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HOW THE INCORPORATION OF ^{14}C IN LEAD WHITE MAKES ITS ABSOLUTE DATING POSSIBLE

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ABSTRACT. Known as lead white, lead carbonates were used as white pigment or cosmetics from the 4th century BC to the 20th century AD. Lead white was produced by the corrosion of metallic lead by vinegar and horse manure up to the 19th c. In order to document the incorporation of carbon in the corrosion mechanism, lead carbonates were produced in the laboratory under monitored experimental conditions using materials with different isotope signatures in ^{14}C and ^{13}C . Six experimental setups were defined combining vinegar, acetic acid, horse manure and fossil CO_2 gas. The corrosion products were characterized by X-ray diffraction. ^{14}C content and $\delta^{13}\text{C}$ values of the initial reactants and the final products were measured by accelerator and isotopic ratio mass spectrometry (AMS and IRSM). The reaction between lead and vinegar or acetic acid resulted in lead acetates with a carbon isotopic signature close to that of the corrosive reagent. In the presence of CO_2 , the carbonation reaction occurred and the cerussite produced had a predominant ^{14}C signature of the carbon dioxide source. These experiments demonstrate that the CO_2 produced by horse manure fermentation is incorporated into the corrosion products, allowing the absolute dating of lead white by the radiocarbon method.

KEYWORDS: cerussite, lead white, pigment, radiocarbon AMS dating, $\delta^{13}\text{C}$.

INTRODUCTION

Lead carbonates—cerussite (PbCO_3) and hydrocerussite ($2\text{PbCO}_3\text{Pb}(\text{OH})_2$)—were employed as cosmetics, eye remedies and white pigment (known as lead white) from the 4th century BC to the beginning of the 20th century (Welcomme et al. 2006; Stols-Witlox 2011; Pérez-Arantegui 2021; Messenger et al. 2022). Craddock (2009), was the first to suggest the use of the ^{14}C content in lead white to distinguish past and modern productions, based on the difference between the carbon sources, derived from plants or fossil fuels. The first ^{14}C dates of manufactured lead carbonates were obtained on cosmetics and paintings by two different groups in France and in Switzerland (Beck et al. 2018, 2019; Hendriks et al. 2019; Beck et al. 2020; Messenger et al. 2020, 2021; Sà et al. 2021) after a first application on a corroded lead coffin by Van Strydonck et al. (2016). These successful results clearly indicate that organic carbon in one form or another—not fully identified yet—is incorporated during the corrosion process when organic matter is present or during the lead white manufacturing process described in the ancient recipes (Welcomme et al. 2006; Stols-Witlox 2014; Gonzalez et al. 2019; Photos Jones et al. 2020).

The production of lead white was based on a corrosion process, combining the actions of a corrosive liquid and carbon dioxide on metallic lead. This production process was first mentioned by Theophrastus in the 4th–3rd centuries BC (in Caley and Richards 1956) and was used up to the 19th century with minor modifications (Stols-Witlox 2014). From the 19th

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Table 1 Materials used for lead white produced by corrosion at LMC14.

| Basic compound | Modern reactant containing ^{14}C | Fossil reactant (^{14}C depleted) | Supplier and additional information |
|----------------------|--|--|--|
| Metallic lead | — | — | Goodfellow 99.95+ (foil 10 cm × 5 cm × 0.2 cm) |
| Corrosive liquid | Vinegar (V) | Acetic acid (Aa) diluted to 10% v/v | CDRC (Lyon, France) VWR chemicals |
| CO_2 source | Horse manure (Hm) | | Private horse owner in St Martin de Nigelles (France). Collected on 15-06-2020 |
| | | Fossil CO_2 (CO_2B) | Alphagaz N48 - ($\text{CO}_2 \geq 99.998\%$) |

century on, new industrial processes were developed for a larger scale production using CO_2 derived from fossil materials (Villon and Guichard 1898–1902).

In order to document the incorporation and pathway of carbon in the corrosion mechanism, lead carbonates were produced in the laboratory under monitored experimental conditions. Various materials, with different carbon isotope signatures in ^{14}C and ^{13}C were selected as corrosive reagents and CO_2 sources. Six experimental setups were defined combining vinegar, acetic acid, horse manure and fossil CO_2 gas.

The corrosion products were characterized by X-ray diffraction. ^{14}C content and $\delta^{13}\text{C}$ values of the initial reactants and the final products were measured by accelerator mass spectrometry (AMS) and isotopic ratio mass spectrometry (IRSM).

MATERIAL AND METHODS

Samples: Lead White Produced at LMC14

The corrosion process is based on three basic compounds: metallic lead, corrosive liquid, and CO_2 source. To monitor the carbon pathway in the reaction, reactants with various carbon isotope signatures were selected (Table 1). The corrosive reagents were the natural vinegar (containing ^{14}C) used in the traditional manufacture and its counterpart depleted in ^{14}C , acetic acid. The two CO_2 sources selected were horse manure (containing ^{14}C), one of the ingredients described in the ancient literature (Stols-Witlox 2014), and its counterpart depleted in ^{14}C , CO_2 gas.

Six experimental conditions were defined (Figure 1), using lead (Pb) and:

1. acetic acid (Aa)
2. vinegar (V)
3. acetic acid and horse manure (Aa+Hm)
4. vinegar and horse manure (V+Hm) [= historical process]
5. acetic acid and fossil CO_2 (Aa+ CO_2B)
6. vinegar and fossil CO_2 (V+ CO_2B)

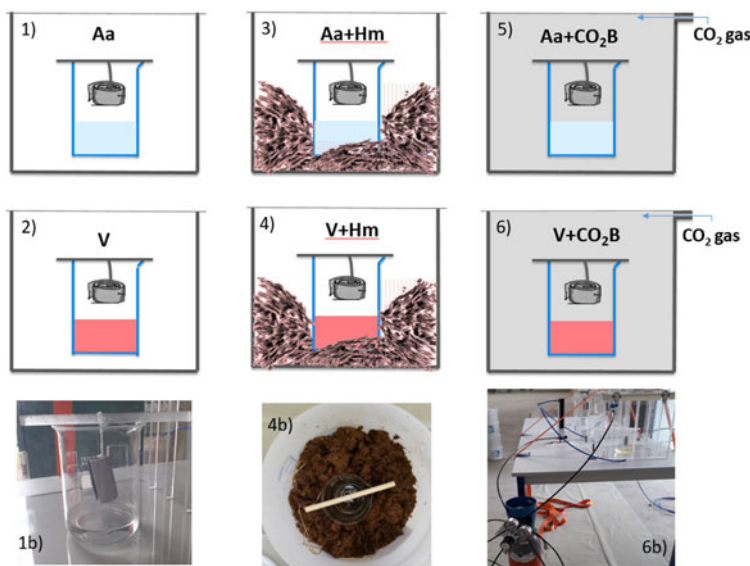


Figure 1 Experimental setups for the production of lead white by corrosion. 1: lead and acetic acid (Aa) (and photo 1b); 2: lead and vinegar (V); 3: lead, acetic acid and horse manure (Aa+Hm); 4: lead, vinegar and horse manure (V+Hm) (and photo 4b); 5: lead, acetic acid and fossil CO_2 (Aa+ CO_2B); 6: lead, vinegar and fossil CO_2 (V+ CO_2B) (and photo 6b).

To expose the lead to the vapors of the corrosive liquid, lead foils were hung over a 500 mL beaker containing 100 mL of acetic acid (10 vol%) or of vinegar. The whole was placed in a not tightly closed 20 L bucket, either empty (setups 1 and 2) or containing horse manure (setups 3 and 4). The temperature was between 20°C and 30°C throughout the process.

For setups 5 and 6, the beakers containing acetic acid (10 vol%) or vinegar were placed in an airtight Plexiglas box in which fossil CO_2 gas was injected under a slight overpressure. The box was regularly refilled to maintain a pressure of ~ 2 atm.

After a few days, a white film formed at the surface of the lead. After several weeks of exposure, complete consumption of the metal foil was observed, and the lead turned into thick, porous and brittle white flakes that no longer adhered to the metal (Figure 2). Samples were taken at different times of exposure and the final products were selected for X-ray diffraction (XRD) and AMS ^{14}C dating. For some samples, IRMS $\delta^{13}\text{C}$ measurements were also carried out.

METHODS

X-Ray Diffraction (XRD)

Corrosion products were analyzed by XRD using a RU-200B (Rigaku) rotating anode X-Ray generator equipped with a Mo anode ($\lambda = 0.7093 \text{ \AA}$). The beam was focused on the sample with a beam size of 100 μm and a photon flux of about 2.107 ph/s. XRD data were collected on a Pilatus 300K (Dectris) hybrid pixel detector in transmission mode with a 2θ range from 2 to 35°. 2D images were circularly integrated using the FIT2D software and phase identification was carried out with Diffrac-EVA software (Bruker) integrating a reference database from ICDD.



Figure 2 Lead white produced after one month of exposure of lead to vinegar and horse manure (setup 4). The corresponding diffractogram is presented in Figure 3b.

AMS ^{14}C

Between 25 to 35 mg of white powder were thermally decomposed at 400°C on a dedicated CO_2 collection line (Beck et al. 2019; Messenger et al. 2020; Dumoulin and Moreau, [submitted](#)). CO_2 was graphitized at 600°C using H_2 and iron catalyst (Vogel et al. 1984). The $^{14}\text{C}/^{12}\text{C}$ ratio was measured by AMS using the LMC14/ARTEMIS facility, a 3MV NEC Pelletron (Moreau et al. 2020; Beck et al. 2023). Oxalic acid II was used for normalization and the international intercomparison samples FIRI H and FIRI I for validation. ^{14}C ages were calculated using the Mook and van der Plicht (1999) recommendations and expressed in pMC (percent of Modern Carbon). Radiocarbon results were calibrated using Oxcal 4.4.4 with the Bomb NH1 21 curve (Hua et al. 2022).

IRMS $\delta^{13}\text{C}$

$\delta^{13}\text{C}$ values were measured offline with an IsoPrime 100 mass spectrometer. Between 200 and 350 μg of sample were loaded in homemade vials. Before use, they were pumped under vacuum to reach a pressure greater than 5.10^{-12} mbar. Samples were then treated with 0.2 mL of anhydride phosphoric acid solution at 90°C under vacuum. After normalization to international standards, the results were expressed in ‰, with respect to the Vienna Pee Dee Belemnite (V-PDB) reference.

For some samples, it was not possible to obtain IRMS $\delta^{13}\text{C}$ due to limited access to the mass spectrometer. For these cases, AMS $\delta^{13}\text{C}$ values were reported after checking that the results obtained by the two methods on some samples were reasonably comparable (see Table 3 in the results section). However, under no circumstances should these AMS $\delta^{13}\text{C}$ values be used as absolute values.

Table 2 ^{14}C content in pMC and AMS $\delta^{13}\text{C}$ of the reactants. For comparison, the contemporaneous ^{14}C content of the atmospheric CO_2 is indicated. It was estimated by measuring the ^{14}C content of nuts collected in France in 2020.

| | Reactant | AMS ^{14}C (pMC) | AMS $\delta^{13}\text{C}$ (‰) | Number of measurements and lab code |
|------------------------------|---|------------------------------|----------------------------------|--|
| Corrosive liquid | Vinegar (V) | 100.8 ± 0.3 | -18.8 | 1 Ly-45893 |
| Corrosive liquid | Acetic acid (Aa) diluted to 10% v/v | < 0.246 | -43.6 | 2 SacA63097, SacA63098 |
| CO_2 source | Horse manure (Hm) | 100.4 ± 0.5 | -28.9 | 2 SacA60850, SacA60851 |
| CO_2 source | Fossil CO_2 gas (CO_2B) | 0.206 ± 0.041 | -35±3 | 10 |
| Atmospheric CO_2 | | 100.8 ± 0.4 | -8 (from literature) | Mean value of 6 ^{14}C measure- ments on nuts collected in France in 2020 SacA61412, SacA61413, SacA64712, SacA64713, SacA64718, SacA64719 |

RESULTS

^{14}C Content and $\delta^{13}\text{C}$ Value of the Initial Reactants

The results of the initial reactants are given in Table 2. The carbon contents of horse manure (100.4 ± 0.3 pMC) and natural vinegar (100.8 ± 0.3 pMC) show compatible results within 2σ , indicating that these two elements are contemporary. These values are also consistent with the contemporaneous atmosphere recorded in 2020 and measured on nuts collected in France (100.8 ± 0.4 pMC). CO_2 gas, usually used as a blank, gives a mean ^{14}C content of 0.206 ± 0.041 pMC. The industrial acetic acid ^{14}C content is very low, close to the ^{14}C detection limit.

The $\delta^{13}\text{C}$ values of horse manure and vinegar, -29‰ and -18‰, are in the range of organic matter, whereas the $\delta^{13}\text{C}$ values of CO_2 gas and acetic acid, -35‰ and -43.6‰ respectively, are characteristic of materials derived from fossil fuels.

Chemical Structure of the Final Products

A white powder was obtained for all the setups due to the corrosion of the metallic lead foil (Figure 2). Two main products were determined by XRD after 2 months of exposure: lead acetate trihydrate, $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3(\text{H}_2\text{O})$ (Figure 3a) for setups 1, 2, and 5 and cerussite, PbCO_3 (Figure 3b) for setups 3, 4, and 6 (Table 3).

Lead acetates were detected for setups 1 and 2 where lead was submitted to the vapors of vinegar or acetic acid (CH_3COOH), as also observed by Gonçalves et al. (2010). The formation of the trihydrate form was promoted when water vapor condensed (Gonzalez et al. 2019) following the reaction:

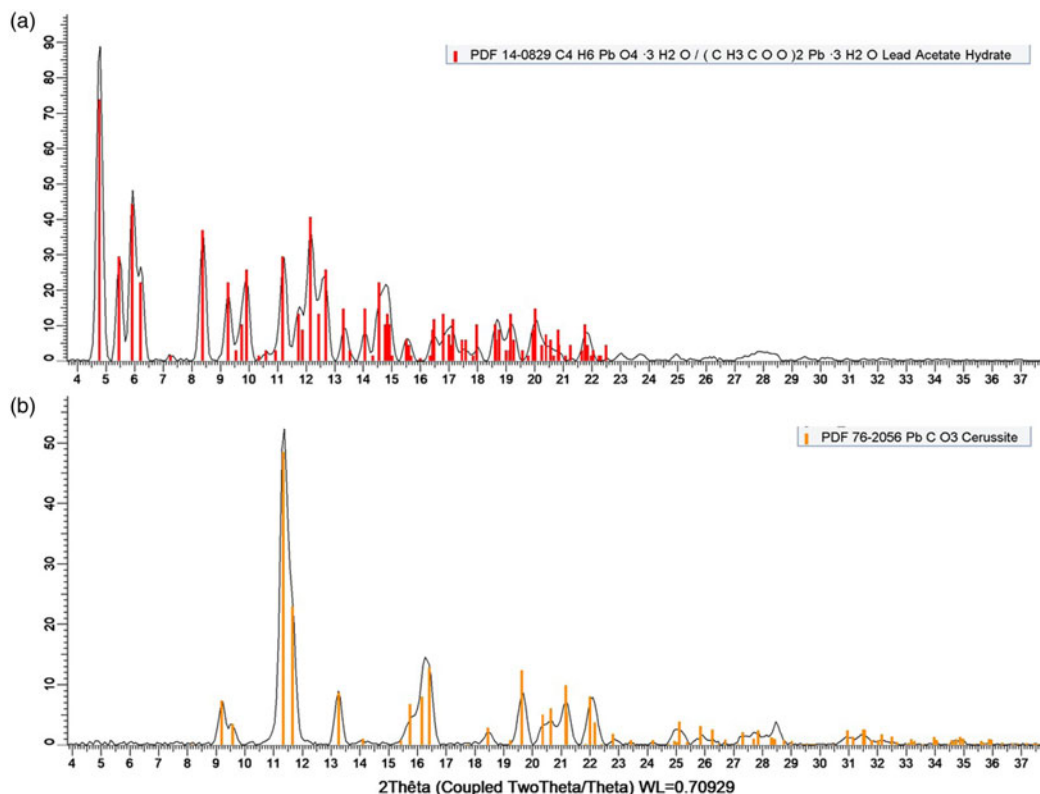
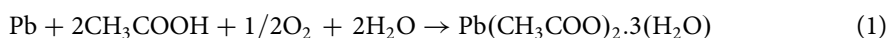


Figure 3 X-ray diffractograms of the white powder collected from: (a) setup 2 showing the production of lead acetate trihydrate (setups 1 and 5 show the same pattern), (b) setup 4 showing the production of cerussite (setups 3 and 6 show the same pattern).



In presence of horse manure and vinegar or acetic acid (setups 3, 4), pure cerussite (PbCO_3) was formed from the second day of exposure. The formation of lead carbonate indicates that the supply in CO_2 , produced here by fermentation of the manure, was enough for the reaction



to be complete. No other intermediate compounds described by Gonzalez et al. (2019), such as plumbonacrite ($\text{Pb}_5(\text{CO}_3)_3\text{O}(\text{OH})_2$) and hydrocerussite ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) were observed, even in the early stages of the reaction.

When CO_2 gas was injected, two different results were obtained. For setup 5 with acetic acid, corrosion took place very slowly and only a thin layer of lead acetate was detected. In contrast, in presence of vinegar (setup 6), lead carbonate (cerussite) was obtained. Several hypotheses can be put forward to explain this difference: experimental failure (lack of CO_2 in setup 5) and/or a possible role played by the microorganisms contained in vinegar (setup 6) as an additional source of CO_2 as suggested by Sanchez-Navas et al. (2013) and Photos-Jones et al. (2020).

Table 3 Composition, ^{14}C content in pMC, IRMS and AMS $\delta^{13}\text{C}$ of the reaction products after 53 to 120 days of exposure (120 days for setups 1 and 2; 73 days for setups 3 and 4; 53 for setups 5 and 6). Composition was determined by XRD after 64 days for setup 1; 53 days for setups 2, 5, 6; 10 and 73 days for setups 3 and 4.

| Setup number and label | Initial reactants | | Corrosion products | | | | |
|-------------------------|---------------------|----------------------------|----------------------|-------------------------------|-------------------------------|--------------------------------|-----------|
| | Corrosive reagents | CO ₂ sources | Composition | ^{14}C content (pMC) | AMS $\delta^{13}\text{C}$ (‰) | IRMS $\delta^{13}\text{C}$ (‰) | Lab code |
| 1. Aa+0 | Acetic acid 10% v/v | — | Lead acetate hydrate | 10.42 ± 0.05 | -39.6 | — | SacA66517 |
| 2. V+0 | Vinegar | — | Lead acetate hydrate | 103.394 ± 0.205 | -17.4 | — | SacA66518 |
| 3. Aa+Hm | Acetic acid 10% v/v | Horse manure | Cerussite | 94.352 ± 0.200 | -50.1 | -50.28 | SacA61872 |
| 4. V+Hm | Vinegar | Horse manure | Cerussite | 101.073 ± 0.254 | -49.0 | -49.89 | SacA63384 |
| 5. Ac+CO ₂ B | Acetic acid 10% v/v | Fossil CO ₂ gas | Lead acetate hydrate | 0.359 ± 0.033 | -39.1 | -36.43 | SacA61878 |
| 6. V+CO ₂ B | Vinegar | Fossil CO ₂ gas | Cerussite | 4.59 ± 0.06 | -44.1 | -46.82 | SacA61879 |

^{14}C Content and $\delta^{13}\text{C}$ Value of the Final Products

The results obtained for the final products are presented in Table 3. For setups 1 and 2, the samples were taken after 4 months of exposure. Lead acetate formed from lead and vinegar has a ^{14}C content of 103.394 ± 0.205 pMC and a $\delta^{13}\text{C}$ value of -17.4% . Lead acetate formed from lead and acetic acid has a ^{14}C content of 10.42 ± 0.05 pMC and a $\delta^{13}\text{C}$ value of -39.6% . The $\delta^{13}\text{C}$ values are of the same order of magnitude as those of the initial ingredients (vinegar $\delta^{13}\text{C}$ value = -18.8% ; acetic acid $\delta^{13}\text{C}$ value = $-35 \pm 3\%$), but the ^{14}C contents are slightly higher (vinegar ^{14}C content = 100.8 ± 0.3 pMC; acetic acid ^{14}C content = 0.206 ± 0.041 pMC). These results are probably due to external contamination by environmental CO_2 or by the other setups nearby, occurring during the long time of exposure. For setup 1, measurement after one week of exposure only seems to confirm this interpretation with a ^{14}C content of 1.558 ± 0.125 pMC and a $\delta^{13}\text{C}$ value of $-36 \pm 4\%$ (SacA61010, not reported in Table 3) very close to those of acetic acid. For setup 2, the result is above the current atmospheric level, but no other source of ^{14}C has been identified so far. For setups 1 and 2, it can be inferred that $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3(\text{H}_2\text{O})$ has a similar carbon isotope signature to that of the corrosive liquid. No significant $\delta^{13}\text{C}$ fractionation was observed. These results confirm that lead acetate was produced by the reaction of the acid vapors on lead according to reaction (1).

Lead acetate was also obtained in the case of setup 5 when acetic acid and fossil CO_2 gas were used. The ^{14}C content is 0.359 ± 0.033 pMC and the $\delta^{13}\text{C}$ value -36.43% . These values are similar to those of the initial ingredients, but as both acetic acid and fossil CO_2 gas have a very similar carbon isotope signature, it is not possible to estimate the contribution of each component to the formation of lead acetate in that case.

For setups 3, 4, and 6, the samples were taken after ~ 2 months of exposure. The cerussite produced in setup 3 from lead, acetic acid and horse manure has a ^{14}C content of 94.4 ± 0.2 pMC and a $\delta^{13}\text{C}$ value of -50.3% . In setup 4 where vinegar is present, the ^{14}C content is 101.1 ± 0.3 pMC and the $\delta^{13}\text{C}$ value is -49.9% . In setup 6, the cerussite produced from lead, vinegar and fossil CO_2 gas has a ^{14}C content of 4.59 ± 0.06 pMC and a $\delta^{13}\text{C}$ value of -46.8% . The ^{14}C content of the cerussite produced shows values around 100 pMC when horse manure was involved whatever the corrosive reagent used (vinegar or acetic acid), and a low value when fossil CO_2 gas was used with vinegar (Table 3). These results clearly indicate the predominant influence of CO_2 when lead carbonate is produced according to reaction (2).

In these three setups, carbonation was achieved and pure cerussite was obtained, mostly carrying the ^{14}C signature of the initial CO_2 . However, the influence of the corrosive reagent can be seen when looking in detail at the pMC values for setups 3 and 4. The ^{14}C content of cerussite from setup 4 was 101.1 ± 0.3 when horse manure was used with natural vinegar, whereas the ^{14}C content of cerussite from setup 3 was 94.4 ± 0.2 when horse manure was used with acetic acid (<0.25 pMC). The latter value reflects the presence of traces of acetic acid between the flakes of lead white or minor phases ($<5\%$) not seen by XRD, carrying the ^{14}C signature of acetic acid. The same observation can be made in the reverse situation (setup 6) where the cerussite produced by fossil CO_2 gas (0.21 ± 0.04 pMC) with natural vinegar (100.8 ± 0.3) has a ^{14}C content of 4.6 ± 0.1 pMC.

About the $\delta^{13}\text{C}$ results, contrary to lead acetate, cerussite produced using horse manure shows a strong fractionation: very depleted $\delta^{13}\text{C}$ values of -50.3% and -49.9% were obtained although the initial ingredients had $\delta^{13}\text{C}$ values of -18.8% (vinegar) or -43.6% (acetic acid) and -28.9% (horse manure). The $\delta^{13}\text{C}$ signature is lower than expected for the organic matter from an

animal's diet, which is generally between -32% and -10% (Amelung et al. 1999; Sponheimer et al. 2003; Inacio et al. 2013). Hendriks et al. (2020) and Messenger et al. (2022) obtained similar results, with $\delta^{13}\text{C}$ values between -45 and -40% for lead whites prepared with the same process but provided by other suppliers.

Low $\delta^{13}\text{C}$ values are not well documented for carbon dioxide. Botz et al. (1996) reported $\delta^{13}\text{C}$ values up to -49.7% for CO_2 emitted during biologic methane formation and Whiticar (1999) indicated values up to -46% for CO_2 produced by methane oxidation. As gas generated by the degradation of organic matter in manure contains both methane and carbon dioxide (Wartell et al. 2012), the low $\delta^{13}\text{C}$ values obtained for cerussite probably reflect the fermentation process. A direct analysis of the $\delta^{13}\text{C}$ of gas would be necessary to confirm this hypothesis.

^{14}C Dates for Lead White (Cerussite)

When cerussites were produced from acetic acid and/or fossil CO_2 (setups 3, 5, 6), apparent old ages were found due to the presence of dead carbon in the initial ingredients. The calculation of absolute dates is therefore not relevant in these cases.

For cerussite produced according to the process described in the ancient recipes using natural vinegar and horse manure (setup 4), the ^{14}C content was converted into calendar dates using the post-bomb atmospheric NH1 21 calibration curve (recorded up to 2019 only). Two dates were obtained due to the shape of the bomb peak: 1955 and 2017-... Despite the limited expansion of the calibration curve, the second interval can be considered to be in agreement with the manufacturing date in 2020. This result is consistent with the level of ^{14}C recorded in the atmosphere for this given year.

Together with the pioneering works of Hendriks et al. (2019) and Beck et al. (2019) on other lead white reproductions, this result demonstrates that the radiocarbon dates for these pigments produced following the historical corrosion process are accurate and meaningful.

CONCLUSION

Lead white was produced in the laboratory according to ancient recipes involving metallic lead, vinegar and horse manure. For comparison, alternative materials depleted in ^{14}C —acetic acid and fossil CO_2 gas—were also selected to discriminate the function of each ingredient. The reaction between lead and vinegar or acetic acid resulted in lead acetates with a carbon isotopic signature close to that of the corrosive reagent. In the presence of CO_2 , the carbonation reaction occurred and the lead carbonates produced (cerussite here) had a predominant ^{14}C signature of the carbon dioxide source.

As a result, lead white formed by the corrosion process involving vinegar and horse manure has the ^{14}C content of its initial ingredients. This experimental result confirms the possibility of dating lead white by the ^{14}C method and definitely supports the studies conducted on cosmetics or paintings (see introduction). However, a significant fractionation in ^{13}C was observed, which is not fully explained yet.

In conclusion, when all the ingredients are biogenic, as was the case before the 19th century, the date of manufacture of lead white can be reliably determined.

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