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THERMAL DECOMPOSITION OF LEAD WHITE FOR RADIOCARBON DATING OF PAINTINGS

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ABSTRACT. Lead carbonates were used as cosmetic and pigment since Antiquity. The pigment, known as lead white, was generally composed of cerussite and hydrocerussite. Unlike most ancient pigments, lead white was obtained by a synthetic route involving metallic lead, vinegar and organic matter. Fermentation of organic matter produces heat and CO₂ emission, leading to the formation of carbonates. As lead white is formed by trapping CO₂, radiocarbon (¹⁴C) dating can thus be considered. We have developed a protocol to prepare lead white. We selected modern pigments for the experiment implementation and ancient cosmetic and paintings for dating. After characterization of the samples by XRD, thermal decomposition of cerussite at various temperatures was explored in order to select the appropriate conditions for painting samples. CO₂ extraction yield, SEM and XPS were used to characterize the process. Thermal decomposition at 400°C was successfully applied to mixtures of lead white with other paint components (oil as binder, calcite as filler/extender) and to historical samples. We obtained radiocarbon measurements in agreement with the expected dates, demonstrating that thermal decomposition at 400°C is efficient for a selective decomposition of lead white and that paintings can be directly ¹⁴C-dated by dating lead white pigment.

KEYWORDS: cerussite, gilt leather, lead white, painting, radiocarbon dating, thermal decomposition.

INTRODUCTION

Lead carbonates were one of the major materials used in art and archaeology from Antiquity to the 19th century. Various phases of lead carbonate were used as ingredients in cosmetics and paints. Cerussite (PbCO₃) and phosgenite (Pb₂Cl₂CO₃) were employed in cosmetic powders by ancient Egyptians, Greeks and Romans (Lucas 1930; Walter et al. 1999; Welcomme et al. 2006; Martinetto et al. 2001; Katsaros et al. 2010). Cerussite and hydrocerussite (Pb₃(CO₃)₂(OH)₂) were the compounds of lead white (Welcomme et al. 2007; de Viguerie et al. 2009; Beck et al. 2010; Gonzalez et al. 2017a), which was the most widely used white pigment until its poisonous effect restricted its manufacture in the 20th century (Gettens et al. 1993). Lead carbonates exist as natural minerals and as manufactured compounds. The production of cerussite is described in several historical written sources in Antiquity (Theophrastus, Dioscorides, Pliny the Elder) and from the Renaissance to the 19th century (Stols-Witlox 2014). The historical method of preparing lead white pigment is based on the process generally known as the “stack process” where metallic lead is exposed to vapors of acetic acid and carbon dioxide (Stols-Witlox 2014; Gonzalez et al. 2017b). Lead corrodes, forming lead acetate and lead carbonates. At the end of the process, the surface of the metal is covered with flakes of lead white. From Antiquity to the 19th century, the acetic acid was in the form of vinegar

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and carbon dioxide gas came from the fermentation of natural organic matter such as horse manure or tanner bark (Pulsifer 1888; Stols-Witlox 2014). Considering this method, we recently demonstrated that radiocarbon (^{14}C) was incorporated during the synthesis and we successfully dated lead carbonates in ancient cosmetics (Beck et al. 2018). Here, we aim to extend the method to paintings as also proposed by Hendriks et al. (2019) in a recent publication¹. Dating lead white pigment can be an alternative or a complement to ^{14}C measurements on canvas, wood or binder for their authentication (Caforio et al. 2013; Fedi et al. 2014; Hendriks et al. 2016, 2018; Brock et al. 2018).

The preparation of carbonate samples for ^{14}C analysis is usually carried out by acid hydrolysis. CO_2 is recovered from carbonate samples using pure phosphoric acid (H_3PO_4). However, in the case of a mixture of carbonates, typically the mixture of lead white with chalk that is very common in paintings (Stols-Witlox 2011), hydrolysis will extract CO_2 from all carbonates. As chalk contains dead carbon, we anticipated that this process would not be suitable for real samples and therefore explored another approach based on thermal decomposition. Carbonates undergo thermal decomposition to give the metal oxide and carbon dioxide gas (Beck 1950).

Differential thermal analysis of cerussite and hydrocerussite has been extensively studied in the past in various conditions such as CO_2 and inert atmospheres (Warne and Bayliss 1962; Ball and Casson 1975; Ciomartan et al. 1996). Thermal decomposition produces the evolution of CO_2 , the decomposition product being either the corresponding oxide or a basic carbonate, the latter decomposing with further evolution of CO_2 as the temperature is raised. In order to determine the appropriate conditions for the preparation of lead white for ^{14}C dating, we investigated the thermal decomposition of PbCO_3 with two goals in mind: optimizing the CO_2 production yield and collecting CO_2 from lead carbonate only. CO_2 extraction yield, scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS) were used to characterize the process. This procedure was then applied to mixtures of lead white with other paint components (oil as binder, calcite as filler/extender) and to historical samples: a Greek cosmetic from the Louvre Museum and two painted gilt leather wall hangings from a private collection.

MATERIALS AND METHOD

Sample Description and Material Analysis

Modern materials were first used to explore the experimental conditions for the preparation of lead white and then historical samples were prepared and dated. A commercial lead white pigment was obtained from a supplier who reproduces or adapts historical processes. For this study, two types of commercial products were available. For the thermal decomposition experiments, we used a lead white pigment produced according to the historical process, slightly modified: the carbon dioxide gas was provided by the fermentation of sugar and yeast dissolved in water (sample MM). According to the supplier, this method makes it easier to control the amount of CO_2 and to produce a homogenous pigment structure. White flakes were collected, crumbled and milled with water to obtain a fine powder. Then the pigment was washed several times and air dried. X-ray diffraction showed that the lead white powder produced in that condition is composed of pure cerussite (PbCO_3). Mixtures of MM with calcite (sample MM + C) or

¹This article was submitted a few days before the publication of Hendriks et al. (2019).

with linseed oil (sample MM + O) were also thermally studied. The second type of lead white was a modern reproduction of the historical stack process using horse manure. This pigment was made for restoration purposes in 2016 and was used in this study as a test sample (sample MH). X-ray diffraction showed that this lead white powder is composed of cerussite (PbCO_3) and hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) in similar amounts. To further validate the method, three historical samples were prepared and dated: one Greek cosmetic powder (GC) composed of cerussite and dated from the 4th–3rd centuries BC (Hasselin Rous and Huguenot 2017) and two paint samples (GL1 and GL2) taken from two gilt leathers used as decorative wall coverings between the 17th and the 18th centuries (Bonnot-Diconne et al. 2014). The description of the samples and the method used for their characterization are reported in Table 1.

Sample Preparation

Lead white preparation for ^{14}C dating was investigated by studying the thermal decomposition of sample MM composed of cerussite. Samples were heated at different temperatures (from 200 to 800°C) on a manual vacuum line (Figure 1). For each temperature, 20–25 mg of lead white was decomposed in vacuum (5×10^{-6} mbar) for 1 or 2 hr, producing carbon dioxide and water. CO_2 was separated from H_2O using a dry ice/alcohol trap (-78°C) and the pressure of each CO_2 sample was measured to determine the extracted carbon content (Dumoulin et al. 2017). For each temperature, the total released CO_2 was collected in a Pyrex tube sealed after collecting. Residues of the decomposition were preserved for their characterization by SEM (see Supplementary material) and XPS. The XPS device was a VG ESCALAB 220i XL spectrometer with a $\text{Al-K}\alpha$ x-ray source (1486.6 eV).

The same procedure was applied to mixed carbonates containing 25 mg of lead white (PbCO_3) and 10 mg of CaCO_3 (sample MM + C) and to a paint prepared in the laboratory with lead white and linseed oil (sample MM + O). For the test (MH) and the historical samples, the decomposition was carried out at 400°C, according to the results obtained from the preceding experiments and presented in the next section.

As support for the paintings, leather samples were also dated for comparison. They were prepared using the standard acid-base-acid method (0.5 M HCl at 80°C, 1 hr/0.1 M NaOH at 80°C, 1 hr/0.5 M HCl at 80°C, 1 hr), rinsed with ultra-pure water until neutral pH and then dried under vacuum overnight (60°C, 0.1 mbar). CO_2 was obtained by combustion (5 hr, 850°C) in a quartz sealed tube with an excess of CuO (400–500 mg) and a 1-cm Ag wire. CO_2 was finally dried and collected on a semi-automated rig (Dumoulin et al. 2017).

CO_2 of all the samples was then reduced to graphite with hydrogen over iron catalyst. ^{14}C measurements were performed by accelerator mass spectrometry (AMS) using the LMC14/ARTEMIS facility (Moreau et al. 2013). ^{14}C ages were calculated using the Mook and van der Plicht (1999) recommendations and calibrated using OxCal v4.2 (Bronk Ramsey et al. 2013) and the IntCal13 atmospheric calibration curve (Reimer et al. 2013) for past ages and CaliBomb and the Levin curve (Levin and Kromer 2004) for pMC.

RESULTS

The results are presented in two sections. The first section deals with the development of the sample preparation for pure pigment, mixed pigments (lead white and calcite), paint, and

Table 1 Lead white materials and analytical methods used in this study. Cerussite = PbCO_3 ; hydrocerussite = $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$; calcite = CaCO_3 ; ThD = thermal decomposition; XRD = x-ray diffraction; SEM = scanning electron microscopy; XPS = x-ray photoelectron spectroscopy; (*) Hasselin Rous and Huguenot (2017).

Label	Material	Sample information	Date of production or expected age	Composition (main components)	ThD from 200°C to 800°C	ThD at 400°C	XRD	SEM	XPS on residues
MM	Lead white pigment	Modified historical process	End of 2015	Cerussite	x	x	x	x	x
MM + C	Lead white pigment and calcite powder	Mixture of MM with calcite	Modern	Cerussite and calcite	x	x			
MM + O	Paint	Mixture of MM with binder	Modern	Cerussite and linseed oil	x				
MH	Lead white pigment	Reproduction of the historical stack process	2016	Cerussite and hydrocerussite		x	x		
GC	Compact powder	Greek cosmetic	4th–3rd c. BC	Cerussite		x	x (*)		
GL1	Lead white paint layer	Painting on gilt leather 1	Second half of the 17th century	Hydrocerussite		x	x	x	
GL2	Lead white paint layer	Painting on gilt leather 2	Before 1736	Hydrocerussite		x	x	x	

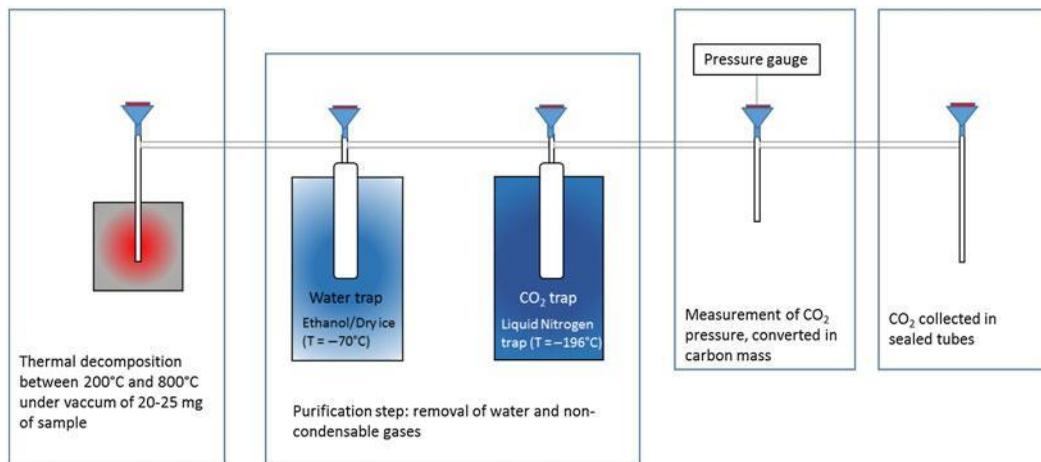


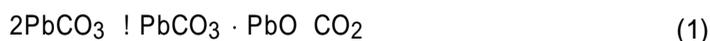
Figure 1 CO₂ collection line for lead carbonate preparation at LMC14.

historical samples. The second section shows the dating results. All the data are reported in Table 2.

Sample Preparation: Carbon Extraction by Thermal Decomposition

Pure Lead White

Total CO₂ released after heating of 20 mg of lead white (samples MM) for 2 hr was collected for each temperature. Figure 2a reports the total carbon content obtained as a function of the temperature. At 200, 250, 300, 350, and 400°C, the amount of collected carbon was 0.1, 0.9, 2.9, 3.2 and 4.4%. The values from 0.1 to 3.2% correspond to the CO₂ release during the first steps of decomposition. At low temperatures, lead white was partially decomposed and two intermediate oxy-carbonates PbCO₃·PbO and PbCO₃·2PbO were obtained according to Equations (1) and (2):



At 400°C, the collected carbon content reached the value of 4.44%, which is close to the carbon content in PbCO₃ (4.49%). This value was constant for temperatures between 400 and 700°C, indicating that the CO₂ release was complete. At these temperatures, the final dissociation of the oxy-carbonate forms lead monoxide (Equation 3).



The formation of PbO was indicated by the reddish and yellow colors of the combustion residues, characteristic of massicot (orthorhombic PbO) (Figure 2c) and confirmed by XPS (Figure 3).

The total decomposition reaction can be summarized by: $\text{PbCO}_3 \rightarrow \text{PbO} + \text{CO}_2$. At 400°C, we can consider that the total recovery of CO₂ means that the total original content of carbon contained in PbCO₃ has been collected. At higher temperature (800°C), the residue melts as

Table 2 Extracted carbon content, carbon mass, pMC, and ^{14}C dating results of modern lead white pigments and historical samples of cosmetic and paintings. Results on leather supports are indicated for comparison.

Label and preparation temp. (°C)	Material	Date of production or expected age	% carbon ($\pm 0.10\%$)	C mass (mg)	pMC	^{14}C date ± 30 (years BP)	Calibrated date (years cal BC/AD; 95.4%)	Lab number
MM-400	Lead white	End of 2015	4.39	1.10	102.2 ± 0.2		1955–1956 & 2013–2016	SacA49833
MM-500	pigment		4.35	1.10	101.8 ± 0.2			SacA49834
MM-600			4.43	1.10	101.5 ± 0.2			SacA52819
MM-700			4.44	1.14	101.8 ± 0.2			SacA52820
MM + C 400		Lead white	Modern	4.34	1.10	102.4 ± 0.2		1955–1956 & 2013–2016
MM + C 700	pigment and calcite in powder		7.69	1.94	58.8 ± 0.2			SacA49843
MM + O 400	Paint	Modern	4.54	1.32	102.2 ± 0.5		1955–1956 & 2013–2016	SacA52825
MH 400	Lead white pigment	2016	3.40	0.71	103.0 ± 0.3		1955–1956 & 2012–2016	SacA51769
GC 400	Compact powder	4th–3rd c. BC	3.35	1.08	76.6 ± 0.2	2140	353–57	SacA48856 (Beck et al. 2018)
GL1 400	Lead white paint layer	Second half of the 17th century	2.4	0.54	96.57 ± 0.22	280	1498–1795	SacA52814
GL1	Leather			0.41	96.62 ± 0.20	275	1514–1798	SacA54660
GL2 400	Lead white paint layer	Before 1736	3.0	0.54	97.34 ± 0.34	215	1644–:::	SacA52830
				0.50	97.42 ± 0.22	210	1646–:::	SacA52813
GL2	Leather				97.60 ± 0.22	195	1648–:::	SacA54661
					98.08 ± 0.24	155	1666–:::	SacA52829

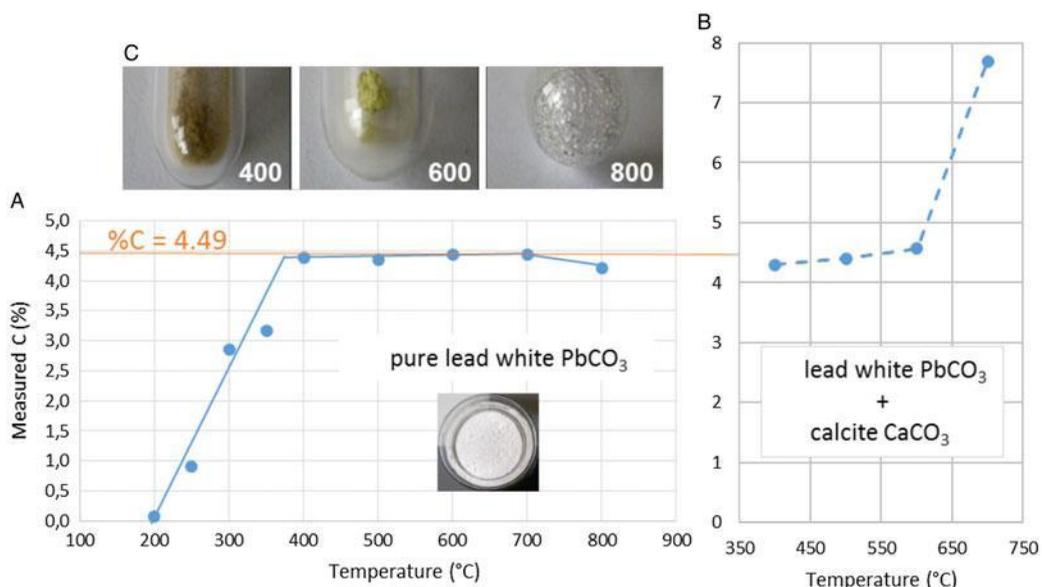


Figure 2 Total amount of carbon released (in absolute percentage with $\pm 0.1\%$ uncertainty) from A) pure lead white (sample MM) and B) a mixture of lead white with calcite (sample MM + C) as a function of the heating temperature. C) From left to right: residues after decomposition at 400, 600, and 800°C

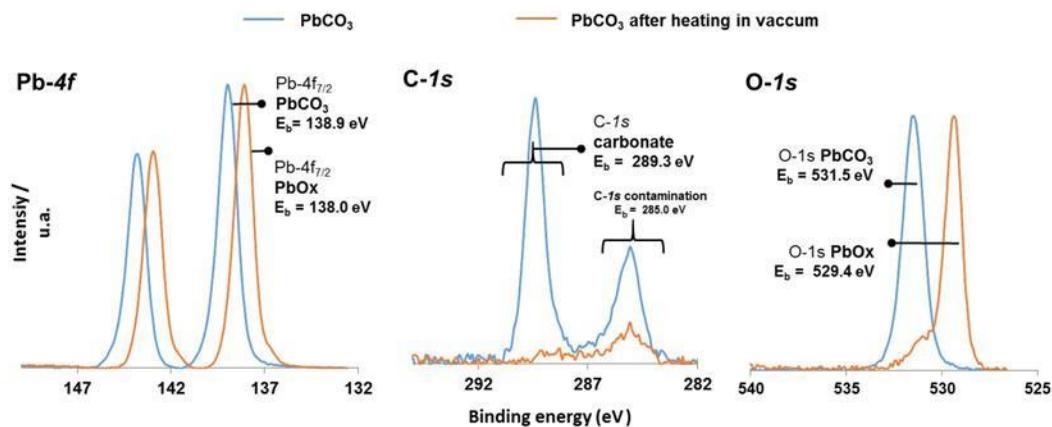


Figure 3 Pb-4f, C-1 s, and O-1 s XPS spectra of lead white before (in blue) and after heating (in orange), showing the vanishing of the carbonate structure and the formation of lead oxide (color images online).

observed in Figure 2c. Decomposition experiments were also conducted for 1 hr, leading to the same results.

Mixed Carbonates: Lead White and Calcite

As all carbonates undergo thermal decomposition to give the metal oxide and carbon dioxide gas, we also investigated the decomposition of mixtures of lead white and calcite between 400 and 700°C (Figure 2b). At 400 and 500°C, the percentage of carbon collected was close to

4.49% corresponding to the CO₂ released by the lead carbonate. At higher temperatures, the content of collected carbon strongly increased, indicating that from 600°C, calcite partially decomposes producing also CO₂. This contamination in dead carbon must be avoided in order to obtain reliable results from lead white. As a result, we selected the temperature of 400°C as the best condition to optimize the CO₂ production yield and to collect CO₂ from lead carbonate only. The choice of this condition was confirmed by heating pure calcite at 400 and 500°C: no release of CO₂ was observed. For future experiments, we plan to implement a two-step procedure to assess the efficiency of the selective separation of lead white and chalk to obtain age determinations for each subsample.

Paint: Lead White and Linseed Oil

The decomposition of the paint was carried out at 400 and 500°C. The percentages of carbon collected were 4.54% and 4.7%, respectively. These values are slightly above 4.49% due to the contribution of the oil. As the linseed oil is generally produced in the same period of time as the pigment, we assume that the contamination by the binder will not significantly alter the dating results.

Test Sample, Ancient Cosmetic and Paintings

The decomposition of the pigment (MH), the cosmetic powder (GC) and the painting samples (GL) was carried out at 400°C. The collected carbon contents were between 2.4 and 3% (Table 2) due to the presence of hydrocerussite (%C = 3.1%).

¹⁴C Measurements

The results of the ¹⁴C measurements are reported in Table 2, in pMC for the modern samples and in years BP for the historical samples. For the modern pigments, we obtained pMC values from 101.5 ± 0.2 to 103.0 ± 0.3, except for the sample MM mixed with calcite and decomposed at 700°C (58.8 ± 0.2 pMC). The high pMC values are in agreement with the dates of the pigment production in 2015–2016. The low pMC value is due to dead carbon contamination since at this temperature, we observed that calcite starts to decompose. These results confirm that the preparation of lead white must be carried out at 400°C to prevent any contamination from calcite decomposition. The presence of oil (sample MM + O) did not affect the result (102.2 ± 0.5 pMC), indicating that the linseed oil was also produced recently.

The Greek cosmetic sample (GC), composed of pure cerussite, was preserved in a small box found in a tomb discovered in Eretria (Greece). This tomb was dated on a numismatic basis from ca. 330 to ca. 266 BC (Hasselin Rous and Huguenot 2017). Two previous ¹⁴C dates measured on an almond seed were also available: 359–112 calBC and 375–203 calBC (Gandolfo and Richardin 2011). The dating of the cerussite powder gives a date range of 353 to 57 BC (95.4%) (Table 2). This date is in agreement with the numismatic result and consistent with the almond seed results as shown by a chi squared test value of $T = 3.7 < 6$ published in Beck et al. (2018).

The two samples of paint layers come from decorated leathers which were used to cover walls. The leather was first gilt with silver leaves and then partially painted. Two specimens painted with lead white were taken at the surface of the leather fragments. According to the historical or stylistic information, the gilt leather #1 dates from the second half of the 17th century and the gilt leather #2 was mentioned in a castle record in 1736.

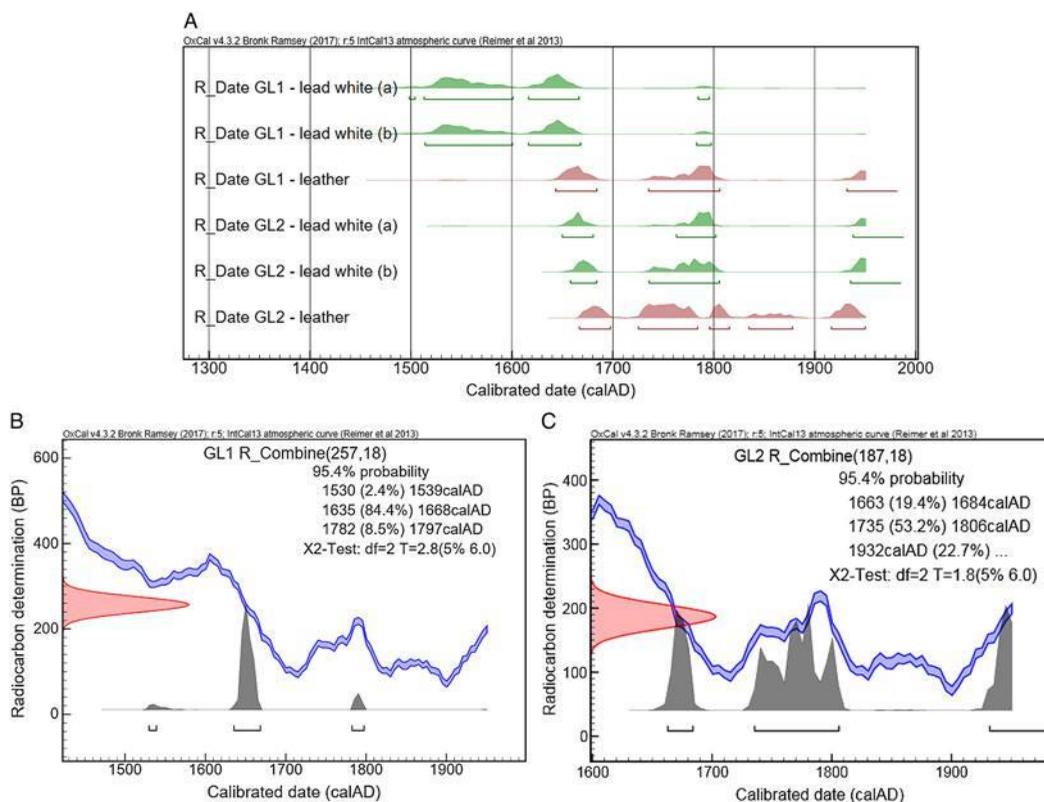


Figure 4 Dating results of the gilt leathers 1 and 2: A) comparison of the age distribution of the leather (in red) and two lead white samples taken from the paint layer (in green); B) and C) combination of the three age distributions obtained on GL1 and GL2. (Please see electronic version for color figures.)

The results on the lead whites and the leathers are reported in Table 2 and compared after calibration in Figure 4a. We can observe a very good agreement between the paint layer dates and the leather date for GL2 but to a lesser extent for GL1. However, the consistency of the dates is demonstrated in both cases by the chi squared test values ($T = 2.8 < 5$ for GL1 and $T = 4.4 < 5$ for GL2). Regarding GL1, manufacture of the lead white pigment earlier than the animal death cannot be excluded.

The dates are also in agreement with the historical information. For GL1, the most probable range of dates (1635–1668 [84.4%]; Figure 4b) is very close to the expected time of its manufacture in the second half of the 17th century. For GL2, due to the fluctuations of the calibration curve, we obtained a large probability distribution. The first interval (1663–1684; Figure 4c) fits with the historical record mentioning that the decor was already in place in 1736. This information makes it possible to exclude the latest dates and suggests that the leather was decorated and painted at the end of the 17th century.

Despite the fluctuations of the calibration curves, we obtained ^{14}C measurements in agreement with the expected dates for modern samples as well as for historical specimens of lead white, whatever the composition (cerussite/hydrocerussite) and the time scale. These results validate

the preparation protocol based on thermal decomposition for producing CO₂. They also confirm that lead white incorporates ¹⁴C during its manufacture.

CONCLUSION

The possibility of ¹⁴C dating lead white pigment has been investigated. The preparation protocol based on the thermal decomposition of lead carbonates was characterized by SEM, XRD and XPS. A decomposition temperature of 400°C was determined to extract CO₂ from lead white and to prevent contamination by other carbonates such as calcite. This selective process is necessary as adulteration of lead white with chalk was often reported in the past to reduce the cost of the paints (Stols-Witlox 2011). For future experiments, we plan to implement a systematic two-step thermal procedure to check the efficiency of the selective separation and obtain age determinations for each subsample of lead white and chalk.

Successful ¹⁴C measurements of modern and historical lead whites have been obtained. An ancient Greek cosmetic powder and two samples taken from paint layers of the 17th century have been dated and the results are in agreement with the expected ages. The results confirm our experimental approach and further validate the assumption that ¹⁴C dating of lead white can be based on the principle of the incorporation of ¹⁴C when its synthesis uses organic reagents. This study demonstrates that paintings can be dated by dating the lead white pigment in addition to the binder and support (canvas or wood). Support ages can be subjected to discussion regarding possible reuse and the binder can be contaminated by varnish or later restorations. Combining ¹⁴C dating of these three components—pigment, binder, support—may provide a more reliable age for the paintings and stronger evidence for their authentication.

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SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit <https://doi.org/10.1017/RDC.2019.64>

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