



# Plumbonacrite Identified by X-ray Powder Diffraction Tomography as a Missing Link during Degradation of Red Lead in a Van Gogh Painting\*\*

Frederik Vanmeert, Geert Van der Snickt, and Koen Janssens\*

**Abstract:** Red lead, a semiconductor pigment used by artists since antiquity, is known to undergo several discoloration phenomena. These transformations are either described as darkening of the pigment caused by the formation of either plattnerite ( $\beta$ - $\text{PbO}_2$ ) or galena ( $\text{PbS}$ ) or as whitening by which red lead is converted into anglesite ( $\text{PbSO}_4$ ) or (hydro)cerussite ( $2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$ ;  $\text{PbCO}_3$ ). X-ray powder diffraction tomography, a powerful analytical method that allows visualization of the internal distribution of different crystalline compounds in complex samples, was used to investigate a microscopic paint sample from a Van Gogh painting. A very rare lead mineral, plumbonacrite ( $3\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2\cdot\text{PbO}$ ), was revealed to be present. This is the first reported occurrence of this compound in a painting dating from before the mid 20th century. It constitutes the missing link between on the one hand the photoinduced reduction of red lead and on the other hand (hydro)cerussite, and thus sheds new light on the whitening of red lead.

X-ray powder diffraction (XRPD) mapping can be used to identify, visualize and to a certain extent quantify the different crystalline components that are present in complex heterogeneous paint systems.<sup>[1]</sup> At state-of-the-art synchrotron radiation facilities this can be done on the (sub)micrometer scale. In the past 10 years, combined microscopic X-ray fluorescence and X-ray powder diffraction ( $\mu\text{XRF}/\mu\text{XRPD}$ ) mapping experiments performed on samples extracted from works of art have been used for the identification of various pigments and artist materials,<sup>[2]</sup> as well as their degradation products,<sup>[3]</sup> and even the imaging of a complete painting.<sup>[4]</sup> However, an intrinsic limitation of two-dimensional (2D)

mapping remains the loss of depth information as projection images are obtained. Therefore, in order to investigate the stratigraphy of a paint system, typically a cross-section of a paint sample needs to be prepared, consuming to a lesser or greater extent part of the (often unique or very rare) sample. With  $\mu\text{XRPD}$  tomography the inner distribution of the crystalline components present in such samples can be visualized without physically cross-sectioning the material under investigation.<sup>[5]</sup> Although the capabilities of this technique have been demonstrated on various complex materials,<sup>[6]</sup> it has been scarcely used on cultural heritage samples.<sup>[7]</sup>

In this work we performed combined  $\mu\text{XRF}/\mu\text{XRPD}$  imaging of a minute sample obtained from the painting *Wheat Stack Under a Cloudy Sky* by Vincent van Gogh (October 1889, oil on canvas, Kröller-Müller Museum, NL). The sample consists of a severed pustular mass revealing a bright orange-red core (about 100  $\mu\text{m}$  in diameter) surrounded by a light blue tinted layer and a gray outer layer that partially covers the pustular mass (Figure 1). This outer layer consists of finely grained particles, rich in both Zn and Pb (Figure 2a), that were applied onto the original blue paint layer which is made up of coarse grains (Figure 2c). The compound-specific distribution maps (Figure 2b) show that this gray layer contains a mixture of the pigments zinc white (zincite,  $\text{ZnO}$ ) and lead white (hydrocerussite,  $2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$ ). Although both white pigments were part of Van Gogh's palette,<sup>[8]</sup> this outer layer was not originally present but was added later, probably during retouching. While the lead white used in this outer layer consists only of basic lead carbonate, a different lead white composition is found in the light blue layer

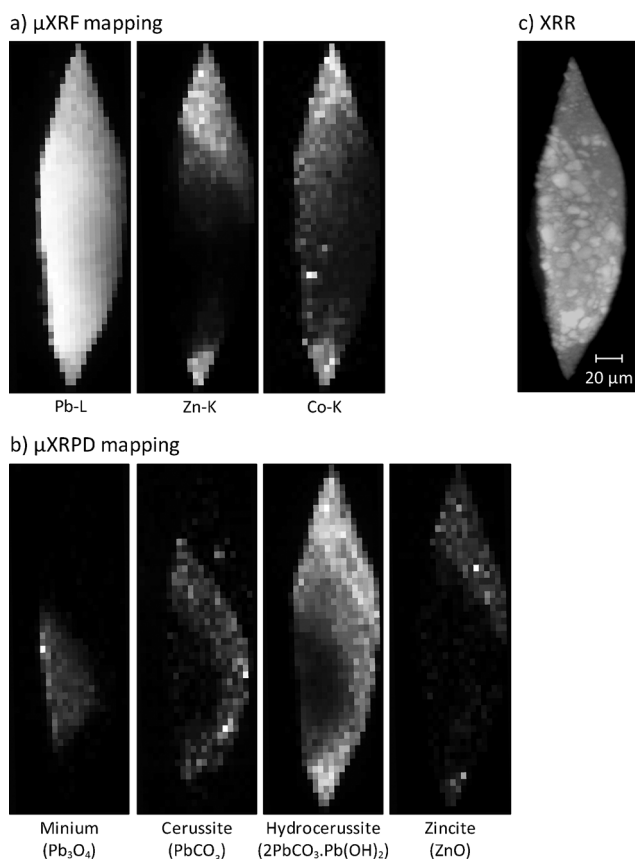
[\*] F. Vanmeert, Dr. G. Van der Snickt, Prof. Dr. K. Janssens  
Antwerp X-ray Analysis, Electrochemistry and Speciation  
University of Antwerp  
Groenenborgerlaan 171, 2020 Antwerp (Belgium)  
E-mail: koen.janssens@uantwerpen.be  
Homepage: <https://www.uantwerpen.be/en/rg/axes/>

[\*\*] The authors acknowledge L. Van der Loeff and M. Leeuwestein (Kröller-Müller Museum) for providing the paint sample. We thank Dr. J. Jaroszewicz (WUT) for performing the CT measurements. This research was carried out at the light source PETRA III at DESY, a member of the Helmholtz Association (HGF). We thank Dr. G. Falkenberg and the members of his team for their assistance in using beam line P06. We acknowledge financial support from the University of Antwerp GOA projects "XANES meets EELS" and "SOLARPaint", as well as from BELSPO (Brussels) Project S2-ART and FWO (Brussels) project "ESRF-Dubble".

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201411691>.



**Figure 1.** a) Photograph of *Wheat Stack Under a Cloudy Sky* by Van Gogh (October 1889, oil on canvas, Kröller-Müller Museum, NL). The sample area is indicated by the white circle. b) Detail of the severed pustular mass on the painting surface. c) Detail of the paint sample.

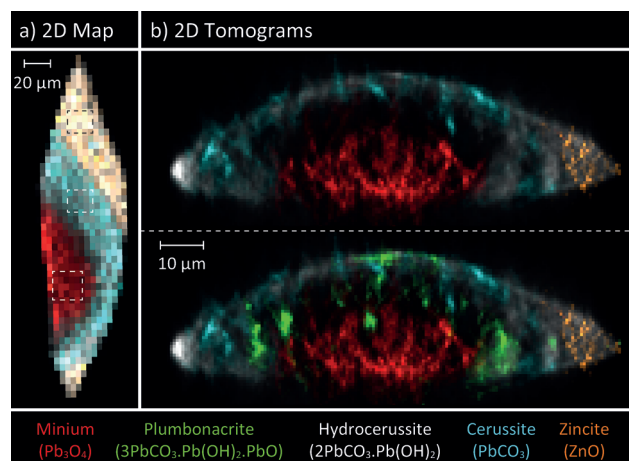


**Figure 2.** a) Elemental and b) phase-specific 2D distribution images of the severed pustule. Map size:  $80 \times 255 \mu\text{m}^2$ ; Pixel size:  $4 \times 5 \mu\text{m}^2$ . c) X-ray radiography (XRR) image obtained from an X-ray absorption tomography dataset (experimental parameters see Supporting Information).

underneath that contains both neutral (cerussite,  $\text{PbCO}_3$ ) and basic lead carbonate (hydrocerussite). The blue color of this layer could originate from cobalt blue, a pigment frequently used by Van Gogh, as a significant Co XRF signal is observed. In the bright red core of the pustule, a third lead-containing pigment identified as red lead is present. Figure 3a shows the composite projected distribution of the above-mentioned crystal phases.

Red lead, most commonly designated with the term *minium*, is a semiconductor pigment used since ancient times and is thought to be one of the first artificially prepared pigments.<sup>[9]</sup> Minium corresponds to the lead(II,IV) oxide mineral of composition  $\text{Pb}_3\text{O}_4$  and can often be found on artworks in association with lead monoxide, either litharge (tetragonal  $\text{PbO}$ ) or massicot (orthorhombic  $\text{PbO}$ ).<sup>[10]</sup> However, the diffraction data did not show any lead(II) oxides in the sample. The red lead pigment is known to be unstable with time. On the one hand, it is thought to play a role in the formation of lead soap protrusions where lead carbonate and lead soaps are formed through the reaction of red lead with the fatty acids present in the oil medium.<sup>[11]</sup> On the other hand, orange, flake-like particles found in and around lead soap protrusions have been identified as minium,<sup>[12]</sup> and are believed to have formed by remineralization usually together

with lead carbonate.<sup>[13]</sup> However, from the large grains shown to be present in the interior of the sample and the large amount of red lead present, it is most plausible that minium is the original material and not a degradation product as a result of protrusion formation. It is also known both from his letters and from the study of paint samples that Van Gogh used minium as a red pigment in his paintings from the Auvers-sur-Oise period.<sup>[8]</sup>



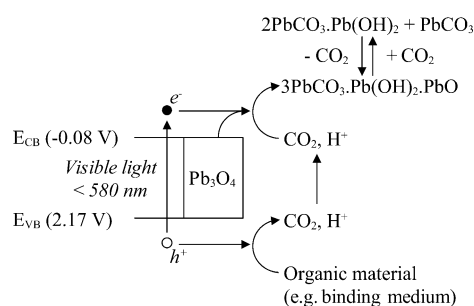
**Figure 3.** Color reconstructions of a) the projected and b) the internal crystalline distribution of the paint sample. Pixel size: a)  $4 \times 5 \mu\text{m}^2$ , b)  $1 \times 1 \mu\text{m}^2$ . The dashed boxes show the regions from which averaged diffractograms were extracted (see Figure S1–3, Supporting Information).

Next to being involved in protrusion formation, red lead can undergo severe discoloration.<sup>[14]</sup> The most frequently encountered color change is described as blackening of the pigment, caused by the formation of either galena ( $\text{PbS}$ ) or plattnerite ( $\beta\text{-PbO}_2$ ). A second, less documented discoloration, visible as whitening or bleaching of the pigment has also been described.<sup>[15]</sup> In this case the alteration products are shown to be either lead carbonate (neutral and/or basic) or lead sulfate ( $\text{PbSO}_4$ ). Both lead carbonates that are formed during the whitening of the pigment are present in the blue covering layer, making it difficult to conclude that whitening of the red lead is taking place. However, the  $\mu\text{XRPD}$  tomograms we obtained reveal a “vacant space” between the minium core and the blue-tinted lead white layer (Figure 3b, top). In fact a fourth lead-containing compound, plumbonacrite ( $3\text{PbCO}_3 \cdot \text{Pb(OH)}_2 \cdot \text{PbO}$ ), is found to be present in the sample (see Figure S4 in the Supporting Information), and is largely situated in this “void”. To some extent an overlap between the lead white layer and plumbonacrite is visible (see also Figure S5, Supporting Information).

Plumbonacrite, a very rare lead carbonate mineral, can be formed in aqueous systems at ambient temperature and pressure and is metastable with respect to litharge ( $\text{PbO}$ ) and hydrocerussite.<sup>[16]</sup> The compound has been commonly reported as a corrosion product, for example in artificial ageing studies of lead samples subjected to acidic environments,<sup>[17]</sup> and on bronzes,<sup>[18]</sup> as well as on naturally aged objects.<sup>[19]</sup> However, literature regarding the presence of

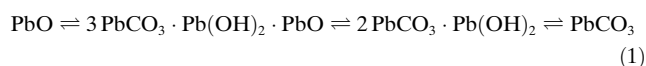
plumbonacrite in paintings or painters materials is very scarce. Plumbonacrite, together with (hydro)cerussite, was identified as a degradation product formed from lead(II) oxides upon artificial ageing.<sup>[20]</sup> It is worth mentioning that plumbonacrite was made synthetically from the mid 20th century.<sup>[21]</sup> Before this date, to the best of our knowledge, this phase was never detected on paintings, either as part of lead white mixtures or as a pure compound.

In our case, the presence of this carbonate-poor lead compound in between the red lead and the carbonate-rich lead white layer strongly suggests that plumbonacrite is present as an intermediate degradation product formed during the whitening of minium. Since PbO, a remnant of the red lead production process,<sup>[14]</sup> is more reactive than Pb<sub>3</sub>O<sub>4</sub>, it may have initiated the degradation process. Alternatively, minium itself can be photoactivated, leading to the reduction of Pb<sup>IV</sup> to Pb<sup>II</sup>. For the latter pathway, we propose an additional step in the photochemical reaction described by Zhou et al.<sup>[22]</sup> (Scheme 1).



**Scheme 1.** Proposed pathway for the photochemical degradation of Pb<sub>3</sub>O<sub>4</sub> under visible light irradiation. Conduction and valence band potentials, respectively  $E_{CB}$  and  $E_{VB}$ , are given relative to the normal hydrogen electrode (NHE).<sup>[22]</sup>

Electron hole pairs are formed between the valence (2.17 V) and conduction band (−0.08 V) of minium upon exposure to visible light ( $\lambda < 580$  nm). The electrons generated in the conduction band can reduce Pb<sup>IV</sup> present in minium to Pb<sup>II</sup> which in turn reacts with CO<sub>2</sub> to form one or more lead carbonate compounds.<sup>[22]</sup> The required CO<sub>2</sub> can be formed in situ through the oxidative decarboxylation of free fatty acids present in for example, the binding medium.<sup>[11]</sup> Atmospheric CO<sub>2</sub> may also easily penetrate through the porous paint layers; its influence has been proven to affect the whitening of red lead.<sup>[15]</sup> Here we propose an intermediate step in the fixation of CO<sub>2</sub> where a gradual uptake of CO<sub>2</sub> leads to the formation of plumbonacrite. Depending on the availability of CO<sub>2</sub>, the initially formed plumbonacrite layer can take up more CO<sub>2</sub> to form hydrocerussite and finally cerussite. Indeed, such a gradual uptake of CO<sub>2</sub> by lead(II) oxide has been shown to exist.<sup>[16b]</sup>



Different stages of equilibrium (1) can be observed at different locations in Figure S5 (Supporting Information).

Thus, our observations are fully consistent with the results obtained by Taylor and Lopata,<sup>[16b]</sup> who studied the solubility and stability of the PbO–CO<sub>2</sub>–H<sub>2</sub>O system; our results complete the photoinduced degradation pathway of minium.

## Experimental Section

The  $\mu\text{XRF}/\mu\text{XRPD}$  imaging experiments were performed at the microprobe station of the P06 Hard X-ray Micro/Nano-Probe beam line (PETRA III, DESY, Germany) (see Figure S6, Supporting Information). A photon energy of 21 keV was selected by means of a Si(111) double crystal monochromator. The beam was focused to  $0.5 \times 0.5 \mu\text{m}^2$  (hor.  $\times$  vert.) employing a Kirkpatrick–Baez mirror optic. Fluorescence radiation was recorded by a Vortex-EM silicon drift detector placed perpendicular to the incident X-ray beam. Simultaneously diffraction signals were recorded in transmission geometry using a PILATUS 300 K area detector at a distance of approximately 15 cm behind the sample. Initial calibration of the diffraction setup was performed using a LaB<sub>6</sub> reference sample. The software package PyMCA was used for spectral fitting of the fluorescence data,<sup>[23]</sup> while whole pattern fitting of the diffraction data as well as the  $\mu\text{XRF}$  and  $\mu\text{XRPD}$  computed tomography reconstructions were performed using XRDUA.<sup>[5b]</sup> This software package provides several methods for obtaining crystalline-specific distributions from a large number of diffraction patterns typically obtained in  $\mu\text{XRPD}$  imaging experiments.<sup>[7]</sup> The virtual cross-section of the paint sample was reconstructed using the maximum-likelihood expectation-maximization (MLEM) algorithm. Additional details regarding the  $\mu\text{XRF}/\mu\text{XRPD}$  tomography experiment as well as the computed X-ray absorption tomography measurement can be found in the Supporting Information.

Received: December 5, 2014

Revised: January 22, 2015

Published online: February 20, 2015

**Keywords:** degradation · pigments · red lead · tomography · X-ray diffraction

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