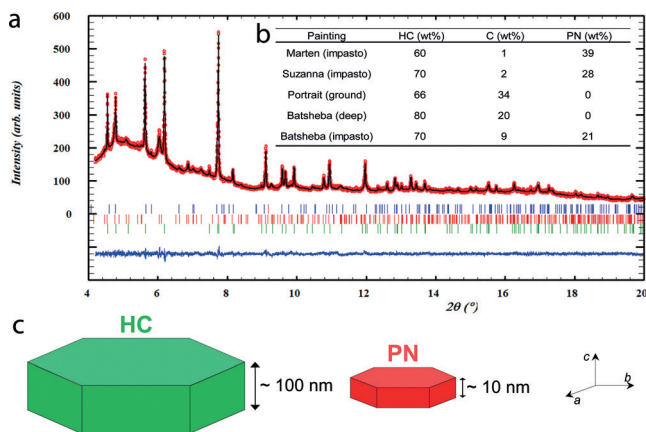
Figure 2. a) Rietveld plot for sample from the *Portrait of Marten Soolmans*, experimental (red circles), calculated (black line), difference (blue line), Bragg positions for C (blue), HC (red) and PN (green). b) Weight percentages for HC, C, and PN. c) Mean dimensions of HC and PN crystallites, produced after Rietveld refinement of the sample.

impasto layers), at the ID22 beamline (ESRF, France). XRD patterns revealed the presence of HC and C in the ground/underlayer samples, as expected (Figure 2a,b). More surprisingly, plumbonacrite, $Pb_5(CO_3)_3O(OH)_2$ (PN), was detected but specifically in impasto samples (>20 wt%). PN is extremely rare in historic paint layers. Its more notable

occurrence was linked to degradation of the red lead (minium) pigment in a Van Gogh painting.[6] It has also been reported in 20th-century paint samples, following the development of new production methods for lead white.[7] However, its presence in older artworks has not been reported. It is notably absent in the large corpus (>35) of historical lead white paints recently studied.[5,8] Another interesting result was the marginal amount (<10 wt%) of C in these samples, with HC as the main crystalline phase (Figure 2b).

To tackle the possible origins of PN, complementary analyses were carried out. For one sample (*Portrait of Marten Soolmans*), high quality HR-XRD patterns were acquired over 4 h. Rietveld refinement was performed and used to model the crystallites morphologies and sizes at the nanometric scale. For PN, the crystallite length in the c-axis (l_c) is circa 10 nm. Conversely, the HC crystals in the same impasto were significantly larger ($l_c \approx 100$ nm) (Figure 2c).
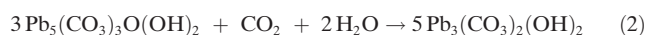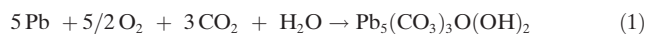
In parallel, μ-XRD phase maps were collected at the ID13 beamline (ESRF) on three other samples, two prepared as resin-embedded thick cross-sections and one prepared as a thin (10 μm) section. The objective was to localize the various Pb phases at the micron scale and obtain their distribution within the paint stratigraphies and also within each layer. The sample collected from the *Bathsheba* painting is exceptional, as it presents the lead white impasto layer on top of a lower lead white layer (Figure 3a). HC was detected in both layers, C only in the lower paint layer and PN specifically in the impasto (Figure 3b). This confirmed the unique phase composition of impastos. Moreover, other maps collected from samples from the *Portrait of Marten Soolmans* and the *Susanna* paintings more precisely revealed the distribution of tiny (ca. 5 μm) aggregates of PN crystals homogeneously throughout the impasto layer (Figure 3c,d). This homogeneous distribution does not support the idea that PN would result from a cleaning process as it would result in a higher conversion of PN at the surface of the layer and
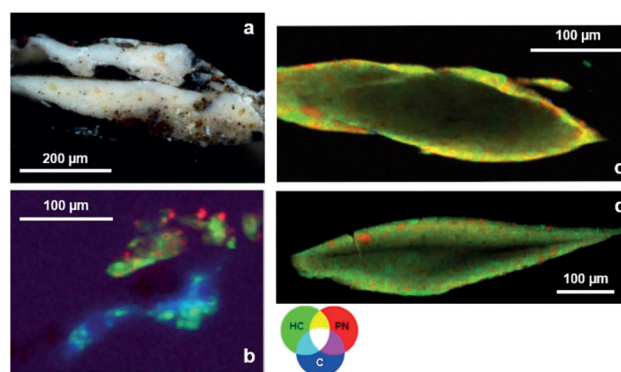
Figure 3. a) Microscopy image of the *Bathsheba* sample prepared as a polished cross-section (resin block), showing two white layers, impasto on top of an underlayer. b) μ-XRD phase maps acquired on a thin section from the *Bathsheba* sample (see the Supporting Information for the section preparation). c,d) μ-XRD phase maps acquired from a cross-section c) from the thickly painted rosette in the *Portrait of Marten Soolmans* and d) from the white drapery of *Susanna* (d). Because of the sample's thickness when prepared as resin blocks, the samples appear more opaque in the centre.

indicates that the presence of PN and the specific HC/C ratio in impasto is a marker of a specific preparation recipe.

Our first hypothesis was that PN could originate from the lead white pigment itself. In previous reconstructions of the historical recipes of lead white synthesis, we revealed that PN is indeed an intermediate crystalline phase in the traditional corrosion process of metallic lead leading to the formation of lead white (HC and C),[9] more specifically following Equations (1–3):

$$5\,Pb\ +\ 5/2\,O_2\ +\ 3\,CO_2\ +\ H_2O \rightarrow Pb_5(CO_3)_3O(OH)_2 \qquad (1)$$

$$3\,Pb_5(CO_3)_3O(OH)_2\ +\ CO_2\ +\ 2\,H_2O \rightarrow 5\,Pb_3(CO_3)_2(OH)_2 \qquad (2)$$

$$Pb_3(CO_3)_2(OH)_2\ +\ CO_2 \rightarrow 3\,PbCO_3\ +\ H_2O \qquad (3)$$

Multi-phased LWs result from an incomplete carbonation, C (cerussite) being the final product. Under these conditions, the CO_2 supply controls not only the global carbonation but also the proportions of the various phases insofar as the reactions at stake require unequal amounts of CO_2. For instance, the formation of PN from lead requires 3/5 CO_2 molecules per lead atom, versus only 1/15 for HC and 1/3 for C in the subsequent transformations. This mechanism is particularly detrimental to PN, which transforms readily into HC, thus explaining the absence of the former.

The PN film at the metal's surface always remains very thin (less than 1 μm based on the transmission of the lead XRD peaks at 1.54 Å, data not shown), and therefore cannot be found in the pigment in such high amounts as those measured (> 20 wt%). In addition, a fortuitous epitaxial relationship exists at the interface between the metallic lead and PN, whereas HC and C tend to naturally separate from PN (Figure 4). If a paint manufacturer would have accidently scraped PN, HC and C together, metallic Pb would certainly be attached to PN. These greyish PN/Pb clusters would immediately be washed away during the acidic pigment cleaning. These two considerations rule out the hypothesis of the contamination of lead white by PN during synthesis in the case of Rembrandt's impastos.

Likewise, a second hypothesis of an HC,C→PN reaction during the post-synthesis processing steps of the pigment is unlikely. PN is only stable in alkaline conditions (pH > 10);[10] and, to our knowledge, lead whites were generally washed in
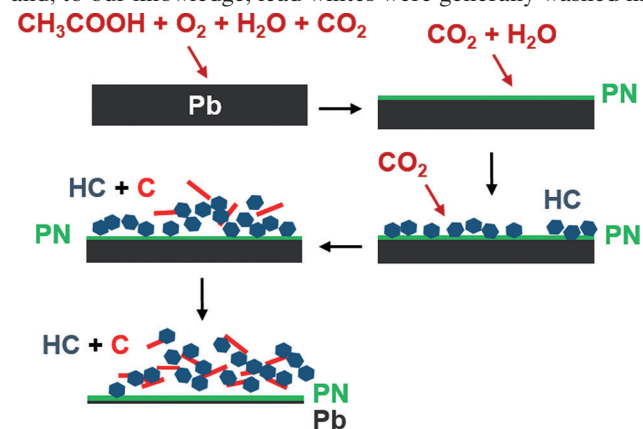
Figure 4. Schematized corrosion steps in the historical synthesis of lead white.

vinegar and/or water, not in the high-pH medium required to form PN.[9]

Our third hypothesis to explain the presence of this unusual phase is an in situ formation within the impasto layers, in alkaline conditions. The homogeneous dispersion of PN in the form of nanometric crystals points to this phenomenon.

The composition of the impasto layers and in particular the HC:C ratio is another indication of the alkalinity of the paint. In historical paints, lead white is almost always composed of a mixture of HC and C. The proportion of these two phases can be modulated during the synthesis and post-synthesis treatments, in particular by washing/grinding in vinegar and heating in water.[5] The synthesis process of lead white used during the Dutch Golden Age is remarkably stable and notably yields a pigment with a "classic" ratio HC:C > 70:30 (w%),[9] in agreement with the one measured in the two ground/underlayers studied herein (Figure 2). The much lower proportion of C (stable at pH < 6) in the impasto layers, therefore points to conversion of C into PN, triggered by an alkaline paint environment.

As discussed elsewhere, the lead from lead pigments and driers diffuses into the oil, forming a lead ionomer by binding to the oil carboxylic acids groups.[11] The binder's chemical conditions (in particular alkalinity) would be such that they would favor the recrystallization of Pb^{2+} in the form of PN crystals. This alkaline binding medium condition also supports the presence of a low C%, as it favors the conversion of C→ HC. In the present case, one possibility could be that Rembrandt may have used litharge (PbO) in the preparation of the impasto binding medium. The use of PbO as a drier by 17th century Dutch golden age painters, notably by Rembrandt and his circle in their media preparation is reported in few studies of historical sources.[4] In that report, among several hypotheses, the authors propose that Rembrandt and his followers were using heat-bodied oils to achieve the necessary texture to build impastos. As quoted in ref. [4], in 1687, John Smith recommended "heating the oil with finely powdered litharge for one hour until it was almost the thickness of treacle". Effectively, reconstructions of historical recipes of "boiled oils/olio cotto/fat oil" resulted in paste-like media completely different from the original fluid oil.[12] PbO acts both as a basic reagent for the oil saponification and as an oil drier.[13] In particular, one of these reconstructions is based on the huile de litharge recipe given by De Mayerne to produce a "thickened, rapidly drying, litharge oil [...], which does not split or crack, 1633".[14] The recipe prescribes a PbO/oil/water ratio of 1:4:4 (w%). This medium was synthesized and used to reconstruct a ground layer, without addition of any other lead compounds (in particular lead white).[15] The paint was reanalyzed by μ-XRD after nine years of natural ageing: PN was detected, not only in a large lead soap protrusion but also in all the medium, and exhibited a homogeneous distribution throughout the paint layer, impressively similar to Rembrandt's impastos[13] (Figure S2 in the Supporting Information). Moreover, recent μXRD analyses showed that PN can form in oil in a rather short time scale (details are given in the Supporting Information). For this experiment, some PbO particles were dispersed in

a droplet of heated oil and left to age at 60°C. After three months, no PbO was detectable while PN and HC were clearly identified (Figure S3). This is in agreement with the nanometric structure of PN in Rembrandt's impasto, indicative of a germination phenomenon triggered by a rapid equilibrium shift. It also demonstrates that PN can form in rather dry oils (at least it does not require addition of water in the paint medium), and without preliminary introduction of lead carbonates in the medium.

Another hypothesis mentioned in ref. [4] is that impastos can be created using a high amount of pure lead white pigment and untreated linseed oil. However, PN was never detected by the authors in the numerous non-impasto pure lead white paint layers they analyzed (historical and reconstruction samples with untreated linseed oil), encouraging us to discard this possibility.

In conclusion, our HR-XRD/µ-XRD characterization demonstrates a specific composition of Rembrandt's lead white impastos; that is, the presence of an unusual phase, PN, and a very high HC:C ratio. These two elements strongly suggest that Rembrandt mastered the rheology of paint in his impastos by the use of an alkaline lead-based medium, possibly by the use of litharge-treated oil. PN could result from the carbonation of PbO drier (CO_2 could come from the atmosphere or could be generated by decarboxylation of a fatty acid or fatty acid soap[15]) and/or from the alkalinization of C and HC from the lead white pigment. Further experiments are required to determine whether Rembrandt could have used a special quality of lead white rich in HC from the start or if the specific HC:C ratio observed is only the result of a transformation of C into PN over time.

This study provides new insights into the artistic process of Rembrandt and yields valuable tools for the long-term preservation and conservation of his masterpieces. As for future perspectives, this work calls for further investigations.

First, the studied corpus is not yet extensive enough to affirm that impastos systematically contain PN. Rembrandt might have used other recipes, based for example, on the addition of calcite.[16,17] Other lead white/ impasto samples from other paintings by Rembrandt and from other 17th Dutch Masters, including Vermeer, Hals, and painters belonging to Rembrandt circle will thus be studied.

Second, we plan to reconstruct specific impasto-like samples, preparing and ageing them under CO_2-rich and CO_2-free atmospheres (to assess the origin of carbonates) and in humid and dry conditions (to assess the effect of water of the phase transformation). It will also be important to characterize the structural features and rheological properties of the different (un/aged) model paints. The possible effect of alkaline cleaning treatments should be tested as well.

Conflict of interest

The authors declare no conflict of interest.

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