UvA-DARE (Digital Academic Repository)

Synchrotron micro-XRD and micro-XRD-CT reveal newly formed lead-sulfur compounds in Old Master paintings

Gonzalez, V.; van Loon, A.; Price, S.W.T.; Noble, P.; Keune, K.

DOI

[10.1039/d0ja00169d](https://doi.org/10.1039/d0ja00169d)

Publication date

2020

Document Version

Final published version

Published in

Journal of Analytical Atomic Spectrometry

License

Article 25fa Dutch Copyright Act

[Link to publication](#)

Citation for published version (APA):

Gonzalez, V., van Loon, A., Price, S. W. T., Noble, P., & Keune, K. (2020). Synchrotron micro-XRD and micro-XRD-CT reveal newly formed lead-sulfur compounds in Old Master paintings. *Journal of Analytical Atomic Spectrometry*, 35(10), 2267-2273.
<https://doi.org/10.1039/d0ja00169d>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)

Cite this: *J. Anal. At. Spectrom.*, 2020, **35**, 2267

Synchrotron micro-XRD and micro-XRD-CT reveal newly formed lead–sulfur compounds in Old Master paintings†

Victor Gonzalez, ^{*,a} Annelies van Loon, ^{ab} Stephen WT Price, ^c Petria Noble^a and Katrien Keune^{ad}

The *in situ* formation of lead–sulfur inorganic compounds in historical oil paintings can have a strong detrimental effect on an artwork's physical and visual integrity. In this paper, paint micro-samples collected from several paintings from the Rijksmuseum (Amsterdam) and Mauritshuis (The Hague) collections were probed using a combination of synchrotron micro-XRD and micro-XRD-CT. This permitted precise identification of the chemical nature of the *in situ* formed crystalline compounds as well as charting their distribution within paint layers at the microscopic level. This provided new information on the origin of the ions involved in the crystallization of the various newly formed mineral lead–sulfur products. The formation of palmierite $K_2Pb(SO_4)_2$, anglesite $PbSO_4$ and lanarkite $Pb_2(SO_4)O$ in historical samples can thus be connected to the paint stratigraphic build-up, environmental conditions and potential past restoration treatments.

Received 16th April 2020
Accepted 21st July 2020
DOI: 10.1039/d0ja00169d
rsc.li/jaas

Introduction

Old Master oil paintings are dynamic systems, in which various chemical reactions take place over time. Typical reactions occurring between the intrinsic paint materials, *e.g.* the inorganic components of the paint (pigments, driers) and carboxylic acid groups of the oil binder can result in the *in situ* formation of a variety of new compounds. Among the most common are the reaction products that form between saturated fatty acids (palmitic and stearic acid) and lead-containing pigments or driers, also called lead soaps.¹ Lead-based inorganic pigments and driers were omnipresent in the palette of painters until the 20th century, in particular lead white² (a mixture of lead carbonates: hydrocerussite $Pb_3(CO_3)_2(OH)_2$ and cerussite $PbCO_3$), red lead³ (lead(II,IV) oxide Pb_3O_4), lead-tin yellow⁴ (lead-stannate, type I: Pb_2SnO_4 and type II: $PbSn_{1-x}Si_xO_3$), litharge/massicot⁵ (lead II oxides, $PbO-\alpha$ and $PbO-\beta$), and lead acetate⁶ ($Pb(CH_3COO)_2$). These lead components provide a continuous source of lead ions and are therefore frequently associated with the formation of lead

soaps, which can manifest in paintings as inclusions (lumpy agglomerates), increased transparency of the paint layers and as whitish crusts on the paint surface.^{7–10}

Recently, other inorganic lead-based products were detected in paint stratigraphies, using both macro^{11–14} and micro-scale^{10,15–23} analysis: lead–sulfur compounds. Those compounds were not used by Old Masters, and were thus not originally present in the paint composition.^{24,25} An important conclusion was that the formation of inorganic degradation products could derive from both internal (original paint materials) and external reactants (for example, gasses present in the environment).

This leads to an important hypothesis: the spatial distribution of lead–sulfur products within paint stratigraphies is a critical parameter from which the availability and mobility of internal and external reactive components can be deduced, and the chemical conditions of their *in situ* crystallization can be inferred. To tackle this, we used a combination of synchrotron micro 2D X-ray diffraction (SR- μ -XRD) and synchrotron micro X-ray diffraction computed tomography (SR- μ -XRD-CT) to identify and chart the distribution of lead–sulfur products at the micro-scale in historical paint stratigraphies. More specifically, we mapped the presence of lead–sulfur non-original crystalline phases such as anglesite²⁶ ($PbSO_4$), palmierite²⁷ ($K_2Pb(SO_4)_2$) or lanarkite²⁸ ($Pb_2(SO_4)O$) in the paint layers. This permits us to obtain new information on the formation mechanisms and evolution over time of those compounds. Gathering precise knowledge of these products is essential today to guide conservation strategies and ensure an efficient preservation of historical oil paintings.

^aRijksmuseum, Conservation & Science Department, Hobbemastraat 22, 1071 ZC Amsterdam, The Netherlands. E-mail: gonzalvic@gmail.com

^bMauritshuis, Paintings Conservation Department, Plein 29, 2511 CS The Hague, The Netherlands

^cFinden Ltd, Merchant House, 5 East St Helen Street, Abingdon, Oxfordshire, OX14 5EG, UK

^dVan't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1090 GD Amsterdam, The Netherlands

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0ja00169d

Experimental

Materials

Minute paint fragments were collected from paintings from the collections of the Rijksmuseum and the Mauritshuis, embedded in resin blocks and polished to reveal the layer structures of the paintings. The obtained samples are better known as paint cross-sections. This paper will focus on three samples collected from the following paintings: the *Portrait of Maria Cornelisz* (1680–1719) by Jan Weenix (Rijksmuseum SK-A-4959), the *Portrait of Marten Soolmans* (1634) by Rembrandt van Rijn (Rijksmuseum SK-A-5033) and the *Hay Wagon* (c.1650) by Philips Wouwerman (Mauritshuis inv. 218). All three paintings were affected by different types of degradation. The Weenix painting exhibits severe cupping and delamination. As a result, flakes of paint are actively delaminating from the canvas, severely compromising the physical integrity of the artwork. A paint sample was collected from the left edge of the painting. During the recent treatment of the Rembrandt painting, an old, insoluble conservation layer (identified as an aged egg-white varnish) was observed in many dark areas on the paint surface. A sample was taken from the black cloak. Finally, the degradation observed in the Wouwerman painting manifests itself as whitish spots/inclusions in the blue sky. Those inclusions are composed of crumbly material, resulting in a general loss of cohesion of the affected paint surface. A paint sample containing such an inclusion was collected from the sky.

Methods

All samples were examined using light microscopy (LM), imaging ATR-FTIR and SEM-EDX beforehand, to localize the Pb-containing layers and to determine in which layer the degradation products had formed. They were then analysed by SR- μ -XRD and SR- μ -XRD-CT at beamline I18 of the DIAMOND Light Source (Didcot, UK). SR- μ -XRD and SR- μ -XRD-CT both rely on the use of a micrometric synchrotron beam to collect XRD patterns at each pixel (or voxel) of an area (or volume).²⁹ With SR- μ -XRD, 2D distribution maps of the crystalline compounds present in the samples are obtained, revealing the build-up of various paint layers. SR-XRD-CT enables to “slice” through the sample, thus potentially revealing the three-dimensional build-up of the inorganic compounds present. Cross-sections were positioned on a motorized xyz stage, in front (10° angle) of a 13 keV (0.9537 Å), 2×10 ($H \times V$) μm^2 beam. Samples were raster scanned with a 2×2 μm step size over a 2D map, 5 s per pixel. At each pixel, a two-dimensional diffraction pattern (Debye–Scherrer rings) was recorded in reflection mode, on a Photonic Science CMOS camera. A μ -XRF signal was simultaneously recorded using a Vortex ME-4 silicon drift detector, providing elemental information. The diffraction rings were then converted into 1D patterns by azimuthal integration using the DAWN software.³⁰ This allowed to obtain a full diffractogram at each pixel: the distribution of the crystalline phases for the entire mapped area was thus achieved. For one sample (the Wouwerman painting), SR- μ -XRD-CT in transmission mode was also performed.^{3,16} To avoid strong attenuation of the diffraction

signal by the resin surrounding the paint fragment, the cross-section was polished before analysis, until only a very faint amount of shielding matter was present (method described in ESI of ref. 16). The sample was positioned vertically on the tip of a needle, and rotated in front of the 13 keV beam. Two CT slices of 220×220 μm^2 were collected with the same 2×2 μm^2 step size.

The XRDUA software package³¹ was used to handle μ -XRD data. In the case of SR- μ -XRD-CT, after processing using the Savu processing pipeline³² for the reconstruction, the PyMCA software³³ (ROI Imaging Tool plugin) was used to better visualize the main crystalline phases present in the slice recorded through the micro-sample.

Results

Micro-XRD

Weenix. The delamination of the entire paint stratigraphy of the Weenix painting takes place at the interface of the ground with the canvas. The stratigraphy of the analysed sample consists of five layers identified as: a porous lower ground composed of a mixture of earth pigments and gypsum (layer 1 in Fig. 1C), a second ground consisting of a mixture of earth pigments, chalk and lead white (layer 2), a thin organic-rich intermediate layer (layer 3), a paint layer containing a mixture of smalt (a cobalt silicate-potash glass pigment) and lead white (layer 4) and finally, a varnish layer (layer 5).

SEM-EDX was performed and revealed a thin light grey deposition layer rich in sulfur and lead at the interface of the two grounds, layers 1 and 2 (Fig. 1D). The collected μ -XRD data permitted to precisely identify the crystalline compounds present. The earth pigment present in the first and second ground layers (layers 1 and 2) was found to be goethite (FeO(OH)) (Fig. 2E); hydrocerussite and cerussite were also identified as a component of the layers 2 and 4 (Fig. 2C and D); calcite is part of the second ground, mainly present in the upper part of the layer (Fig. 2F), and gypsum was also confirmed to be present as expected in the first ground (Fig. 2G). Regarding

Fig. 1 (A) Jan Weenix, *Portrait of Maria Cornelisz*, 1680–1719, oil on canvas, H 126.5 $\times$ W 109 cm, Rijksmuseum, (B) detail raking light showing cupped paint layer, (C) UV image of cross-section collected from the left edge of the painting showing 5 layers, (D) SEM-BSE image of detail area of the cross-section (red box in C) showing a Pb and S-rich deposition layer at the interface between layers 1 and 2.

Fig. 2 Selected SR- μ -XRD maps collected from the Weenix paint cross-section showing the distribution of the following crystalline phases (A) anglesite PbSO_4 , (B) palmierite $\text{K}_2\text{Pb}(\text{SO}_4)_2$, (C) hydrocerussite $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, (D) cerussite PbCO_3 , (E) goethite $\text{FeO}(\text{OH})$, (F) calcite CaCO_3 , (G) gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

lead-sulfur compounds, the thin crystalline interface between layers 1 and 2 was determined to be anglesite (Fig. 2A), while mainly palmierite was detected at the interface between the paint and varnish and in the varnish (layer 5, Fig. 2B). Smalt is amorphous, and cannot be identified by XRD.

Rembrandt. A μ -XRD map was collected from the Rembrandt sample in order to characterize the insoluble degradation products observed on the surface of the painting. The following paint layers were identified in the cross-section: a paint layer composed of lead white, carbon black and chalk (layer 1 in Fig. 3E), followed by a paint layer containing a mixture of lead white, ivory black and earth pigment (layer 2) and finally the ivory black layer of the cloak (layer 3). The ground layers, which

Fig. 3 (A) Rembrandt van Rijn, *Portrait of Marten Soolmans*, 1634, oil on canvas, H 210 $\times$ W 136 cm, Rijksmuseum, (B) detail cloak, ultraviolet light image showing the strongly fluorescent egg-white varnish, (C) detail cloak, stereomicroscope image showing cracked and degraded egg-white layer that appears as brown 'islands' on the paint surface, (D) ultraviolet light image of cross-section from the cloak showing several conservation layers including old egg-white varnish on top of the original paint layers, (E) SEM-BSE image of the same cross-section revealing three paint layers (1, 2, 3), showing Pb and S-rich zones (brightest areas), also in the egg white varnish layer (4) and at the interface between original and conservation layers (white arrow).

Fig. 4 Selected SR- μ -XRD maps collected from the Rembrandt cross-section showing the distribution of the following crystalline phases (A) hydrocerussite $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, (B) cerussite PbCO_3 , (C) whitlockite $\text{Ca}_9(\text{PO}_4)_6\text{PO}_3\text{OH}$, (D) anglesite PbSO_4 , (E) palmierite $\text{K}_2\text{Pb}(\text{SO}_4)_2$.

consist of a lead-white containing grey layer on top of a reddish brown lower ground, are missing in this sample. On top of the original paint layers are several "conservation layers", the lowest and oldest one is a proteinaceous (egg white) layer along with starch residues and degradation products, followed by (oil-) resin varnish layers (layer 4).³⁴ Here again, SEM-EDX detected the presence of lead and sulfur, in this case in the proteinaceous layer.

Compared to the Weenix sample, the μ -XRD maps of the Rembrandt sample highlight a different distribution of lead-sulfur products within the paint stratigraphy. While the distribution of palmierite (Fig. 4E) closely follows the original paint layers (at the interface of layers 3 and 4 in Fig. 4E), interestingly, anglesite has formed deeper in the original stratigraphy, reaching the lead white-containing background paint layer (layer 2), as seen in Fig. 4D. Whitlockite is associated with ivory black (Fig. 4C).

Wouwerman. The cross-section from the Wouwerman painting is composed of three paint layers: a lead white priming/upper ground (layer 1 of Fig. 5C, the lower (chalk) ground is not present in this sample), a blue underpaint layer containing lead white and smalt (layer 2) and a blue paint layer containing lead white and ultramarine (layer 3). The inclusions

Fig. 5 (A) Philips Wouwerman, *The Hay Wagon*, c.1650, oil on panel, H 40 $\times$ W 48 cm, Mauritshuis, (B) detail of blue sky, stereomicroscope image showing the presence of whitish spots (inclusions) on the painting surface, (C) dark field image of cross-section from the sky showing the inclusion, (D) SEM-BSE image of the cross-section showing the Pb, K and S-rich inclusion that formed in the blue underpaint of the sky (layer 2).

Fig. 6 SR- μ -XRD maps of the cross-section from the Wouwerman painting showing the distribution of the following crystalline phases: (A) hydrocerussite $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, (B) cerussite PbCO_3 , (C) palmierite $\text{K}_2\text{Pb}(\text{SO}_4)_2$.

(ca. 100 μm diameter) have a brownish translucent appearance in cross-sections (Fig. 5C). SEM-EDX analysis revealed the presence of potassium and sulfur together with lead. In the BSE image of the cross-section, these appear as light grey amorphous areas surrounding the dark grey angular smalt particles within the inclusion (Fig. 5D).

A μ -XRD map of the entire cross-section was recorded and permitted to identify palmierite as the main constituent of the inclusion (Fig. 6). The distribution of hydrocerussite and cerussite did not reveal different ratios of the two phases in layers 1, 2 and 3. In other words, it seems that an identical lead white pigment was used for the three layers.^{2,35}

Micro SR-XRD-CT

In order to obtain more precise insight into the mineral phases present in the vicinity of the inclusion, the Wouwerman sample was also analysed with SR- μ -XRD-CT. The obtained μ -XRD-CT map revealed the presence of lanarkite $\text{Pb}_2(\text{SO}_4)\text{O}$, in addition to palmierite, within the inclusion (Fig. 7). This specific phase was not visible in the μ XRD 2D-maps: this highlights the interest of performing CT to detect minor crystalline compounds within microscopic paint stratigraphies, as the collection of structural data from many different projections results in the increased sensitivity to minor phases in the measured diffraction signal.¹⁶

Discussion

Through structural mapping analysis of three paint cross-sections, a variety of lead-sulfur degradation products were identified. The key question stemming from these findings is

the source of the Pb, K and S ions necessary for the formation and crystallization of these products. The precise spatial charting at the micro-scale of the crystalline phases present provides convincing evidence to answer this question.

Weenix

In the case of the Weenix sample, two possible sources for the S ions can be identified: the gypsum present in the first ground (layer 1 in Fig. 1D), as well as in atmospheric SO_2 . Regarding the K ions, they could originate from the smalt pigment (layer 3), as smalt is known to release K ions as a result of aging.³⁶ Another potential source of K ions could be aluminosilicate compounds often present as traces in earth pigments (in this case in the goethite present in layers 1 and 2). Those S and K ions could combine with Pb ions from the lead white (layer 2), to form anglesite and palmierite. Since K ions (from smalt) were not available at the interface between the grounds, layers 1 and 2, anglesite was formed. It is interesting to note that palmierite is segregated to the surface of the paint, and is not present in the entire bulk of the paint layer. This last result, combined with the fact that the surface of the painting is not in contact with the deeper gypsum layer, points to an origin of S ions from atmospheric SO_2 , as proposed in previous works.¹⁶ Conversely, in the case of anglesite between layer 1 and 2, the S ions could indeed simply originate from the underlying gypsum layer (1). However, lead-sulfur products are hardly found at the interfaces of gypsum containing layers, based on the numerous SEM-EDX analysis we carried on 17–18th c. Dutch oil paint samples. Another important consideration in the case of the Weenix sample is the nature of the canvas support. As the painting is unlined and has a relatively coarse, plain weave canvas with an open structure, the porous ground layer is more exposed to atmospheric SO_2 , as penetration from the back of the canvas is relatively easy. We therefore do not exclude a possible atmospheric origin for the S ions that recombined at the interface of layers 1 and 2 to form anglesite.

The proposed chemical mechanisms for the formation of anglesite and palmierite can be summarized as:

Fig. 7 SR- μ -XRD 2D tomogram obtained from a slice of the Wouwerman cross-section showing the presence of hydrocerussite $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (HC, red), palmierite $\text{K}_2\text{Pb}(\text{SO}_4)_2$ (P, green) and lanarkite $\text{Pb}_2(\text{SO}_4)\text{O}$ (L, blue).

Wouwerman

Regarding the Wouwerman sample, the most obvious source of free Pb ions appears clear as the layer in which the inclusion has formed (layer 2) is composed of lead white (as shown by the presence of hydrocerussite and cerussite). Again, we propose that the primary source of K ions are the smalt particles present in the blue underpaint (layer 2 on Fig. 5C). One cannot, however, exclude the ultramarine pigment from the top paint layer (Fig. 3) as a potential source of K and S ions, as was observed in other examples of ultramarine paints that did not contain smalt.³⁷ Indeed, natural ultramarine, while mostly composed of lazurite $((\text{Na,Ca})_8(\text{AlSiO}_4)_6(\text{SO}_4,\text{S,Cl,OH})_2)$, usually

comprises multiple other potassium-containing minerals.³⁸ Apart from lazurite however, no other inorganic pigment could act as source of S ions, encouraging us to propose again that atmospheric SO₂ played this role. The influence of a past conservation treatment can be also included as a possible factor. More specifically, solutions of (diluted) sulphuric acid have been known to be used for cleaning paintings in the 19–20th centuries,³⁹ although there is no evidence for this in the treatment records of this painting.

As detected by μ -XRD-CT, the Wouwerman sample is also characterized by the presence of lanarkite. A reaction can be proposed for the formation of this compound:

For reaction (3) to take place, water molecules must be available. Paint layers are porous materials: depending on the environmental conditions a painting was subjected to, more specifically the relative humidity, they can adsorb and hold a certain amount of moisture. This moisture can remain trapped, thus acting as a source of water.⁴⁰

We were surprised not to detect leadhillite $\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$ in this sample as this compound is usually associated with lanarkite and hydrocerussite.²⁸ Explanation for this could stem for a very faint amount of the crystalline material within the sample. It was reported that lanarkite is stable only at low CO₃²⁻ contents, which is in agreement with the distribution of this compound within the palmierite cluster, where no carbonate groups are present.

Rembrandt

In the case of the Rembrandt sample, the two lead-sulfur compounds detected exhibit two different distributions. Palmierite is only present at the surface of the paint layers and in the egg white varnish (Fig. 4E), while anglesite seems to be distributed throughout the entire stratigraphy (Fig. 4D). In this case, S ions could originate not only from the atmosphere, but also from the egg-based conservation layer. No S-containing pigments such as gypsum or organic lake pigments (precipitated on an alum substrate), which could act as another source of S ions, were detected. Regarding the origin of palmierite, an important clue is the lack of any internal K ions source within the paint stratigraphy. Combined with the localization of this crystalline phase to the paint surface, this points to a previous conservation treatment as a possible source of K ions. In particular, historical sources mention that potash was frequently used prior to the 20th century as a cleaning product for the surface of historical paintings.³⁹ The deeper distribution of anglesite within the paint stratigraphy again points to a combination of free Pb ions with atmospheric SO₂ or S ions from the egg-based layer. In the case of this artwork, it is important to mention that the canvas is wax-resin lined and densely woven. In addition, the double ground (not present in the studied sample) is very compact. In contrast to the Weenix painting (open weave canvas, porous ground), those two factors could explain why the penetration of atmospheric S ions was only possible from the surface of the painting, which would explain why anglesite is present at the top of the stratigraphy and seems to continuously grow towards the bottom,

reaching as far as layer 2 in Fig. 3E. The question as to whether this dynamic process is still occurring is of course of particular interest for conservators and the long term preservation of this masterpiece. Environmental conditions in museums have greatly improved during the last decades, resulting in a very low availability of atmospheric S ions that might react within the paint stratigraphy.²³ In addition, potash and lye solutions are already for a long time no longer used as cleaning agents.

General discussion

An important observation is the difference in morphology of the newly crystallized products detected in this work. For example, while palmierite re-crystallized as a thin, intermediate layer in the Weenix painting, it is present as large, globular inclusions in the Wouwerman. While several works have proposed mechanisms to explain the formation of protrusions, *e.g.* phase-separation mechanism or diffusion driven processes towards crystallization nuclei,^{41,42} explaining such differences remains difficult, as multiple factors have to be considered, as it was highlighted in this work.

First, the local environmental conditions of conservation (temperature, relative humidity (RH), pH) play an important role in the *in situ* formation of crystalline products in paint layers. In particular, as noted by Aze *et al.*, sulfation by atmospheric SO₂ is governed by complex reactions, during which S(IV) $\rightarrow$ S(VI) oxidation occur in aqueous phase.⁴³ The sulfation of lead carbonate compounds thus require high moisture content. Other authors agree on the capital role of RH in the complex mechanisms governing atmospheric SO₂ attack on model systems of historical pigments (iron and lead oxides)⁴⁴ and cements.⁴⁵ It is worth mentioning that some of these works have reported the formation of anglesite in mural painting model stratigraphies as a thin surface layer, the same morphology as observed in the Weenix and Rembrandt paintings.⁴⁶ In the case of the paintings studied in this work, we favour the hypothesis of a “dry” deposition of SO₂ on the painting, followed by an oxidation producing SO₄²⁻ that can in turn react with Pb²⁺ ions towards various crystalline lead-sulfate compounds, as hypothesized⁴⁴ by Maguregui *et al.*

Secondly, different sources of ions have to be considered: original painting materials (inorganic pigments, dryers, organic binders...), atmospheric gases, and past conservation treatments. It is important to note that this research does not consider potential sources of Pb or S ions that could however be relevant for other artworks. For example, all three paintings sampled were painted using linseed oil, as it was usual for Dutch Golden Age artworks. However, different types of organic binders (for example egg-based tempera) could act as yet another source of S ions. In other words, in addition to a precise preliminary study of the paint build-up, gathering as much information on the conservation history of a studied painting is important to propose sound chemical hypotheses.

Thirdly and finally, we think that the structural characteristics of the canvas (densely woven, lined or not...) have an effect on the diffusion rate of those atmospheric gases within paint layers and should be considered in the future.

Conclusions

This paper showcases the potential of SR- μ -XRD and SR- μ -XRD-CT to discriminate inorganic degradation products in complex paint stratigraphies at the micro-scale. The capability to precisely determine where these *in situ* compounds have formed appears essential to propose sound hypotheses regarding the source of the free Pb, K and S ions necessary to their formation. Those hypotheses are in turn valuable clues to reveal additional information about the conservation history of the studied artwork, and provide precious insights for the future conservation of historical easel paintings.

From a wider perspective, this work highlights the high variety of chemical reactions involving lead-based inorganic products within historical paint layers. This encourages us to continue our efforts towards better knowledge of the chemistry of lead in those complex inorganic/organic systems. In particular, identifying the kinetics of these reactions presents an immense interest for the long term preservation of oil paintings. This can only be achieved by complementing results obtained on historical samples, such as the ones presented in this paper, with research results gathered on carefully designed model systems.⁴⁷ In the case of lead-sulfate compounds, our first step will consist in testing several environmental conditions (T, RH, pH...) as well as conducting a study on the possible variation of the diffusion coefficient of SO₂ in paint layers with different compositions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors give thanks to AzkoNobel and the '3D understanding of degradation products in oil paintings' project by the Netherlands Institute for Conservation, Art and Science (NICAS) NWO Programme for funding. We acknowledge Diamond Light Source for providing beamtime, and thank Dr Konstantin Ignatyev and Dr Sylvia Britto for support at beamline I18. We thank Dr Frederik Vanmeert for help with the XRDUA software. We are indebted to our colleagues Anna Krekeler, Gwen Tauber, Susan Smelt, Marjolein Hupkes, Sepha Wouda and Oleg Karuvits at the Rijksmuseum, UvA and Mauritshuis for preliminary samples analyses and valuable insights on the studied paintings. We thank Dr Marine Cotte and Dr Joen Hermans for many interesting discussions on chemical reactions involving within paint layers.

Notes and references

- 1 *Metal Soaps in Art*, ed. F. Casadio, K. Keune, P. Noble, A. van Loon, E. Hendriks, S. A. Centeno and G. Osmonds, Springer, 2019.
- 2 V. Gonzalez, G. Wallez, T. Calligaro, M. Cotte, W. De Nolf, M. Eveno, E. Ravaud and M. Menu, *Anal. Chem.*, 2017, **89**, 13203.
- 3 F. Vanmeert, G. van der Snickt and K. Janssens, *Angew. Chem., Int. Ed.*, 2015, **54**(12), 3607.
- 4 C. Sandalinas and S. Ruiz-Moreno, *Stud. Conserv.*, 2003, **49**, 41.
- 5 M. Cotte, E. Checroun, W. de Nolf, Y. Taniguchi, L. de Viguierie, M. Burghammer, P. Walter, C. Rivard, M. Salomé, K. Janssens and J. Susini, *Stud. Conserv.*, 2017, **62**, 2.
- 6 L. Carlyle, *The Artist's Assistant: Oil Painting Instruction Manuals and Handbooks in Britain, 1800-1900, with Reference to Selected Eighteenth-century Sources*, Archetype Publications, London, 2001.
- 7 P. Noble and A. van Loon *Art Matters Netherlands Tech. Stud. Art*, 2007, vol. 4, p. 19.
- 8 C. Higgitt, M. Spring and D. Saunders, *National Gallery Technical Bulletin*, 2003, vol. 24, p. 75.
- 9 K. Keune and J. Boon, *Stud. Conserv.*, 2007, **52**(3), 161.
- 10 A. van Loon, P. Noble and J. Boon in *ICOM-CC 16th triennial conference preprints*, Paintings Working Group, Lisbon, 2011, pp. 1–10.
- 11 F. Vanmeert, N. de Keyser, A. van Loon, L. Klaassen, P. Noble and K. Janssens, *Anal. Chem.*, 2019, **91**, 7153–71561.
- 12 J. Simoen, S. De Meyer, F. Vanmeert, N. de Keyser, E. Avranovich, G. Van der Snickt, A. van Loon, K. Keune and K. Janssens, *Heritage Sci.*, 2019, **7**, 83.
- 13 K. Janssens, S. Legrand, G. Van der Snickt and F. Vanmeert, *Elements*, 2016, **12**(1), 39.
- 14 S. De Meyer, F. Vanmeert, R. Vertongen, A. van Loon, V. Gonzalez, G. van der Snickt, A. Vandivere and K. Janssens, *Heritage Sci.*, 2019, **7**, 67.
- 15 J. J. Boon, *Microsc. Microanal.*, 2013, **19**, 1408.
- 16 S. W. T. Price, A. Van Loon, K. Keune, A. D. Parsons, C. Murray, A. M. Beale and J. F. W. Mosselmans, *Chem. Commun.*, 2019, **55**, 1931.
- 17 D. Saunders, M. Spring and C. Higgitt in *ICOM-CC 13th triennial meeting proceedings*, Rio de Janeiro, 2002, pp. 455–463.
- 18 F. Piqué in *Conservation of ancient sites on the silk road, Proceedings of an International Conference on the Conservation of Grotto Sites*, ed. N. Agnew, Los Angeles, 1993, pp. 348–361.
- 19 J. L. Perez-Rodriguez, C. Maqueda, M. C. Jimenez de Haro and P. Rodriguez-Rubio, *Atmos. Environ.*, 1998, **32**(6), 993–998.
- 20 G. Silvester, A. Burnstock, L. Megens, T. Learner, G. Chiari and K. Van den Berg, *Stud. Conserv.*, 2014, **59**(1), 38.
- 21 G. Van der Snickt, K. Janssens, J. Dik, W. De Nolf, F. Vanmeert, J. Jaroszewicz, M. Cotte, G. Falkenberg and L. Van der Loef, *Anal. Chem.*, 2012, **84**, 10221.
- 22 S. Hageraats, K. Keune, M. Thoury and R. Hoppe in *Conservation of Modern Oil Paintings*, ed. K. J. van den Berg *et al.*, Springer, 2020, pp. 275–288.
- 23 A. van Loon, L. E. Hartman, J. Van den Burg, R. Haswell and C. Pottasch in *Metal Soaps in Art*, ed. F. Casadio, K. Keune, P. Noble, A. Van Loon, E. Hendriks, S. A. Centeno and G. Osmonds, Springer, 2019, pp. 283–296.
- 24 N. Eastaugh, V. Walsh, T. Chaplin and R. Siddall in *Pigment Compendium: A Dictionary and Optical Microscopy of Historic Pigments*, Butterworth-Heinemann, London, 1st edn, 2008.

- 25 D. Bomford, J. Kirby, A. Roy, A. Rüger and R. White in *Art in the Making – Rembrandt*, National Gallery Publications, London, 1998.
- 26 M. Miyake, I. Minato, H. Morikawa and S. I. Iwai, *Am. Mineral.*, 1978, **63**, 506.
- 27 R. G. Tissot, M. A. Rodriguez, D. L. Sipola and J. A. Voigt, *Powder Diff.*, 2001, **16**, 97.
- 28 F. A. Abdul-Samad, J. H. Thomas, P. A. Williams and R. F. Symes, *Mineral. Mag.*, 1982, **46**, 499.
- 29 V. Gonzalez, M. Cotte, F. Vanmeert, W. de Nolf and K. Janssens, *Chem.-Eur. J.*, 2020, **26**(8), 1703.
- 30 J. Filik, A. W. Ashton, P. C. Y. Chang, P. A. Chater, S. J. Day, M. Drakopoulos, M. W. Gerring, M. L. Hart, O. V. Magdysyuk, S. Michalik, A. Smith, C. C. Tang, N. J. Terrill, M. T. Wharmby and H. Wilhelm, *J. Appl. Crystallogr.*, 2017, **50**, 959.
- 31 W. De Nolf, F. Vanmeert and K. Janssens, *J. Appl. Crystallogr.*, 2014, **47**, 1107.
- 32 R. C. Atwood, A. J. Bodey, S. W. T. Price, M. Basham and M. Drakopoulos, *Philos. Trans. R. Soc., A*, 2015, **373**(2043), 20140398.
- 33 M. Cotte, T. Fabris, G. Agostini, D. Motta Meira, L. de Viguerie and V. A. Solé, *Anal. Chem.*, 2016, **88**, 6154–6160.
- 34 P. Noble, E. Van Duijn, E. Hermens, K. Keune, A. Van Loon, S. Smelt, G. Tauber and R. Erdmann, *Rijksmuseum Bulletin*, 2018, **66**, 308.
- 35 S. De Meyer, F. Vanmeert, R. Vertongen, A. van Loon, V. Gonzalez, J. Delaney, K. Dooley, J. Dik, G. Van der Snickt, A. Vandivere and K. Janssens, *Sci. Adv.*, 2019, **5**(8), eaax1975.
- 36 M. Spring, C. Higgitt and D. Saunders, *National Gallery Technical Bulletin*, 2005, vol. 26, p. 56.
- 37 The National Gallery, Vermeer and technique, <https://www.nationalgallery.org.uk/research/about-research/the-meaning-of-making/vermeer-and-technique/altered-appearance-of-ultramarine>, accessed April 2020.
- 38 J. Plesters, *Stud. Conserv.*, 1966, **11**(2), 62.
- 39 M. Stols-Witlox, *ICOM-CC 16th triennial conference preprints, Theory and history of conservation working group*, 2011, p. 1.
- 40 G. K. van der Wel and O. C. G. Adan, *Prog. Org. Coat.*, 1999, **37**(1–2), 1–14.
- 41 J. J. Boon, F. Hoogland and K. Keune in *AIC PSG postprints*, ed. H. Mar Parkin, AIC, Washington 2007, vol. 19, pp. 16–23.
- 42 J. Hermans, K. Keune, A. Van Loon and P. Iedema in *Metal Soaps in Art*, ed. F. Casadio, K. Keune, P. Noble, A. Van Loon, E. Hendriks, S. A. Centeno and G. Osmonds, Springer, 2019, pp. 47–67.
- 43 S. Aze, J.-M. Vallet, A. Baronnet and O. Grauby, *Eur. J. Mineral.*, 2006, **18**, 835–843.
- 44 M. Maguregui, U. Knuutinen, I. Martinez-Arkarazo, K. Castro and J. M. Madariaga, *Anal. Chem.*, 2011, **83**(9), 3319–3326.
- 45 G. Ramakrishnan, Q. Wu, J. Moon and A. Orlov, *Chem. Eng. J.*, 2017, **319**, 57–64.
- 46 S. Aze, J.-M. Vallet, M. Pomey, A. Baronnet and O. Grauby, *Eur. J. Mineral.*, 2007, **19**, 883–890.
- 47 L. Baij, L. Chassouant, J. Hermans, K. Keune and P. Iedema, *RSC Adv.*, 2019, **9**, 35559.