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Unravelling the spatial dependency of the complex solid-state chemistry of Pb in a paint micro-sample from Rembrandt’s Homer using XRD-CT†

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The surface of many Old Master paintings has been affected by the appearance of whitish lead-rich deposits, which are often difficult to fully characterise, thereby hindering conservation. A paint micro-sample from Rembrandt’s Homer was imaged using X-ray Diffraction Computed Tomography (XRD-CT) in order to understand the evolving solid-state Pb chemistry from the painting surface and beneath. The surface crust was identified as a complex mixture of lead sulfates. From the S : Pb ratios throughout the paint layer, we can conclude that S is from an external source in the form of SO₂, and that the nature of Pb–SO₄ product is dependent on the degree of diffusion/absorption of SO₂ into the paint layers.

Several degradation phenomena disturbing the appearance of many Old Master paintings can be associated with the formation of lead soaps, of which the protrusions-small aggregates of lead soaps that ‘protrude’ through the paint surface- are the most researched.¹ Lead soaps or carboxylates are the consequence of reactions between lead pigments or driers and reactive carboxylic acid groups of the oil binder. This paper focuses on the formation of insoluble, whitish deposits on the surface of oil paintings (efflorescence), as yet another degradation phenomenon related to lead soaps.

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Typical XRD measurements (with mm-sized beams) show lead white to be a mixture of cerussite and hydrocerussite, however the 2 micron resolution available at synchrotrons is able to spatially resolve the individual micro crystallites and their distributions within the paint layer. The use of SR microscopy has been successfully applied to characterise paint fragments by both FTIR and XRD 2-D mapping,¹ showing chemical and phase distributions, and also by 3D X-ray tomography (absorption contrast),⁵ providing information on voids and grain distribution within the paint layer. Mapping however, essentially interrogates the sample surface, thus is unable to provide the necessary depth information. In that regards, recently, a combination of XRD with computed tomography (XRD-CT†) has been demonstrated to be a powerful method for obtaining depth contrast and to identify with a spatial resolution in the μm, amongst other phases, plumbonacrite (3 PbCO₃·Pb(OH)₃·PbO) in a ca. 250 μm-wide, unembedded protrusion in Wheat Stack Under a Cloudy Sky (1889) by Vincent van Gogh.⁷
In this study, $\mu$XRD-CT is used to address a fundamental question on the nature and formation of the whitish surface deposits rich in Pb, K and S—present in the form of sulfate as demonstrated by FTIR and Raman—found in Rembrandt’s Homer (1663), Mauritshuis, The Hague. The deposits in this particular painting have been a topic of in-depth study since its last treatment in 2005/06. The last orangey ground layer (1) (thickness $\sim$15 $\mu$m) sits approximately between 80 and 95 $\mu$m beneath the surface of the paint and consists primarily of calcite ($\text{CaCO}_3$) and earth pigments. It corresponds to the yellow phase in Fig. 2. The distribution of calcite over the first slice is plotted in Fig. 3b (see also Fig. S7 and S8, ESI†). This is followed by a second ground layer (2) ($\sim$20 $\mu$m) of mostly lead white that has converted into lead soaps. The loss of the original highly scattering particulate lead white pigment is significant, as can be seen by the less dense, amorphous character of the layer in the SEM-BSE images (Fig. S2, ESI†). The smallest crystallites are known to react first, leaving only a few large, highly scattering agglomerates remaining. Fitting of the XRD-CT identifies hydrocerussite (basic lead carbonate), as well as lead soaps (fitted as lead palmitate and lead azelate—PbC$_4$H$_7$(O$_2$) in the second ground layer (Fig. 2, 3e, f and Fig. S4, S5, ESI†). The maps of hydrocerussite and cerussite do not overlap (Fig. 3f and g). Hydrocerussite is the main component of lead white. Lead white can also contain a small fraction of cerussite (lead carbonate), usually varying between 5 and 10%, but it seems that most of the cerussite originally present in the second, lead white-containing ground layer has reacted away. The presence of lead soaps in the second, upper ground corroborates prior FTIR results (band at $\nu_{\text{as}}$-spacings are not well resolved. As such the largest intensity ca. 1520 cm$^{-1}$ characteristic of the lead carboxylate group $\nu_{\text{as}}$COO). The XRD patterns have a large background signal above 10 Å (in part due to the detector, but also due to the resin encapsulating the samples), and so reflections with large $d$-spacings are not well resolved. As such the largest intensity reflections (i.e. $>6$ Å) identified by Robinet and Corbel cannot be used to assign the lead soaps present. However the pattern fitting matched well with structures reported by Catalano and Plater. A dark undermodelling paint (3) (bone black and earths; $\sim$15 $\mu$m) was applied on top of the ground layers, followed by a reddish paint (4) (red earth, red lake, bone black, smalt; $\sim$30 $\mu$m) and a small-containing glaze (5) ($\sim$15 $\mu$m).
The distribution of lead species throughout the sample as revealed by XRD-CT helps to build a theory about how insoluble lead-rich surface deposits may form. Fig. 4 shows a schematic diagram for the formation of the different Pb phases. Lead is solubilized from the lead white ground. It either reacts with free carboxylic acid groups in the oil medium or interacts with atmospheric compounds. Sulfate formation is the preferential reaction in the upper paint layers. Leadhillite and lanarkite, as well as cerussite, were found deeper beneath the paint surface. The S: Pb ratio being greatest at the surface, suggests that external sources, most likely in the form of SO₄, are the origin of the sulfur. Combustion from domestic heating in the past may have released sulfurous gases into the atmosphere, as did the industrial revolution. The SO₂ is absorbed in or at the surface of the paint, where it readily oxidizes and reacts with moisture to form sulfates. The presence of sulfur at/near the paint surface has previously been identified in other paintings. The Pb-phases also show the involvement of CO₃²⁻ ions in the formation of cerussite and leadhillite products. CO₂ from the atmosphere can form CO₃²⁻ ions, a comparable process as for SO₂. However, the CO₂ is not absorbed at the surface as much as SO₂, and therefore diffuses deeper into the paint structure. We see comparable processes in large lead soap aggregates inside the painting, where lead soap is converted into lead carbonate and CO₂ is expected to play an important role. The availability of SO₄²⁻ and CO₃²⁻ ions and pH of the moisture in the paint system determine the lead phase formed. High SO₄²⁻ and acidic environment favour anglesite formation over leadhillite and cerussite. This situation reflects the conditions at the paint surface, where anglesite and palmitite are the dominant Pb phases. Formation of leadhillite, lanarkite and cerussite require slightly different reaction conditions. Leadhillite is only stable at neutral environment, whereas cerussite is more likely to form at high CO₃²⁻ content and alkaline environment. The basic sulfate salt, lanarkite, is thermodynamically stable only at very low CO₃²⁻ content. Since historical paints are highly heterogeneous systems, the degree of alkalinity or acidity inside the system, as well as the amounts of SO₄²⁻ and CO₃²⁻, can locally change and thereby influence the Pb phases formed. In turn, the chemical reactions that take place in the paint may also influence the local chemical environment, favouring the formation of other Pb phases. This can explain the variety of Pb phases including some rare minerals that co-exist deeper beneath the paint surface. A remaining question is how has the palmitite formed from the Pb and K species. As earlier analysis of samples of Homer showed, the smalt used in the paint has almost completely discoloured due to the K leaching out to form water-soluble and

Fig. 3 Maps of the location of the major Pb containing phase for the Rembrandt fragment (slice 1). (a) palmitite, (b) anglesite, (c) lanarkite, (d) leadhillite, (e) lead palmitate, (f) hydrocerussite, (g) cerussite, (h) calcite. Dashed yellow outline over each phase marks the approximate boundaries of the sample as defined by the absorption reconstruction, and act as a guide to identify the relative location of each phase within the sample. Where possible the major reflection has been used to create the map of the phase (Table S2, ESI†), however this is not always possible, and so in certain cases a less intense reflection was used, this resulted in higher background noise (e.g. lanarkite). NB some streak artefacts are still present even after the application of the mean trimmed filter to the raw data (see ESI†), indicating the presence of large single crystals, e.g. hydrocerussite.

Fig. 4 Schematic diagram showing the formation and localisation of the different Pb phases in the painting.
highly mobile K soaps. Previous research has shown that K soaps preferentially deposit at the paint surface. Although the small layer is relatively thin in this sample (5–10 μm), SEM-EDX mapping reveals a concentration of K at the surface away from the small particles (Fig. S2, ESI†). Exposure of K to SO2 will also readily form water-soluble K sulfates. Pb ions seem to trap the K soaps/sulfates leading to the formation of insoluble crusts of palmierite. This process is probably similar to the formation of Pb-rich rims around organic lake pigment particles, the K2SO4-rich substrate adsorbing the migrated Pb and acting as direct reaction side for the formation of palmierite. The sulfates of Pb and Pb-K are highly insoluble in water or organic solvents, so it is not very likely that they migrate towards the surface once formed. This means that the anglesite and palmierite preferentially locate where they have formed, i.e. more towards the paint surface. Depending on how much K is available the ratio of anglesite to palmierite will change.

XRD-CT has been able to identify the different crystalline structures present, giving a clearer picture as to the nature of the Pb deposits, not just on the surface of the painting, but through the whole layer. The need for the mean trimmed filter applied to the data (see ESI!) strongly suggests that many of the crystallites identified are of dimensions equal to or larger than the beam size (2 μm), however the common presence of diffraction rings also indicates that much of the remineralisation that occurs results in many small (<1 μm) crystallites. The deeper understanding of the nature and likely pathway of formation of these sulfate and carbonate deposits has implications for the conservation treatment. The source of sulfur is historical, therefore, no new sulfurous deposits are expected to be formed if the crust will be removed. In this case study, however, a complete removal of those products would not be possible without damaging the original paint layer, since the surface deposits and the paint are so closely intertwined. In general, this case study demonstrates the complex Pb chemistry that takes place in mature oil paintings over time.

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Conflicts of interest
There are no conflicts to declare.

Notes and references


