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# Synchrotron-based high angle resolution and high lateral resolution X-ray diffraction reveals lead white pigment qualities in Old Masters paintings

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**ABSTRACT:** Micro-samples collected on 27 major paintings by Old European Masters dating from the 14<sup>th</sup> to the late 19<sup>th</sup> c. were analyzed using Synchrotron-based X-ray diffraction. Two complementary analytical configurations were used at beamlines ID22 (high-angle resolution) and ID21 (high lateral resolution), in order to highlight markers of the different grades of the lead white pigments (mixture of cerussite  $\text{PbCO}_3$  and hydrocerussite  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ). Rietveld analysis and crystalline phases mapping at the micro-scale revealed the composition and microstructure of the pigments, shedding light on the preparation recipes and pigment choices of the artists through History.

Until the 20<sup>th</sup> c., lead white has been one of the most employed pigments in easel paintings<sup>1</sup>. Lead white is commonly composed of two crystalline phases, cerussite  $\text{PbCO}_3$  (*C*) and hydrocerussite  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$  (*HC*). Cerussite has an orthorhombic (space group *Pmcn*) aragonite-type structure ( $a = 5.179 \text{ \AA}$ ,  $b = 8.492 \text{ \AA}$ ,  $c = 6.141 \text{ \AA}$ )<sup>2</sup>. Hydrocerussite belongs to the rhombohedral system (space group *R-3m*), with lattice parameters  $a = 5.246 \text{ \AA}$ ,  $c = 23.702 \text{ \AA}$ <sup>3</sup>. In aqueous conditions, the formation of the two phases is *pH* dependent: *C* in acidic ( $pH < 6$ ) and *HC* in basic ( $8 < pH < 10$ ) environment. Morphologies (size and shapes) of the two phase crystallites can significantly vary, but most generally, cerussite crystallites are elongated along the [100] direction<sup>4</sup>, and hydrocerussite tends to crystallize as hexagonal platelets<sup>5,6</sup>.

The synthesis of lead white has remained almost unchanged from the Antiquity until the 19<sup>th</sup> c.<sup>7</sup>. It was traditionally based on the corrosion of metallic lead. Rows of jars containing lead plaques suspended above vinegar were stacked under horse manure: the decomposition of the manure produced  $\text{CO}_2$  and heat<sup>8</sup>. The combination of those reactants with acetic acid vapors induced the formation of cerussite and

hydrocerussite at the surface of the lead<sup>9</sup>. The pigment was collected before being sold to painters.

Historical sources reveal that some synthesis parameters could be adjusted, such as the time of corrosion. In addition, the obtained raw material was almost systematically post-processed by paint manufacturers or painters themselves before being mixed with the organic binder and employed in a painting<sup>10</sup>. Numerous post-synthesis treatments were used in color shops and artist's workshops<sup>11</sup>, such as washing and grinding the pigment in various media (vinegar, water), or heating in water. Obviously, these different processing and post-processing steps impact the chemical and physical characteristic of the final pigment. According to the sophistication degree of the *chaîne opératoire* applied to the pigment, different grades were obtained and proposed at very different prices on color markets<sup>12,13</sup>.

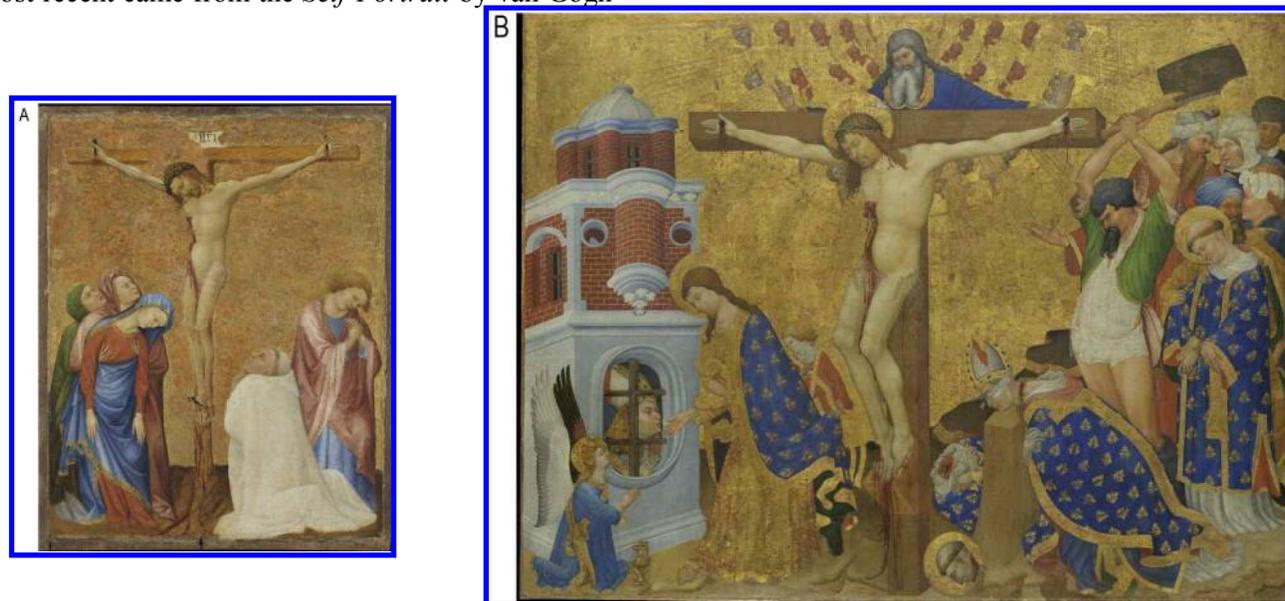
## Scope

The present work aims at detecting potential markers that could reveal the various pigment qualities used in European artworks, painted between the Middle Ages and the 19<sup>th</sup> c. and relate them to production recipes. Indeed, the variation of synthesis conditions and the

1 application of post-synthesis treatments induce  
2 changes in the composition (in particular *HC:C* ratio)  
3 and the microstructure of lead white (crystallites  
4 morphology)<sup>14</sup>. Those two parameters are accessible  
5 in historic paint micro-samples collected on artworks,  
6 using Synchrotron radiation (SR)-based X-ray  
7 diffraction (XRD).  
8

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10 In this work we report results obtained by SR-high-  
11 angular resolution-XRD (SR-HXRD) and SR-high  
12 lateral resolution-XRD (SR- $\mu$ XRD) on a corpus of 36  
13 samples. SR-HXRD is essential to obtain high quality  
14 XRD data (and consequently quantitative phase  
15 composition and crystallite morphologies), however it  
16 requires large and homogeneous samples. As a  
17 complement,  $\mu$ XRD was used for the qualitative  
18 analysis of complex multi-layered samples. The  
19 studied fragments were sampled from major artworks,  
20 preserved in French museums and covering a long  
21 historical period, ranging from the Middle Ages to the  
22 19<sup>th</sup> c. (the oldest sample was collected on the  
23 Louvre's *Cross* by Giotto (1267-1337), while the  
24 most recent came from the *Self-Portrait* by van Gogh  
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(1853-1890) conserved in the Orsay Museum). The  
complete list is presented in Table 1. Within this  
corpus, two artworks from the Louvre Museum  
samples were of particular interest, as the materials  
used during their conception have been documented  
in historical sources. More specifically, the question  
concerns the use of a particular quality of pigment in  
artworks commissioned by the Burgundy court during  
the 14<sup>th</sup> c. The accounts of the court that have been  
recently investigated report the purchase of two white  
pigment types, at different prices: the « *blanc de  
plomb* [= lead white] » and the « *blanc de puille* [=  
puille white] »<sup>15</sup>. The precise nature of *blanc de puille*  
is unknown to art historians: the only certitude is that  
it was bought at a lower price (twice as low) than  
*blanc de plomb*. The first sample has been collected  
on the *Calvaire avec un moine chartreux* (c. 1395)  
(Fig. 1A) by Jean de Beaumetz (1335-1396), the  
second on the *Retable de Saint-Denis* (1416) (Fig.  
1B), by Henri Bellechose (fl. 1415-1444). Historical  
sources indicate that while Bellechose used *blanc de  
plomb*, Beaumetz chose *blanc de puille*.



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Figure 1 : (A) *Calvaire avec un moine chartreux* (c. 1395) by Jean de Beaumetz (Musée du Louvre, © C2RMF, 61 x 48.5 cm).  
(B) *Retable de Saint Denis* (1416) by Henri Bellechose (Musée du Louvre, © C2RMF, 162 x 211 cm)

## 50 MATERIALS AND METHODS

### 51 *Samples*

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Historical samples selected for this work belong to  
the C2RMF samples collection and are paint micro-  
fragments previously collected on masterpieces  
conserved in several French Museums, particularly  
the Louvre and Orsay (Paris, France).

Micro samples have dimensions typically inferior to  
100  $\mu$ m. They were available under two forms: as raw  
fragments (32 samples) and as cross-sections  
prepared by polishing samples embedded in resin  
(two samples).

For HR-XRD experiments, raw samples were placed  
in sealed glass capillaries and positioned directly in

front of the X-ray beam of the ID22 beamline. A limit of the HR-XRD analytical configuration lies in the lateral resolution. With a beam of 1 mm<sup>2</sup>, the whole bulk of the sample is analyzed simultaneously: in the case of complex stratifications, contributions of all the layers are mixed in the obtained diffractogram. In our case, we selected samples with only one layer

containing lead white. In one particular case, it was possible to carefully mechanically separate two superimposed lead white-based layers, in order to analyze them separately (see Table 1, samples 3-a and 3-b), but this process is very tedious and cannot be routinely performed.

Table 1 : Historical micro-samples analyzed by HR-XRD and  $\mu$ XRD

Painter	Artwork	Nature of sample	Analytical method	Label used in figures
Giotto (1266/76-1337)	<i>Crucifix</i> (c. 1315)	Layer	HR-XRD	Giotto
Master of 1333 (active c. 1325-1350)	<i>Retable</i> (1333)	Layer	HR-XRD	Maitre1333
Jean de Beaufort (1335-1396)	<i>Calvaire avec un moine chartreux</i> (c. 1395)	Complete stratigraphy	$\mu$ XRD	Beaufort
Henri Bellechose (active c. 1415-1444)	<i>Retable de Saint Denis</i> (1416)	Complete stratigraphy	$\mu$ XRD	Bellechose
Giovanni da Camerino Boccati (1420-1480)	<i>Vierge à l'enfant et concert d'anges</i> (1463-1480)	Layer	HR-XRD	Boccati
Mantegna (c.1431-1506)	<i>Saint Sébastien</i> (1480)	Layer	HR-XRD	Mantegna
Botticelli (1444/45-1510)	<i>La Vierge et l'enfant avec un ange</i> (c. 1490)	Layer	HR-XRD	Botticelli 1
Botticelli (1444/45-1510)	<i>La Vierge et l'Enfant soutenu par un ange</i> (c. 1467-1510)	Layer	HR-XRD	Botticelli 2
Botticelli (1444/45-1510)	<i>La Vierge à l'enfant</i> (1444/45-1510)	Layer	HR-XRD	Botticelli 3
Leonardo da Vinci (1452-1519)	<i>La Belle Ferronnière</i> (1495-1497)	Ground	HR-XRD	Leonardo 1
Leonardo da Vinci (1452-1519)	<i>La Joconde</i> (1503/06)	Ground	HR-XRD	Leonardo 2
Leonardo da Vinci (1452-1519)	<i>La Vierge, l'enfant Jésus et sainte Anne</i> (c. 1508/10)	Layer	HR-XRD	Leonardo 3-a
Leonardo da Vinci (1452-1519)	<i>La Vierge, l'enfant Jésus et sainte Anne</i> (c. 1508/10)	Layer	HR-XRD	Leonardo 3-b
Leonardo da Vinci (1452-1519)	<i>La Vierge, l'enfant Jésus et sainte Anne</i> (c. 1508/10)	Priming	HR-XRD	Leonardo 3-c
Grünwald (1475/80-1528)	<i>Retable d'Issenheim</i> (c.1512-1516)	Layer	HR-XRD	Grünwald
Lotto (1480-1557)	<i>Le portement de croix</i> (1526)	Layer	HR-XRD	Lotto 1-a
Lotto (1480-1557)	<i>Le portement de croix</i> (1526)	Layer	HR-XRD	Lotto 1-b
Raffaello (1483-1520)	<i>La Belle Jardinière</i> (c. 1507-1508)	Layer	HR-XRD	Raffaello 1
Raffaello (1483-1520)	<i>Portrait de l'artiste avec un ami</i> (c. 1519)	Layer	HR-XRD	Raffaello 2
Raffaello (1483-1520)	<i>La Grande Sainte Famille</i> (1518)	Layer	HR-XRD	Raffaello 3
Bronzino (1503-1572)	<i>Sainte Famille</i> (c. 1550)	Layer	HR-XRD	Bronzino
Parmigianino (1503-1540)	<i>Portrait de jeune homme</i> (c.1520-1530)	Layer	HR-XRD	Parmigianino 1-a
Parmigianino (1503-1540)	<i>Portrait de jeune homme</i> (c.1520-1530)	Priming	HR-XRD	Parmigianino 1-b
Tintoretto (1518-1594)	<i>Le Paradis</i> (1579/80)	Layer	HR-XRD	Tintoretto
Contemporary of Goya	<i>Dernière communion de San José de Calasanz</i> (1819)	Ground	HR-XRD	Goya 1-a
Contemporary of Goya	<i>Dernière communion de San José de Calasanz</i> (1819)	Layer	HR-XRD	Goya 1-b
Goya (1746-1828)	<i>Portrait de la Solana</i> (1794-1795)	Layer	HR-XRD	Goya 2
Goya (1746-1828)	<i>Grande Marquise de Santa Cruz</i> (1798-1799)	Layer	HR-XRD	Goya 3
Monet (1840-1926)	<i>La cathédrale de Rouen. Le portail et la tour Saint-Romain, plein soleil. Harmonie bleu et or</i> (1893)	Ground	HR-XRD	Monet 1a
Monet (1840-1926)	<i>La cathédrale de Rouen</i> (1893)	Ground	HR-XRD	Monet 1b
Monet (1840-1926)	<i>La cathédrale de Rouen</i> (1893)	Transfer layer	HR-XRD	Monet 1c
Monet (1840-1926)	<i>La cathédrale de Rouen. Le portail, soleil matinal. Harmonie bleue</i> (1893)	Ground	HR-XRD	Monet 2
van Gogh (1853-1890)	<i>Le jardin à Auvers</i> (1853-1890)	Ground	HR-XRD	van Gogh 1
van Gogh (1853-1890)	<i>Portrait de l'artiste</i> (1889)	Ground	HR-XRD	van Gogh 2

In order to gain insight on more complex samples, it is necessary to work at a very good spatial resolution (micrometric scale), which was achieved at the ID21 X-ray microscopy beamline: spatial repartition of the crystalline phases can then be retrieved, providing an insight on the entire paint layers' stratification. Accordingly,  $\mu$ XRD was applied to a more reduced corpus, those presenting a complex multilayer structure.

For  $\mu$ XRD experiments, samples were prepared as thin sections (to allow measurements in transmission mode at 8.5 keV). These sections were obtained from historical samples in resin blocks, using a microtome. Their preparation was made difficult by the fact that some of the resin blocks had been prepared decades ago: the resin was not necessarily suitable for microtomy and it was important to preserve as much as the sample cross-section for future analyses. Accordingly, a dedicated protocol was optimized consisting in slicing the cross-section along one of its

sides, perpendicular to the cross-section surface, and perpendicular to the sample strates<sup>16, 17</sup>. In order to preserve the stratification in the thin section, a small piece of sulfur-free tape (Fluxana) is applied on the

### Analytical methods

XRD measurements were performed at two beamlines of the European Synchrotron Radiation Facility (ESRF, Grenoble, France).

*SR-high-angular resolution-XRD.* HR-XRD was carried out at ID22 beamline<sup>18</sup> (ESRF), which is equipped with a 9-channel Si (111) multianalyzer stage. Glass capillaries containing the raw paint micro-samples were placed in front of the  $1 \times 1$  mm<sup>2</sup> beam. The capillaries were rotated at 12 rps during the experiment, to avoid preferential orientation effects. High energy radiation was selected (35 keV, 0.3542 Å) to ensure a good transparency (at this energy, the transmission factor for a micro-sample of 1-3 µg in weight composed of ~50 vol. % lead white is estimated around 60 %). Because of the small size of the samples, 20 min scans were repeated up to a total acquisition time of 1-4 h to record diffractograms with a good signal to noise ratio. The exploitable angular range was  $2 \leq 2\theta$  (°)  $\leq 22$  ( $0.93 \leq d$  (Å)  $\leq 10.14$ ), allowing the measurement of 152 reflections for *C* and 49 for *HC*. The main advantages of this configuration are the excellent angular resolution (0.002°) and the absence of preferential orientation. This permits the recording of high quality datasets: a precise composition can be derived from the Rietveld fitting<sup>19</sup> (error bars of about  $\pm 1$  w% estimated from a *C/HC* calibration mixture) and the modeling of the pigment crystallite morphologies is possible. To achieve that, XRD patterns were analyzed using the Fullprof suite<sup>20</sup>, on the basis of crystallographic data found in the literature for *HC*<sup>3</sup> and *C*<sup>2</sup> (Fig. 2A). Quantitative phase analyses were derived from the scale factors. More particularly, the *HC/(HC+C)* and  $\text{CaCO}_3/(\text{HC}+\text{C})$  weight percentages were calculated to assess the pigment composition. More details on the Rietveld fitting can be found elsewhere<sup>14</sup>.

For the assessment of crystallites sizes, a measurement was considered as reliable only in the case of a sufficient broadening (> 50%), that is for

resin surface, trapping the thin section during the cut. This section can then be protected with an Ultralen foil (Spex Certiprep) avoiding the sample fragment to fall away. The complete protocol is detailed in S. I.

crystallites of size < 1.5 µm (for a full-width at half maximum FWHM of the instrumental peak (LaB<sub>6</sub>) of 0.004° at  $2\theta = 10^\circ$ ). In other words, the modeling is only possible for small crystallites. More particularly, for *HC*, the overview of the mean crystallites sizes is solely based on the thickness of the hexagonal platelets (*l<sub>c</sub>*).

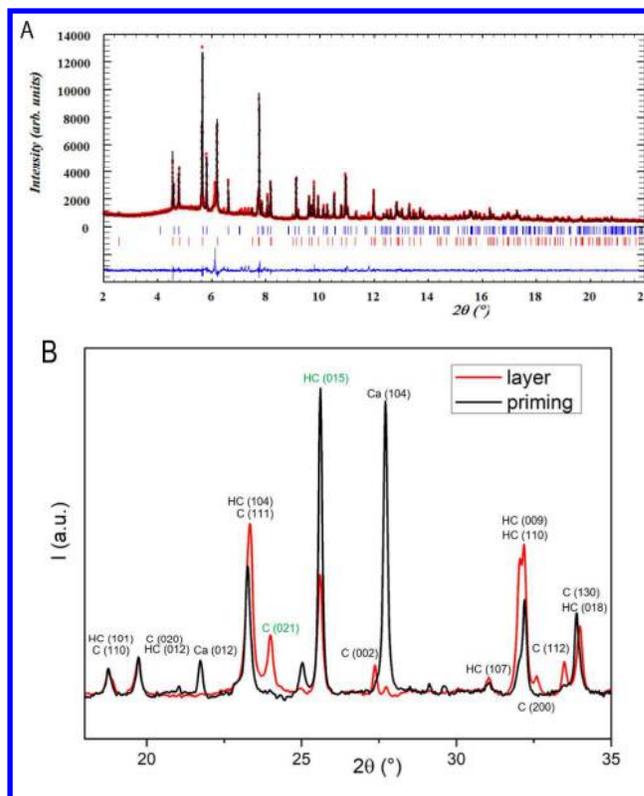


Figure 2 : (A) Rietveld plot for diffractogram recorded by HR-XRD at ID22 (sample Raffaello 1) : experimental (red circles), calculated (black line), difference (blue line), Bragg positions (bars).

(B) Cumulated and azimuthally integrated diffractogram recorded by  $\mu$ XRD at ID21 on layer 3 of sample Beaumetz (cf. Fig 7). Peaks used for quantification (*C*<sub>(021)</sub> and *HC*<sub>(015)</sub>) are indicated in green.

*SR-high lateral resolution-XRD.*  $\mu$ XRD experiments were carried out at the ID21 beamline, ESRF. This beamline offers a combination of multiple micro-analytical X-ray based techniques<sup>21</sup>. For this work, the  $\mu$ XRD branch was used to perform crystalline phase mapping using a  $0.7 \times 1.0$  µm<sup>2</sup> beam. In this mode, the beamline is optimized for an energy of 8.54 keV, 1.4519 Å. 2D diffraction patterns (Debye-Scherrer rings) are recorded in transmission, on a CCD FReLON camera (2048×2048 pixels, 52 µm

1 pixel size) positioned behind the sample. The  
2 diffraction rings are then converted into 1D  
3 diffractograms by azimuthal integration, using the  
4 PyFAI and XRDUAs<sup>22, 23</sup>. Thin-sections are  
5 positioned on a motorized *xyz* stage, perpendicular to  
6 the beam, and are then raster scanned over a 2D map.  
7 At each pixel, a diffractogram is recorded: crystalline  
8 phases distribution for the entire mapped area is thus  
9 performed. The XRDUAs software package was used  
10 to handle  $\mu$ XRD data<sup>24</sup>. In particular, the  
11 diffractogram recorded at each pixel of the map was  
12 fitted on the basis of references for each crystalline  
13 phase of interest. Background correction was also  
14 applied. This allowed obtaining qualitative spatial  
15 distribution of *HC*, *C* and  $\text{CaCO}_3$ . Applying  
16 quantitative analysis such as Rietveld fitting for each  
17 pixel was not reliable since the relatively large size of  
18 some crystal particles (in particular cerussite), with  
19 respect to the beam size ended into highly oriented,  
20 quasi single crystal patterns. As an alternative,  
21 cumulated Debye-Scherrer rings were calculated  
22 using XRDUAs, for an entire selected area of the  
23 crystalline map, more particularly over each layer of  
24 the paint stratification. With this approach, the signal  
25 is averaged over tens of grains, presenting disperse  
26 orientations, the resulting XRD pattern being more  
27 similar to a powder-like pattern. For each cumulated  
28 diffractogram, cerussite, hydrocerussite and calcite  
29 relative amounts were estimated on the basis of  
30 integrated intensities of a single, but strong and non-  
31 overlapped peak (*C* (021), *HC* (015)) (Fig. 2B, Fig.  
32 S.I.2). Values measured on standard mixtures were  
33 used to convert intensity ratios into weight ratios  
34 *HC*/*HC*+*C* (w%). The main asset of  $\mu$ XRD is the  
35 excellent spatial resolution, allowing discriminating  
36 paint layers with thickness of only several microns.  
37 However, several limitations related to the used  
38 geometry (some pigment grains having a size of the  
39 order of the beam size leading to preferential  
40 orientations; limited statistics due to the limited  
41 amount of material contributing to the diffracted  
42 signal) can skew the measured intensities, thus  
43 limiting the accuracy of the calculated composition. It  
44 is reasonable to envision a  $\pm 10$  w% error bar for  
45 *HC*:*C* ratios.

46 Furthermore, the observation of the cumulated  
47 diffractograms indicated a satisfactory statistic

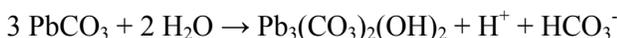
which allowed us to estimate the Scherrer broadening  
for *HC*, on the basis of the (015) and (107) peaks. In  
this case, the instrumental function was evaluated to  
 $0.15^\circ$  ( $2\theta$ ) on the basis of the  $\text{CaCO}_3$  phase present in  
the sample, and FWHM for each peak was evaluated  
by fitting them independently using the Fullprof  
software. Considering a possible error of  $2/100^\circ$   
during the FWHM measurement, the error on the  
crystal thickness is of about 120 nm.

## RESULTS AND DISCUSSION

In order to provide explanations of the observed  
tendencies, the diffraction data obtained on historical  
samples was compared with results gathered on  
models samples. Those models have been obtained by  
reconstitution of the corrosion process and of post-  
synthesis treatments. Experiments will be detailed in  
a forthcoming publication, but we summarize here the  
main conclusions as a basis for the interpretation of  
results obtained on historical samples. First, these  
experiments highlighted the complexity of the  
corrosion process based on the combined action of  
acetic acid vapor,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ : several intermediate  
phases (lead acetates) as well as plumbonacrite<sup>25</sup>  
 $\text{Pb}_{10}(\text{CO}_3)_6\text{O}(\text{OH})_6$  (*PN*) were detected in the first  
stage of corrosion, before their transformation in *HC*  
and *C*. As a rule of thumb, it appears that the lead  
white composition evolves during the corrosion  
process towards carbonate-rich phases, that is, from  
*PN* to *HC*, then *C*, but whereas *HC* and *C* form flakes  
that peel off easily, *PN* only occurs in the thin  
corrosion film that sticks to metal. Therefore, *PN* is  
only rarely observed in the final pigment. Besides,  
these reproductions showed that the amount of *C*  
increases with the corrosion time, as the *HC*  $\rightarrow$  *C*  
transformation keeps going as long as  $\text{CO}_2$  is present.  
So, if the  $\text{CO}_2$  supply was too important, or continued  
after the consumption of the metallic lead, a pigment  
with *C* > *HC* was obtained. However, in a real stack  
process, the supply of  $\text{CO}_2$  necessary to entirely  
convert *HC* into *C* was limited. Indeed, the *HC*  $\rightarrow$  *C*  
reaction consumes five times as much  $\text{CO}_2$  per Pb  
atom than the *PN*  $\rightarrow$  *HC* reaction (see S.I.3):  
synthesizing an important amount of *C* is difficult.  
So, we expect an historical lead white to be mostly  
composed of *HC*.

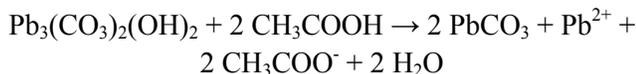
In the same way, in the case of a brief synthesis, the ratio was displaced such as  $HC > C$  (up until  $HC:C = 100:0$  w%). More detailed information on the reaction chain at stake in the stack process is presented in S.I.

Furthermore, the two main post-synthesis treatments frequently described in historical sources (heating in water, washing or grinding in vinegar)<sup>26</sup> were also reproduced on pure  $HC$  and  $C$  powders, to investigate their effects. It was thus observed that heating in water induced the transformation of  $C$  into  $HC$ , according to the following reaction:



The newly formed  $HC$  crystallites were of important sizes, with dimensions up to  $5 \mu\text{m}$  instead of  $< 1 \mu\text{m}$  without this post-process.

Conversely, the treatment in acidic environment of pure  $HC$  led to a formation of  $C$ , following a recrystallization process:



As stated above, we will use those results (summarized in Fig. 3) to explain the composition and microstructure of the lead white pigment used by Old Masters in their paintings, accessible using SR-XRD.

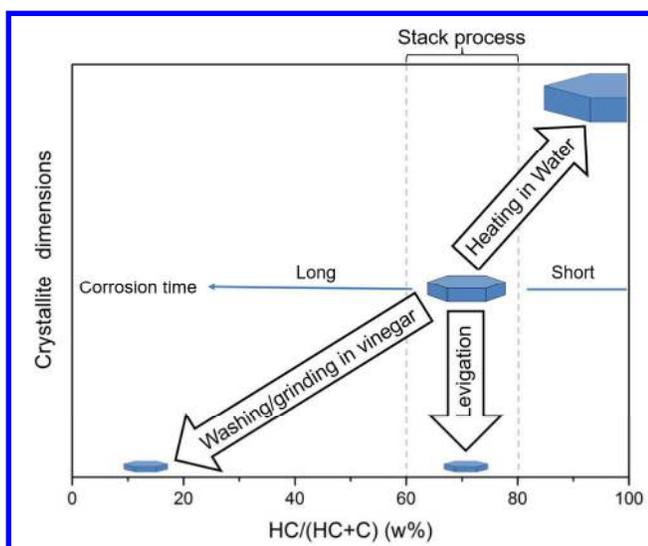


Figure 3 : Composition and microstructure of lead white as a function of synthesis conditions and post-synthesis processes

## HR-SR-XRD

Composition Fig. 4 gives an overview of the compositions ( $HC/HC+C$  w% and  $\text{CaCO}_3/HC+C$  w%) measured on the entire corpus of raw micro-samples.

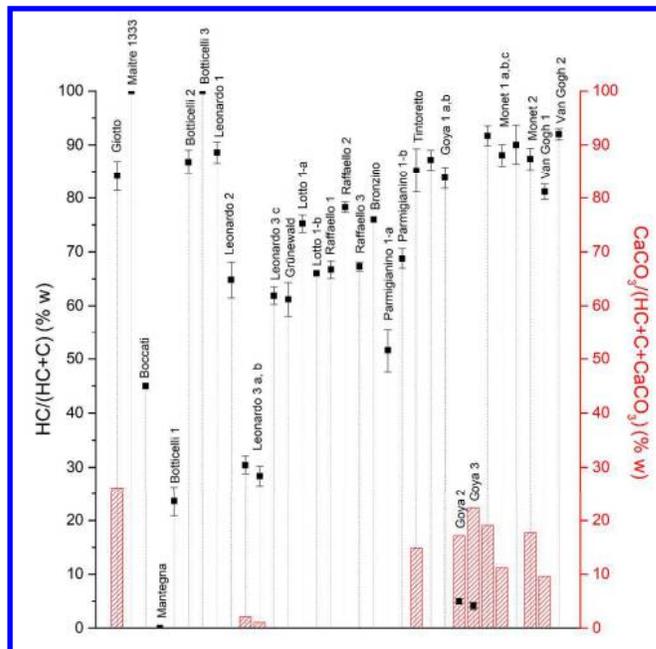


Figure 2 : Composition derived from Rietveld fitting of ID22 data. Hydrocerussite (left scale, black squares) and calcite (right scale, red bars) weight ratios. Samples are plotted in chronological order from left to right

Several observations can be made:

- From the 14<sup>th</sup> to the 19<sup>th</sup> c., most of the samples present a  $HC$ -rich chemical composition ( $HC:C$  ratio between 60:40 and 80:20 w%).
- Lead white pigments produced during the 19<sup>th</sup> c. are all very rich in  $HC$  ( $HC:C > 80:20$  w%).
- Two samples are only composed of  $HC$  (Maitre 1333 and Botticelli 3).
- A small number of samples (8/34) present a  $HC:C < 50:50$  w% ratio, meaning that they contain more  $C$  than  $HC$ .
- Calcite  $\text{CaCO}_3$  is frequently present as an extender of lead white, sometimes in a very important amount ( $> 20$  w%), and this more frequently from the late 19<sup>th</sup> c. (samples collected on paintings by Goya and Monet).

1 Relying on the laboratory reconstitution of the  
2 corrosion process and of the post-synthesis treatments  
3 (cf. Fig. 3), it is possible to propose explanations to  
4 those observations.

5  
6 - The persistence in time of  $HC:C$  ratios comprise  
7 between 60:40 and 80:20 w% is noteworthy. As  
8 stated above, if a lead white synthesis is carried on  
9 until total lead depletion, a  $C > HC$  pigment would be  
10 expected. This persistence could then be explained by  
11 several reasons. First, as stated above, the supply of  
12  $CO_2$  necessary to entirely transform  $HC$  into  $C$  was  
13 limited in a stack. Another explanation is a systematic  
14 harvest of the pigment before complete consumption  
15 of lead. The reason for this could be a special interest  
16 of painters in  $HC$ -rich pigments: recent work suggest  
17 that the specific morphology of  $HC$  crystallites indeed  
18 communicates interesting optical properties to the  
19 pigment<sup>27</sup>. Finally, another possibility is an  $C \rightarrow HC$   
20 evolution of the pigment within paint layers over  
21 centuries, but this seems doubtful, as it would require  
22 a shift of  $pH$  towards basicity, which is unlikely in a  
23 polymerized fatty-acid organic binder. This leads us  
24 to the hypothesis that a pigment with a weight ratio  
25  $HC:C$  comprise between 60:40 and 80:20 w%  
26 corresponds to the standard product obtained by the  
27 stack process.

28  
29 - The very high  $HC$  amounts detected in samples from  
30 the 19<sup>th</sup> c. ( $HC:C > 80:20$  w%) could be explained by  
31 two hypotheses. The first hypothesis is linked to the  
32 rate of the phases formation during this process. As  
33 mentioned before,  $HC$  is the first crystalline phase  
34 that forms abundantly during corrosion. As the  
35 demand for lead white was considerable at this time<sup>28</sup>,  
36 production rates were increased and corrosion times  
37 were curbed at the maximum, which could lead to the  
38 formation of an even more  $HC$ -rich lead white.  
39 Secondly, all of the historical sources describing the  
40 synthesis of lead white during the 19<sup>th</sup> c. insist on the  
41 very thorough washing that was performed on the  
42 pigments in factories<sup>29, 30</sup>: such a post-synthesis  
43 treatment could also lead to an increase of the  $HC$   
44 percentage.

45  
46 - Ratios  $HC:C = 100:0$  w% could result either from a  
47 very brief synthesis or from the heating of the  
48 pigment in water (the  $HC$  crystallites would then have  
49 a large size), as previously stated.

50  
51 - Two main hypotheses can be considered for the  $C$ -  
52 rich samples. The first is that the  $C$  enrichment took  
53 place during the synthesis by the stack process. As  
54 described above, the transformation of all the  $HC$   
55 created during the corrosion in  $C$  could for example  
56 result from a  $CO_2$  supply sufficient for completing the  
57 carbonation, or a long corrosion time. The second is  
58 that a post-synthesis treatment in acidic environment  
59 (by washing or grinding) was used.

60  
61 - Regarding the high amount of calcite sometimes  
62 mixed with the lead white (20 w% of  $CaCO_3$   
63 corresponds to 40% of the pigment volume), it is  
64 possible to deem that such pigments were of lower  
65 quality, as attested by numerous historical sources<sup>31,</sup>  
66 <sup>32</sup>. The fact that most samples from the 19<sup>th</sup> c.  
67 contained calcite mixed with lead white is also in  
68 agreement with sources: the adjunction of this  
69 extender was frequent at those times, when the  
70 production of the lead white pigment could almost be  
71 qualified as industrial.

*Microstructure* When the amount of diffracting  
matter was sufficient (e.g. samples of size  $> 100 \mu m$ ),  
HR-XRD diffractograms of high quality were  
obtained, enabling the modeling of  $HC$  and  $C$   
crystallites, based on the anisotropic broadening. This  
modeling is unprecedented for lead white, as pigment  
crystallites are aggregated when the pigment is mixed  
with the binder, and thus unobservable by classic  
examination techniques used in conservation science  
such as scanning electron microscopy (SEM).

Crystallites shapes were in accordance with the  
expected model for the two phases (elongated  
rhombohedra for  $C$  and hexagonal platelets for  $HC$ ).  
The obtained results can be divided into two temporal  
periods: 14-16<sup>th</sup> c. and 19<sup>th</sup> c., as visible on Fig. 5.

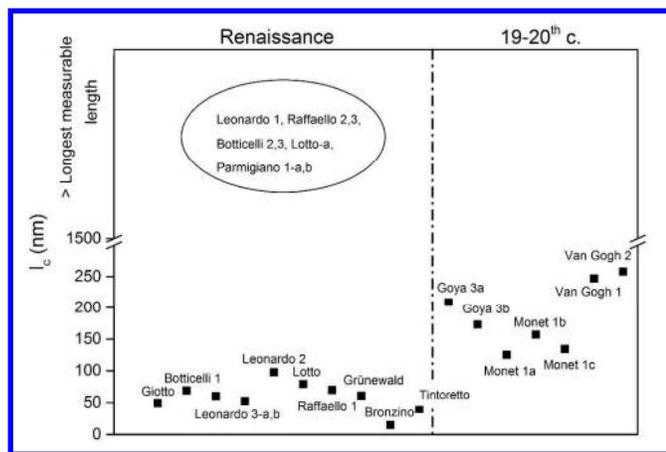


Figure 3 : Evolution of the mean HC crystallite sizes in time. For the 14-16<sup>th</sup> c. group, lead white exhibit either very small or large (superior to the longest measurable length) crystallites.

The first observation is that for lead whites used during the 14-16<sup>th</sup> c., samples split up into a bimodal distribution: a first group is composed of crystallites with sizes inferior to 150 nm, while another is constituted of particles with  $l_c > 1500$  nm, that is to say superior to the longest measurable length.

Providing a definitive explanation of these tendencies is difficult, but several points for reflection can be made. Regarding the 14-16<sup>th</sup> c. period, the only synthesis method then used was the stack process. The presence of two groups of sizes could be ascribed to the use of a post-synthesis treatment. Indeed, heating the pigment in water could account for large-sized crystallites. Conversely, a treatment in vinegar inducing an acidic dissolution of HC crystallites could explain the presence of smaller particles. Finally, levigation of lead white was often performed, in order to select only the finest pigment particles<sup>33</sup>. This post-synthesis treatment could also result in a pigment composed of small crystallites.

Regarding the 19<sup>th</sup> c., it cannot be asserted that the stack process is the only used way to produce lead white. The increase in crystallites size could thus be the result of new synthesis routes developed at this time. However, the stack process was far from being abandoned and we can suppose that the better monitoring of the corrosion conditions (temperature control, gas flows...), or the thorough washing always performed in lead white factories, resulted in larger crystallites.

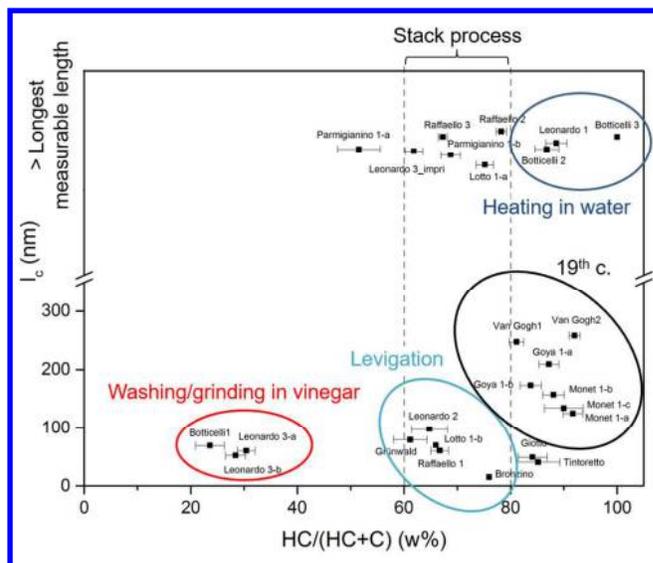


Figure 4 : Plotting of the mean crystallite sizes vs HC/(HC+C) (w%)

The plotting of HC crystallite mean sizes as a function of the HC:C ratio (Fig. 6) proves informative.

A first group of pigments rich in C and composed of small sizes particles appears. This supports the idea that this type of lead white could originate from a post-synthesis treatment in acidic conditions: the recrystallization of small C crystallites is accompanied by the dissolution of all the pre-existing crystallites: remaining HC platelets exhibit small dimensions. A second group of pigments used by artists of the 14-16<sup>th</sup> c. with small crystallites could be the result of a levigation process, that would permit to select only small crystallites without shifting the HC:C ratio. A third group composed of pigments containing HC crystallites of large dimensions and with HC:C > 80:20 w% could account for the heating of the pigment in water. Finally, lead whites used by painters of the 19<sup>th</sup> c. present comparable features (small crystallites with HC:C > 80:20), and could highlight the quasi-industrialization of the lead white synthesis at this time.

#### SR- $\mu$ XRD

Qualitative  $\mu$ XRD crystalline maps were obtained on two samples, taken from the paintings of Beaumetz and Bellechose, as detailed in the introduction. Preliminary SEM observations of these two samples reveal comparable stratigraphies: on a thick Ca-based preparatory layer, successive lead white layers were painted: first a thin priming layer (marked #2 on Fig.

7A and 7B), then a pictorial layer (only one in the case of Beaumetz (#3 on Fig. 7A) and two for Bellechose (#3 and #4 on Fig. 7B). It is worth noting that in the case of Bellechose, a thick lead white-based transfer layer (not visible on the SEM image) is

found below the calcite ground. This layer is not of origin and was not taken into account.

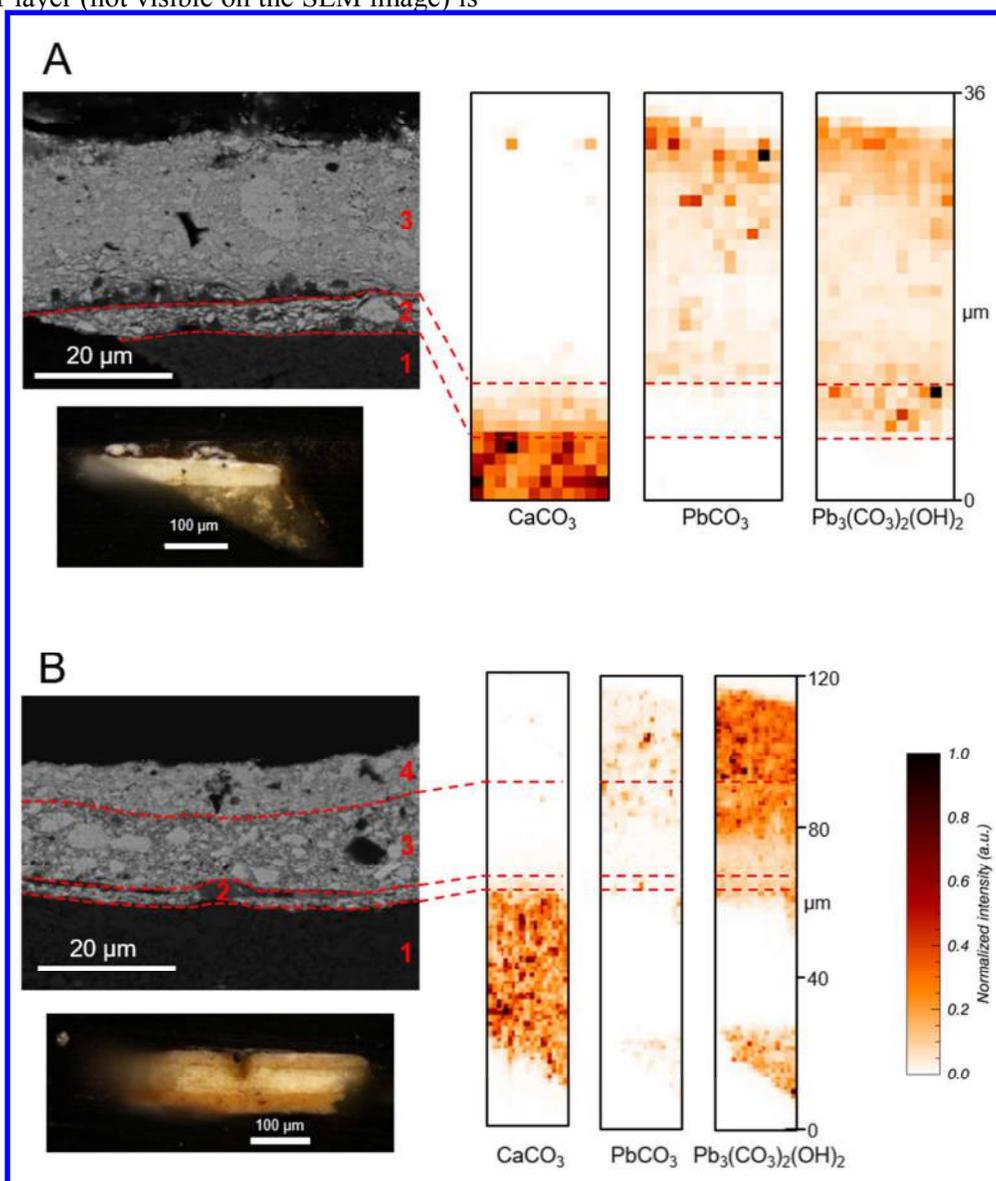


Figure 5 : Mapping of calcite  $\text{CaCO}_3$ ,  $\text{C PbCO}_3$  and  $\text{HC (Pb}_3(\text{CO}_3)_2(\text{OH})_2)$ , for the sample Beaumetz (A) and Bellechose (B). On the Beaumetz sample, above the calcite ground, the impression layer (delimited in red dots) only contains HC. On top the white layer contains a mix of HC and C. On the Bellechose sample, above the calcite ground several lead white layers containing HC and C are superimposed.

For the Beaumetz sample, the phase maps immediately render the stratification of the sample. The preparatory layer is composed of calcite  $\text{CaCO}_3$ . The priming layer is composed of 100% HC. The pictorial layer above is composed of a mix of the two carbonates with the estimated ratio  $\text{HC:C} = 75:25 (\pm 10)$  w%.

For the Bellechose sample, the distinction of specific lead white recipes (i.e. specific  $\text{HC:C}$ ) was not

straightforward, due to the low chemical contrast between adjacent lead white layers #2, 3 and 4. In this case, layers were identified on the basis of the SEM images, showing characteristic pigment grain morphologies (see Fig. 7). Cumulated patterns were calculated over those regions. The following ratios were obtained for the lead white layers: for the priming (layer #2):  $\text{HC:C} = 80:20 (\pm 10)$  w%, for layer #3:  $\text{HC:C} = 90:10 (\pm 10)$  w%, for layer #4:  $\text{HC:C} = 80:20 (\pm 10)$  w%. The limited precision of the ratio

1 estimations does not allow to discriminate potential  
2 pigment qualities between the layers.

3  
4 Regarding lead white microstructure, for the lead  
5 whites used by Beaumetz, in the priming as well as in  
6 the pictorial layer, the broadening corresponds to *HC*  
7 platelets with a thickness of about 400 nm. For  
8 Bellechose, thickness of the *HC* platelets was  
9 estimated to 250 nm for the upper layer (#4) and 400  
10 nm for the intermediate layer (#3). Taking into  
11 account the  $\pm 120$  nm error corresponding to the  
12 FWHM estimation, the obtained thickness still  
13 corresponds to very important crystallite sizes.

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16  
17 Considering all the XRD information gathered on the  
18 two samples, we propose a possible identification on  
19 the *blanc de paille* used by Beaumetz as a lead white  
20 pigment composed of 100% *HC*. This composition is  
21 indeed particularly uncommon, and can either be  
22 linked to a post-synthesis treatment, or to specific  
23 synthesis conditions.

24  
25  
26 We showed that such a composition can be the result  
27 of the pigment heating in water. This first hypothesis  
28 is in agreement with the estimated crystallites sizes.  
29 We can propose that the name *blanc de paille* was  
30 given to a lead white sold in a poor state of  
31 cleanliness and that had to be washed for a long time  
32 by the painter himself, in order to get rid of impurities  
33 (dirt) it contained. This would account for the reduced  
34 price of *blanc de paille*: a low grade pigment  
35 requiring thorough washing to be usable in paintings.

36  
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39 Another hypothesis relies on the examination of  
40 another historic treatise. In this manuscript, the author  
41 affirms that *blanc de paille* was obtained using urine  
42 instead of vinegar during the pigment synthesis. This  
43 could also account for the high *HC* content observed.  
44 Indeed, the amount of  $\text{CO}_2$  in such a synthesis would  
45 be considerably lesser than when vinegar is used. In  
46 the case of such a  $\text{CO}_2$ -deprived corrosion  
47 environment, the formation of hydrocerussite would  
48 conceivably be favored.

49  
50  
51  
52 Finally, other white mineral compounds such as  
53 calcite  $\text{CaCO}_3$  or *gesso*  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  have been ruled  
54 out, as the price of *blanc de paille* remains too high to  
55 designate those cheap materials.

It is worth noting that the only other sample we  
observed with a similar composition also stems from  
the same historic period (Maitre 1333 sample, see  
Fig. 4). The synthesis of *blanc de paille* could thus  
have been time-bound in Europe during the 14<sup>th</sup> c.  
before disappearing.

## CONCLUSION

Using two SR-based XRD analytical configurations  
on historical micro-samples, it was possible to gain  
insight on the various grades of lead white pigments  
used by painters.

Variations of the hydrocerussite/cerussite ratios and of  
pigment crystallite sizes were connected to different  
synthesis conditions, or to post-synthesis treatments  
employed by paint manufacturers and artists of the  
past.

In addition, the use of  $\mu\text{XRD}$  allowed identifying a  
particular pigment used during the 14<sup>th</sup> C., reinforcing  
our knowledge of the use of paint materials during the  
Middle-Ages.

A previous study performed on reference samples has  
highlighted the effects of post-synthesis treatments on  
the pigment optical properties<sup>34</sup>. While many  
questions remain regarding their criteria when  
choosing between various grades of lead white, this  
work allowed taking a step forward in the  
understanding of the pictorial practices of the Old  
Masters.

Regarding methodology, an important consideration  
is the high complementarity of the various SR-XRD  
configurations that were implemented. While the  
excellent data quality of the HR-XRD permits a very  
precise estimation of the studied material composition  
and microstructure, only the spatial resolution of the  
 $\mu\text{XRD}$  allows to distinguish between paint layers at  
the micro-scale.

The main limitation of SR-XRD as used here is that it  
is applied on samples of micrometric dimensions. The  
issue of reproducibility, despite having been  
successfully tested on some samples collected on the  
same painting<sup>14</sup>, remains open. Regarding this issue,  
recent instrumental developments, especially  
crystalline phase mapping at the macro scale are

promising<sup>35</sup>. The combination of those new laboratory-based instruments with methodologies described in this work could provide even more detailed information on the Old Masters pictorial practices.

## ASSOCIATED CONTENT

### *Supporting information available*

Protocol for thin-section preparation at ID21; Calibrating curve based on standard *HC/C* mixtures for the quantification of phases at ID21; Information regarding the chemical reactions at stake during the synthesis and post-synthesis of lead white ; List of historical micro-samples analyzed in this study indicating the museum in which each painting is conserved.

## AUTHOR INFORMATION

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### *Author Contributions*

XRD data was collected during 3 beamtime sessions at the ESRF by V.G., G.W., T.C., M.C., W.D.N and M.M. Data treatment was performed by V.G., G.W. and W.D.N. The ensemble of results was discussed between all authors. The paper was written by V.G., M.C. and G.W. All authors have given approval to the final version of the manuscript.

### *Notes*

The authors declare no competing financial interest.

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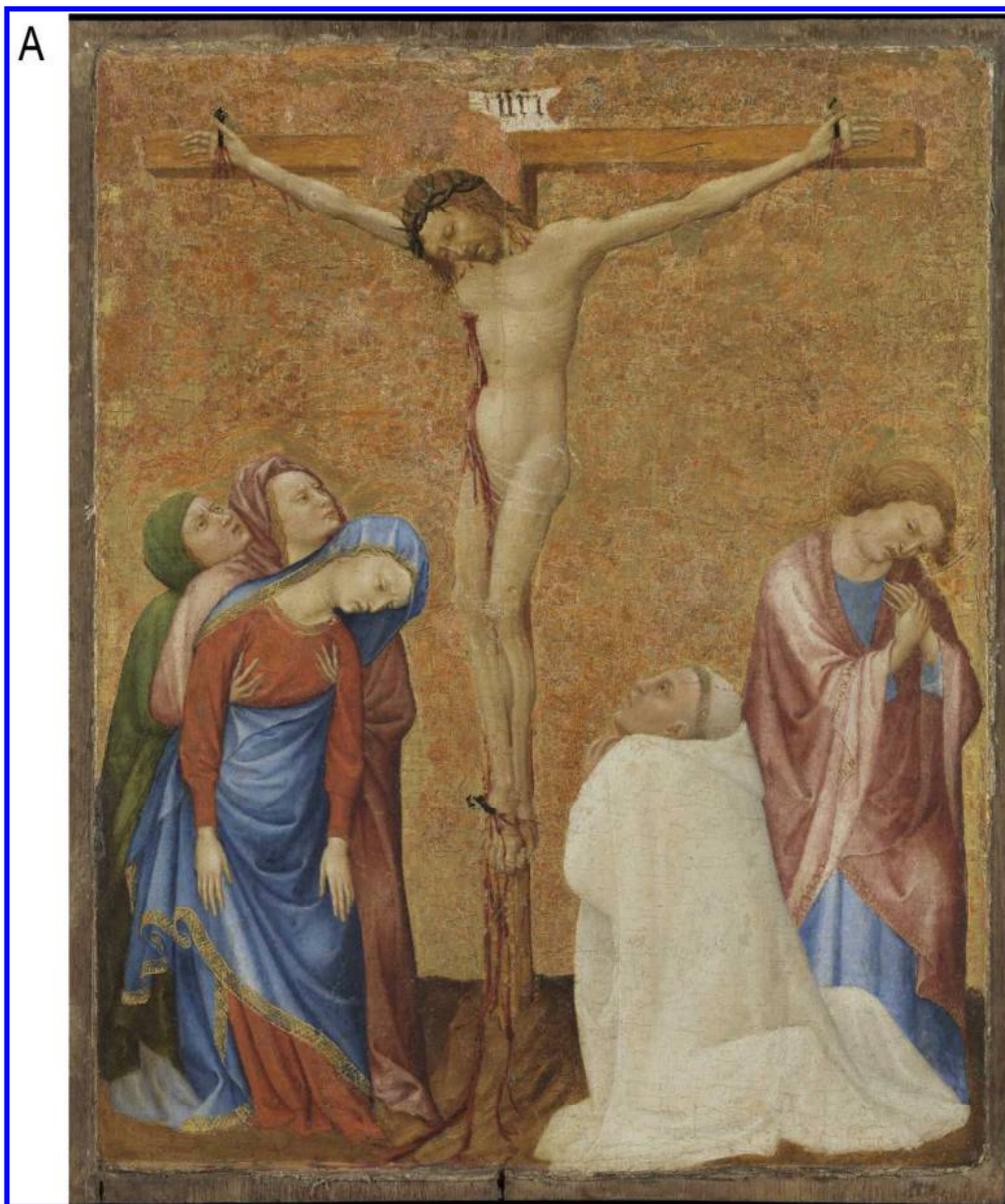
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46 Calvaire avec un moine chartreux (c. 1395) by Jean de Beaufort (Musée du Louvre, © C2RMF, 61 x 48.5  
47 cm)

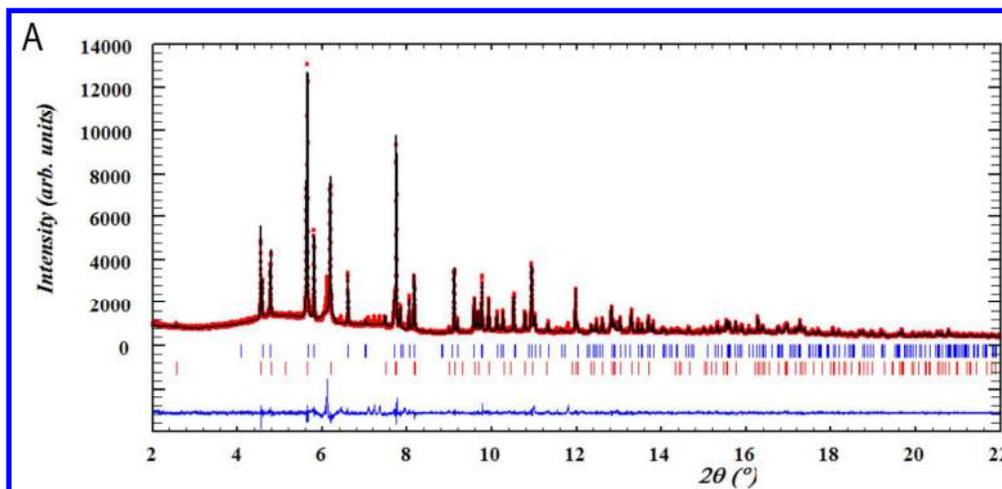
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Retable de Saint Denis (1416) by Henri Bellechose (Musée du Louvre, © C2RMF, 162 x 211 cm)

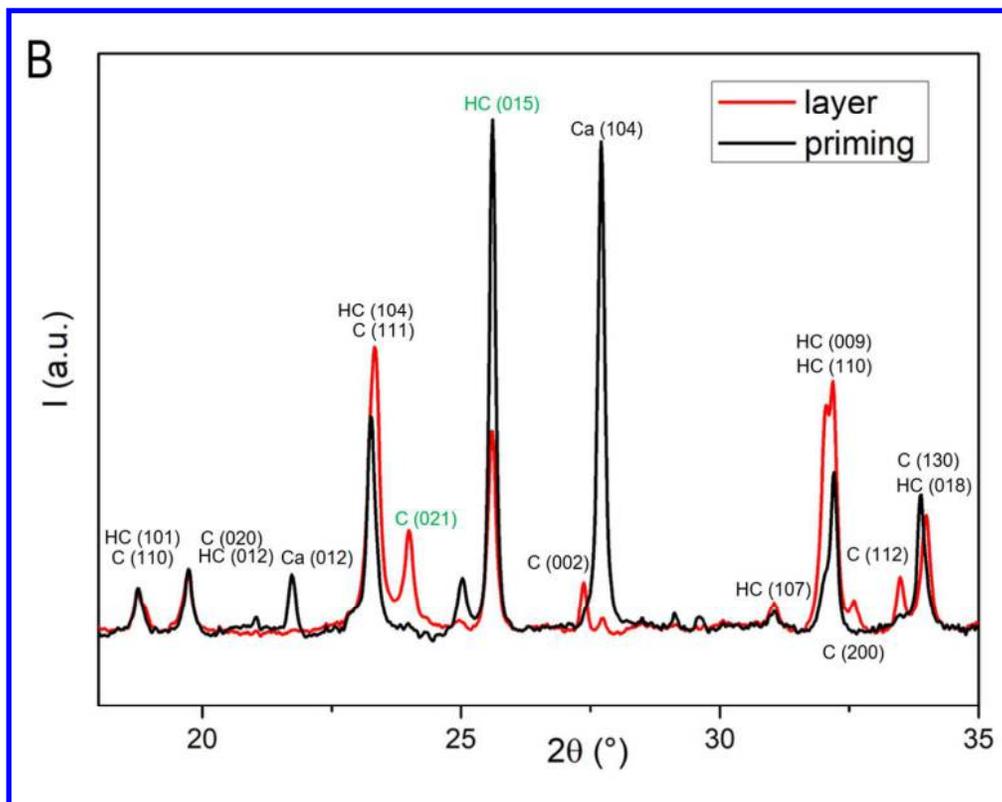
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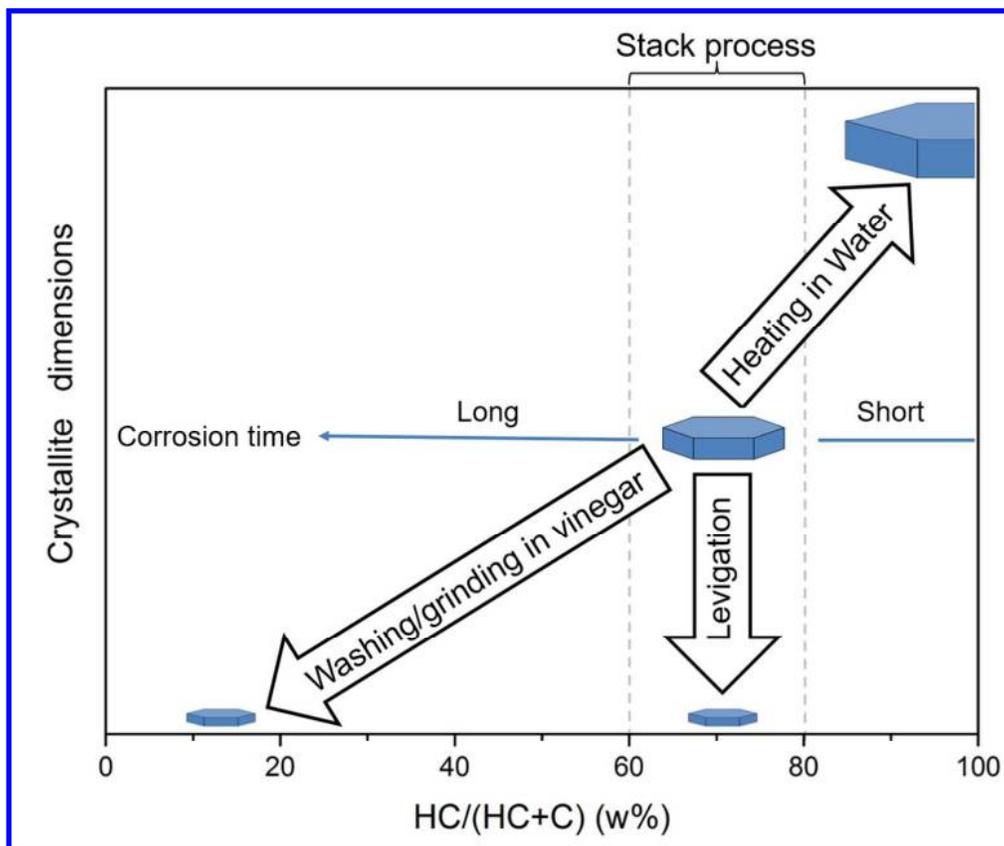
Rietveld plot for diffractogram recorded by HR-XRD at ID22 (sample Raffaello 1) : experimental (red circles), calculated (black line), difference (blue line), Bragg positions (bars)

280x134mm (143 x 143 DPI)



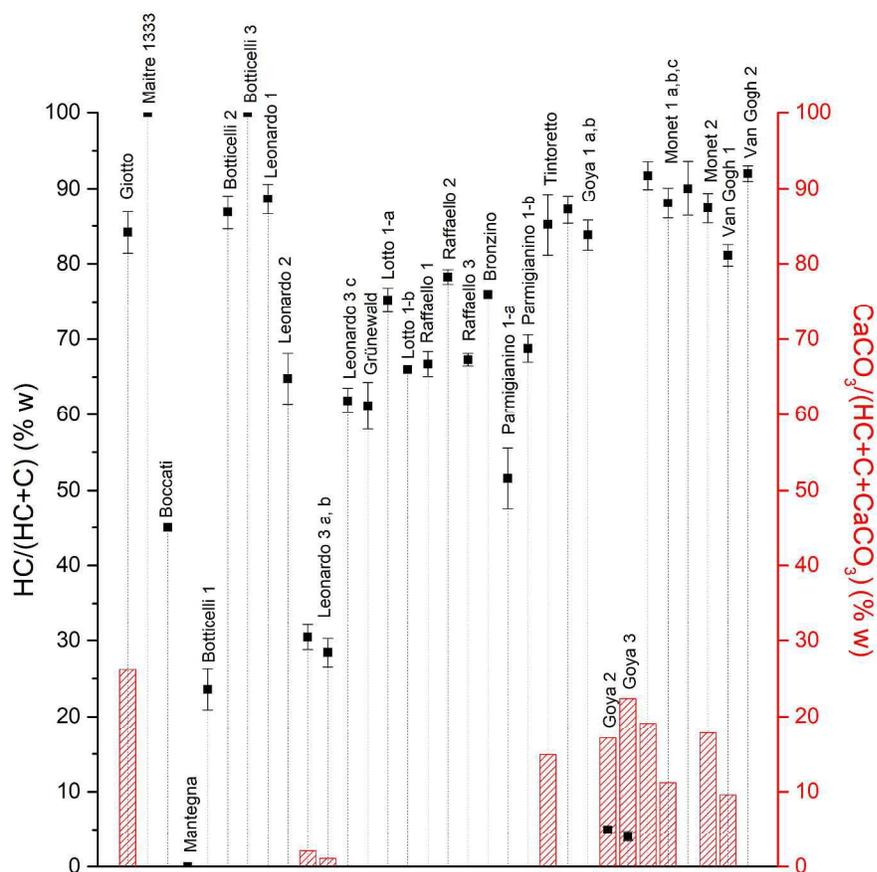
33  
34 Cumulated and azimuthally integrated diffractogram recorded by  $\mu$ XRD at ID21 on layer 3 of sample  
35 Beaumetz (cf. Fig 7). Peaks used for quantification ( $C_{(021)}$  and  $HC_{(015)}$ ) are indicated in green

36 328x260mm (95 x 95 DPI)



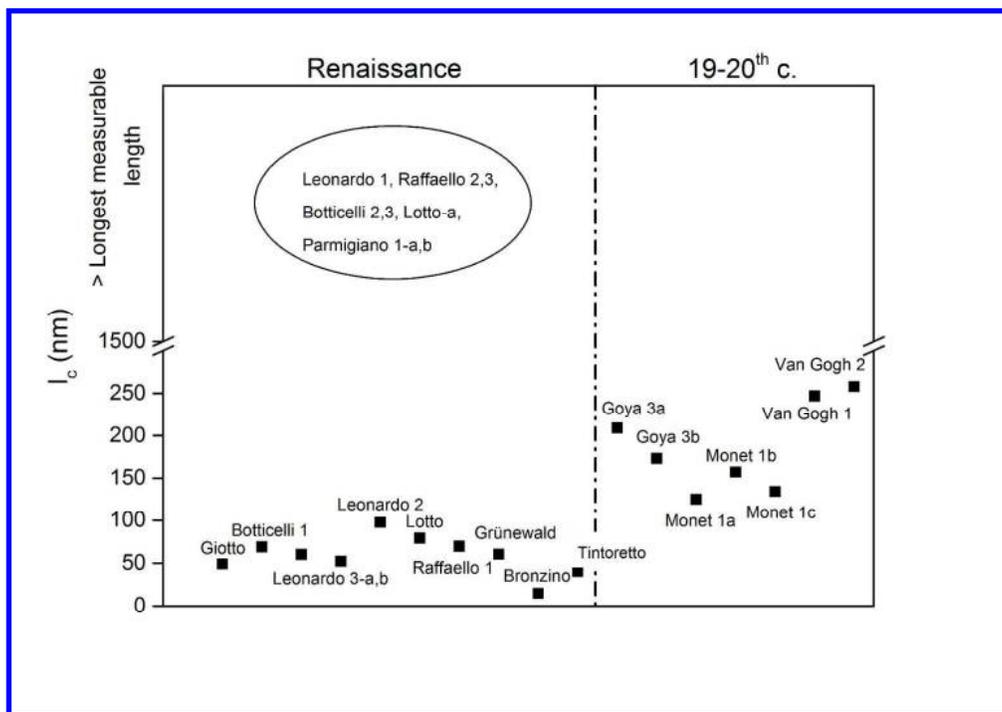
Composition and microstructure of lead white as a function of synthesis conditions and post-synthesis processes

206x172mm (144 x 144 DPI)



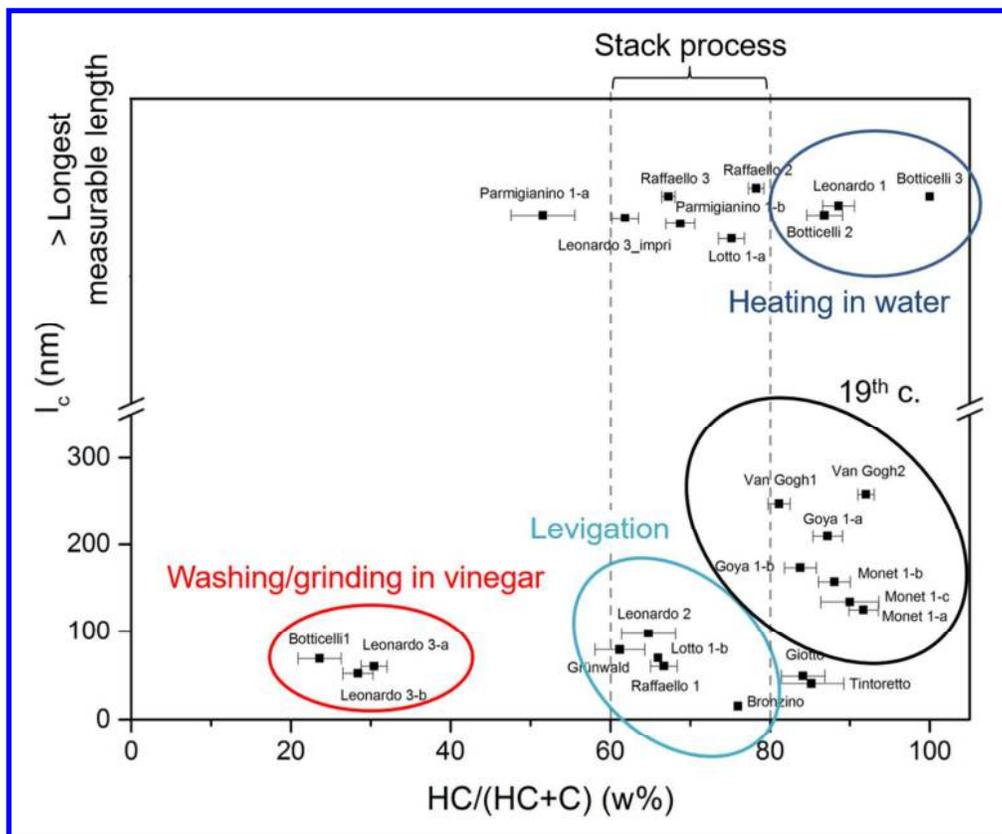
Composition derived from Rietveld fitting of ID22 data. Hydrocerussite (left scale, black squares) and calcite (right scale, red bars) weight ratios. Samples are plotted in chronological order from left to right

289x305mm (299 x 299 DPI)



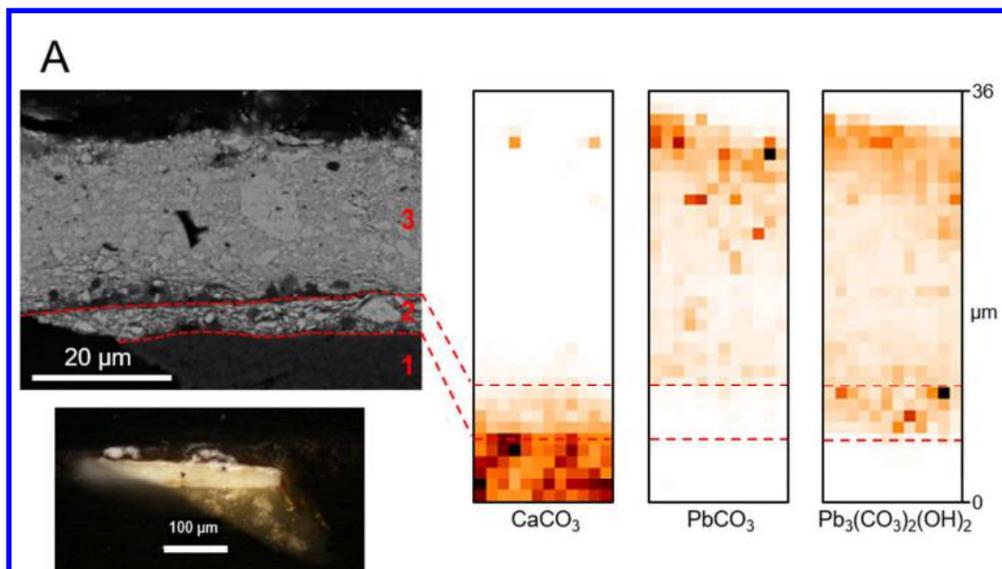
Evolution of the mean *HC* crystallite sizes in time. For the 14-16<sup>th</sup> c. group, lead white exhibit either very small or large (superior to the longest measurable length) crystallites.

288x201mm (300 x 300 DPI)



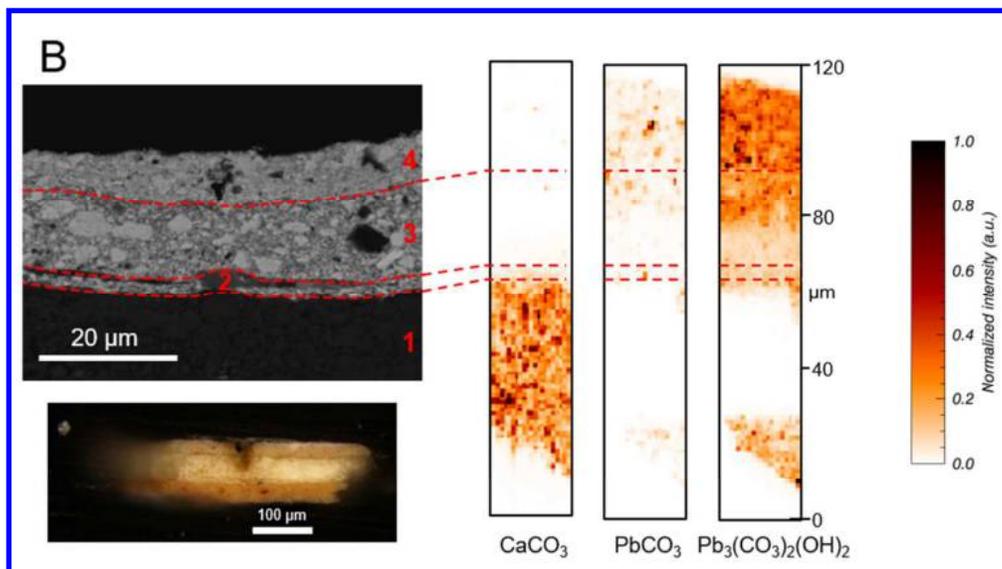
Plotting of the mean crystallite sizes vs  $HC/(HC+C)$  (w%)

214x177mm (144 x 144 DPI)



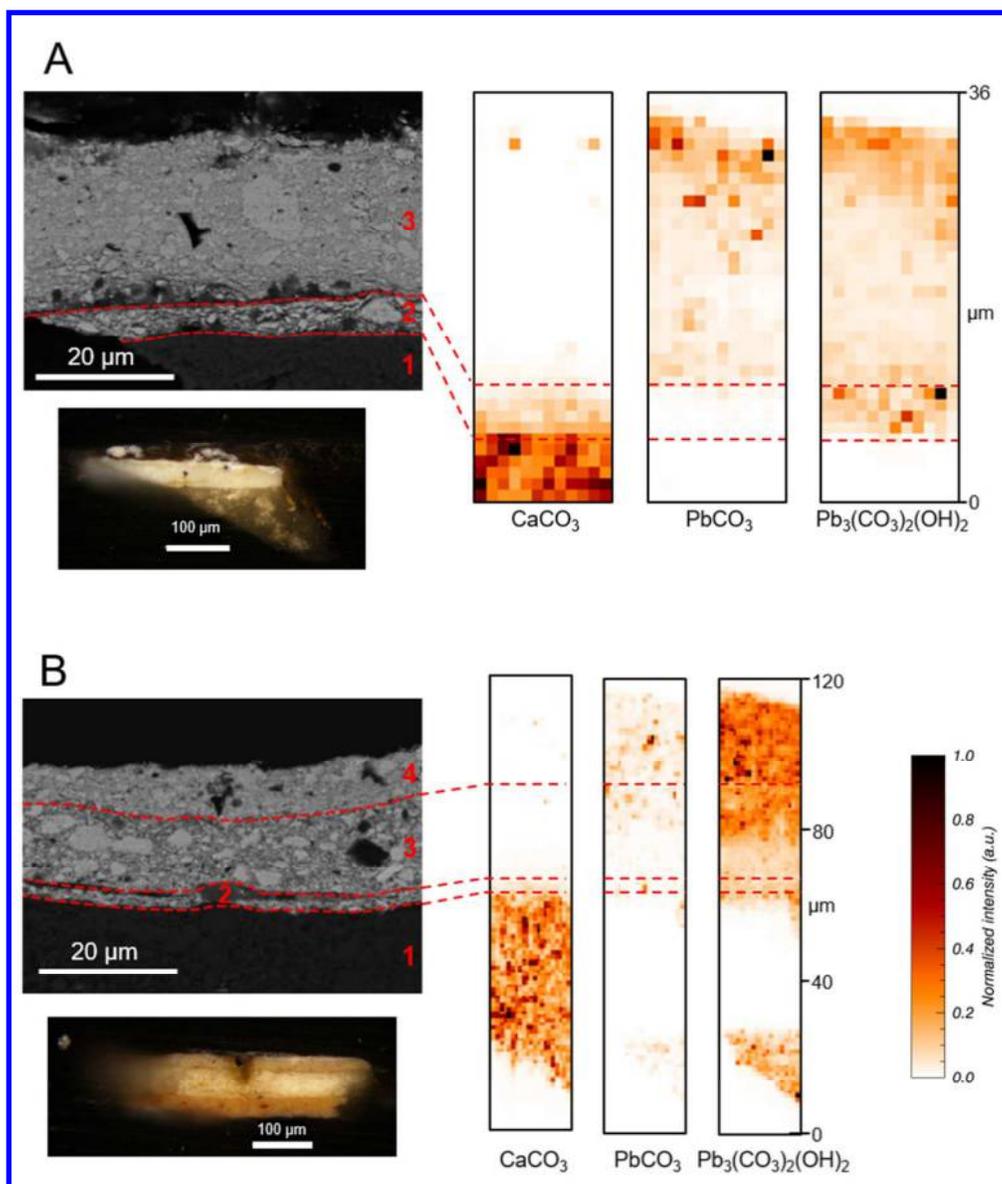
26 Mapping of calcite  $\text{CaCO}_3$ , *C*  $\text{PbCO}_3$  and *HC* ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ), for the sample Beaumetz (A) and Bellechose  
27 (B). On the Beaumetz sample, above the calcite ground, the impression layer (delimited in red dots) only  
28 contains *HC*. On top the white layer contains a mix of *HC* and *C*. On the Bellechose sample, above the calcite  
29 ground several lead white layers containing *HC* and *C* are superimposed.

30 151x84mm (144 x 144 DPI)



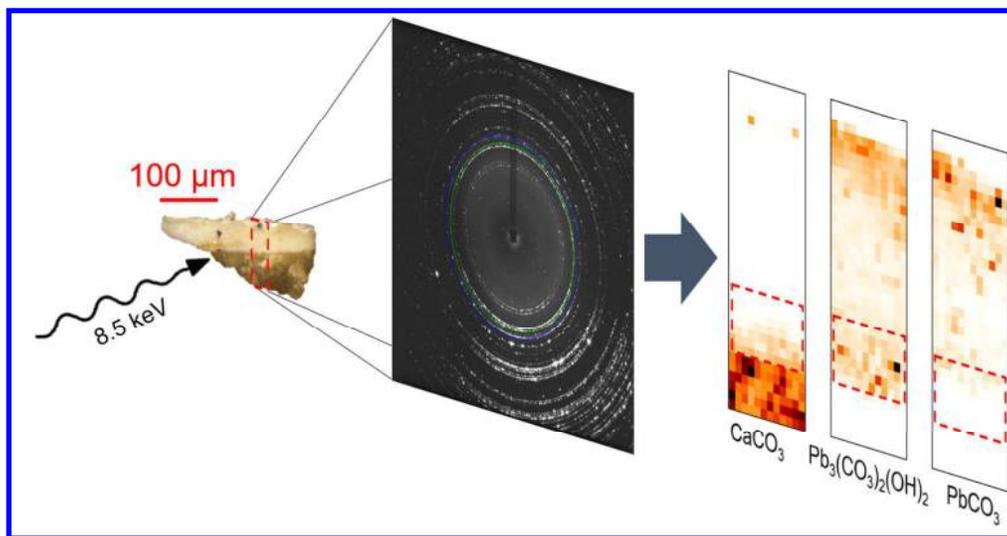
26 Mapping of calcite  $\text{CaCO}_3$ , C  $\text{PbCO}_3$  and HC ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ), for the sample Beaumetz (A) and Bellechose  
27 (B). On the Beaumetz sample, above the calcite ground, the impression layer (delimited in red dots) only  
28 contains HC. On top the white layer contains a mix of HC and C. On the Bellechose sample, above the calcite  
29 ground several lead white layers containing HC and C are superimposed.

30 228x127mm (96 x 96 DPI)



Mapping of calcite  $\text{CaCO}_3$ ,  $\text{C}$   $\text{PbCO}_3$  and  $\text{HC}$  ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ), for the sample Beaumetz (A) and Bellechose (B). On the Beaumetz sample, above the calcite ground, the impression layer (delimited in red dots) only contains  $\text{HC}$ . On top the white layer contains a mix of  $\text{HC}$  and  $\text{C}$ . On the Bellechose sample, above the calcite ground several lead white layers containing  $\text{HC}$  and  $\text{C}$  are superimposed.

228x268mm (96 x 96 DPI)



TOC

241x125mm (149 x 149 DPI)