

ARTICLE

DOI: 10.1038/s42004-018-0034-y

OPEN

Absolute dating of lead carbonates in ancient cosmetics by radiocarbon

Lucile Beck¹, Ingrid Caffy¹, Emmanuelle Delqué-Količ¹, Christophe Moreau¹, Jean-Pascal Dumoulin¹, Marion Perron¹, Hélène Guichard² & Violaine Jeammet³

Lead carbonate is one of the major compounds of art and archeology used as an ingredient in paint and cosmetics since Antiquity. Accelerator mass spectrometry radiocarbon dating is usually applied to organic remains. Here we extend radiocarbon dating to lead carbonate, an inorganic material. We demonstrate that lead carbonates can be dated. We also show that natural and manufactured make-up powders can be discriminated by radiocarbon. We find that cerussite used for cosmetics was a natural mineral during the Egyptian Kingdom and then a synthesized compound manufactured by the ancient Greeks. Furthermore, we confirm that phosgenite was artificially produced by the Egyptians about 3500 years ago. Our results confirm the expertise of ancient Egyptians and Greeks in the chemical synthesis of cosmetics. The detection of radiocarbon in lead carbonate holds great promise for art history and provides a new tool for the authentication of paintings by dating the lead white pigment.

¹Laboratoire de Mesure du Carbone 14 (LMC14), LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, 91191 Gif-sur-Yvette, France. ²Département des Antiquités égyptiennes, Musée du Louvre, Pavillon Mollien, Paris cedex 01 75058, France. ³Département des Antiquités grecques, étrusques et romaines, Musée du Louvre, Paris Cedex 01 75058, France. Correspondence and requests for materials should be addressed to L.B. (email: lucile.beck@cea.fr)

The development of the radiocarbon method has had a profound impact on archeology as it enables the dating of the remains of ancient civilizations. The method is usually applied to organic materials - wood, charcoal, bone, etc. - which incorporate radioactive carbon through photosynthesis or ingestion. However, a few studies have shown that radiocarbon dating can also reveal the age of inorganic manufactured materials. As early as the 1960s, ^{14}C dating was extended to building materials¹. In particular, mortar which incorporates atmospheric carbon dioxide as it hardens, has been extensively studied and used to date churches and Roman buildings^{2, 3}.

More recently, the direct dating of iron was successfully achieved by combining chemical analysis and radiocarbon measurement. During the manufacture of the iron alloy, carbon from charcoal combustion is incorporated by diffusion into the metal and forms cementite (Fe_3C)⁴. This approach has shed new light on the technical skill and intentions of cathedral builders in Europe⁵ and on the chronology of the Angkor temples in Cambodia⁶.

Lead carbonates were used as ingredients in paint and cosmetics. Lead white, a mixture of cerussite (PbCO_3) and hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$), was the most important of all white pigments until the nineteenth century⁷. Lead carbonates were also employed as cosmetics from Antiquity to the eighteenth century^{8, 9}. They were used by ancient Egyptians, Greeks, and Romans¹⁰⁻¹⁵. Understanding the synthetic process of cosmetics production in Antiquity is of great interest for human history and for our knowledge of the development of chemical techniques.

Here we demonstrate the ability of radiocarbon to date archeological and historical lead carbonates and to discriminate natural and synthesized cosmetics. Based on a purposely designed protocol (Methods), radiocarbon measurements are performed on ancient Egyptian and Greek make-up held at the Louvre museum. As they are considered as the earliest synthesized cosmetics, the application of the radiocarbon method is highly meaningful not only to date the compound but also to determine its natural or artificial origin.

We measure the $^{14}\text{C}/^{12}\text{C}$ ratio by accelerator mass spectrometry (AMS) in each cosmetic powder prepared by thermal decomposition and graphitization^{16, 17} (Methods). We show that atmospheric carbon dioxide was incorporated in some lead carbonates during their synthesis. In this way, the radioactive isotope ^{14}C was fixed in the mineral matrix through the carbonate ion and decayed in time after its incorporation, making radiocarbon dating possible. To our knowledge, this study presents the first

absolute dating of lead carbonate. We provide a tool to directly date lead carbonate-based materials such as ancient cosmetics and paintings. Recrystallization of lead carbonate in cosmetics or paintings is unlikely to be problematic for radiocarbon dating as for other carbonates such as shells and some mortar due to lack of exposure to water.

We also show that the quantity of radiocarbon (^{14}C) is the criterion of choice to discriminate natural and synthesized lead carbonates. The results give new insight into the production of white make-up powders in Antiquity and confirm the expertise of ancient Egyptians and Greeks in chemically synthesizing lead carbonate make-up.

Results

Ancient Egyptian and Greek white cosmetics from the Louvre museum. To highlight the novelty of our approach we report here results obtained on well-preserved Egyptian and Greek ancient cosmetics. They are held at the Louvre museum in their original containers in wood, reed or alabaster (Fig. 1). The objects were associated to identified Egyptian or Greek tombs and dated from the 3rd millennium to the 3rd century BC (for more information on the samples, see Methods and Supplementary Table 1). The cosmetics were selected on the basis of their known archeological context and chemical composition. Small samples of powders (10–50 mg) containing two forms of lead carbonate were collected: phosgenite ($\text{Pb}_2\text{Cl}_2\text{CO}_3$) and cerussite. These two compounds were pure or mixed together or associated to other lead minerals: galena (PbS), laurionite ($\text{PbCl}(\text{OH})$), and anglesite (PbSO_4). Galena is an abundant natural mineral, widely distributed in various environments. On the contrary, laurionite and phosgenite are very rare in nature and are considered as the earliest synthesized cosmetics¹⁵. Cerussite exists as a natural mineral, but has also been manufactured. Natural cerussite is found in the oxidation zone of lead deposits. As an artificial compound, the production of “psimythium” (the Greek term for cerussite) or “cerussa” (the Latin term) is described in several written sources from Antiquity, from the 4th century BC to the 1st century AD¹⁸⁻²⁰. Two modern samples of cerussite made according to the historical process were also measured to further validate our methodology (Supplementary Table 5).

Greek Cerussite and Egyptian phosgenite were synthesized in Antiquity. The radiocarbon dating of five samples of powder provided dates coherent with the expected age of the cosmetics (Table 1 and Supplementary Table 2). One sample is a pale pink

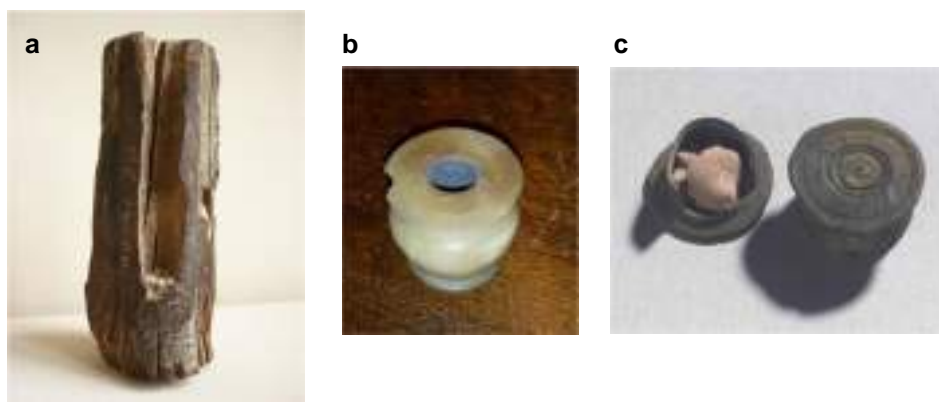


Fig. 1 Egyptian and Greek make-up from the Louvre museum collection. (a) in a wooden cylinder (E 22326, 10 cm high and 4.4 cm diameter), one of the four channels is visible, (b) in an alabaster vase (E 23092, 4.9 cm high, 5.1 cm diameter) and, (c) in a 2.5 diameter wooden box (AGER-CA 508) © Musée du Louvre, LMC14, C2RMF

Table 1 Radiocarbon dates of ancient cosmetics made with cerussite or phosgenite

| Period and Louvre Museum sample label | Main compound | Expected period (years) | pMC | Radiocarbon date ± 30 (years BP) | Calibrated date (years cal BC) –(95.4%) |
|--|----------------------------|---|--------------|----------------------------------|---|
| Greek period AGER-CA508 cosmetics | Cerussite ²¹ | 360-196 calBC ⁴⁰ 330-266 BC ²¹ | 76.60 ± 0.23 | 2140 | 353-57 |
| Egyptian New Kingdom E 22326 cosmetics | a Phosgenite ²⁴ | 18th dynasty: –1550/ –1425 | 66.45 ± 0.24 | 3280 | 1630-1497 |
| | b | | 65.68 ± 0.32 | 3375 | 1763-1534 |
| | c | | 66.79 ± 0.19 | 3240 | 1611-1439 |
| | d | | 68.47 ± 0.21 | 3040 | 1397-1216 |
| Egyptian New Kingdom E 22326 container | Wood | Amenhotep III: 1423-1348 calBC ^{22, 23} | 67.21 ± 0.26 | 3190 | 1514-1412 |

These Egyptian and Greek cosmetics are composed of cerussite (PbCO₃) or phosgenite (Pb₂Cl₂CO₃). The radiocarbon date of the Egyptian wood cylinder containing the phosgenite powders is reported for comparison. See Supplementary Tables 1, 2, 4 for more details.

blush powder (AGER-CA508, Fig. 1c) composed of cerussite. It 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 BC²¹. The other four powders are mainly composed of phosgenite and were placed in four distinct channels of a wooden cylinder (E 22326, Fig. 1a) engraved with the cartouches of Amenhotep III and his wife Queen Tiye. The dates of Amenhotep III's accession and the end of his reign are estimated to be 1423–1386 calBC and 1385–1348 calBC, respectively^{22, 23}.

For the Greek cerussite sample (AGER-CA508) we obtained a date range of 353 to 57 BC (95.4%) (Fig. 2a). This date is consistent with the numismatic result and in agreement with two previous radiocarbon dates measured on an almond seed (AGER-CA518) from the same tomb²¹ (Fig. 2b).

The radiocarbon dates of the four phosgenite Egyptian powders (E 22326) are between 1763 and 1216 calBC (Fig. 3). The powders are preserved in four distinct channels of the container and do not have exactly the same composition²⁴. The relative scatter on the dating results may suggest different production periods. If somewhat large, the range nevertheless includes the radiocarbon date of the container (1514–1412 calBC, see Table 1) and the dates ascribed to Amenhotep III. However, we have to keep in mind that the date obtained on the wood might not accurately reflect the period of use due to the inbuilt effect as well as a possible material reuse due to the scarcity of wood in Ancient Egypt²⁵. The container may have been carved from reclaimed wood that had previously been used for other purposes.

The fact that the measured radiocarbon dates of these cosmetics match with the expected dates is strong evidence that atmospheric carbon dioxide was incorporated at the time of formation of the lead carbonates and that the carbonate formation occurred in a period close to that of the use of the cosmetics. Through the absorption of CO₂, the radioactive isotope ¹⁴C was fixed in the carbonate ion, and decayed over time. The present radiocarbon content of the phosgenite samples ranges from 65.7 ± 0.3 to 68.5 ± 0.2 pMC (percentage of modern carbon). The mean value of the four samples (66.8 ± 1.2 pMC) is consistent with the radiocarbon content of the wooden container (67.21 ± 0.26 pMC).

The radiocarbon measurements thus provide two key results: the age and the signature of the artificial production of the cosmetics.

Ancient Egyptian cerussite is a natural mineral. The radiocarbon dates of seven Egyptian powders composed of mixtures of galena, laurionite, anglesite, cerussite, and phosgenite are much older than the period considered (Table 2 and Supplementary Table 3). As galena, laurionite, and anglesite do not contain

carbon, the radiocarbon measurements concern phosgenite and cerussite exclusively. The two samples containing galena and cerussite give dates from 8793 to 7142 calBC. As they are much older than the expected age (3000–1000 BC), these results evidence a natural origin of the Egyptian cerussite. Cerussite is abundant in nature as a secondary mineral formed by the natural weathering of galena exposed to air or water²⁶. The measured radiocarbon dates thus correspond to its *in situ* formation about 10 kyears ago and indicate that these cosmetics are composed of a natural association of galena and cerussite.

The radiocarbon dates of the five samples containing galena, cerussite and phosgenite are also older than expected, but to a significantly lesser extent (4700–3300 calBC). These intermediate ages are coherent with a combination of the old ages of the natural cerussite and the “pharaonic ages” of the synthesized phosgenite. We interpret this result to mean an intentional combination of natural cerussite associated to galena with synthetic phosgenite.

Discussion

Radiocarbon measurements on ancient cosmetics provide two key results: the production process of the lead carbonate powders and, when synthesized, the date when they were produced.

Our results show two distinctive cases: we find much older radiocarbon dates than the period of use for the Egyptian cosmetics composed of mixtures of lead compounds, and radiocarbon dates in agreement with the expected dates for Greek and Egyptian make-up in pure cerussite or pure phosgenite.

In the first case, for the cosmetics composed of a mixture of cerussite and galena, radiocarbon dates give ages that are too old. This result is the fingerprint of a natural cerussite since geological carbonates contain very low amounts of ¹⁴C. Cerussite is a common alteration product of galena, associated to secondary minerals and other carbonates in oxidized zones of deposits. The weathering of galena exposed to air and water involves the formation of anglesite. In presence of calcareous soil or carbonated water, cerussite is also found. Galena deposits in Egypt occur mainly along the Red Sea coast²⁷. The site of Gebel el-Zeit was one of the main mines exploited in Antiquity²⁸. The mines are located on the calcareous slope of the wadi and in the superficial zones, galena is partially transformed into cerussite²⁹. The mine of Gebel el-Zeit was exploited in the second millennium BC, from the 12th dynasty up to the end of the New Empire (ca 2000–1200 BC)³⁰. Minerals containing galena and secondary minerals were collected at this period and used as cosmetics without chemical transformation. The color, from black to light gray, was probably adjusted by selecting various mineral blends, depending on the proportion of black galena and grayish natural cerussite and

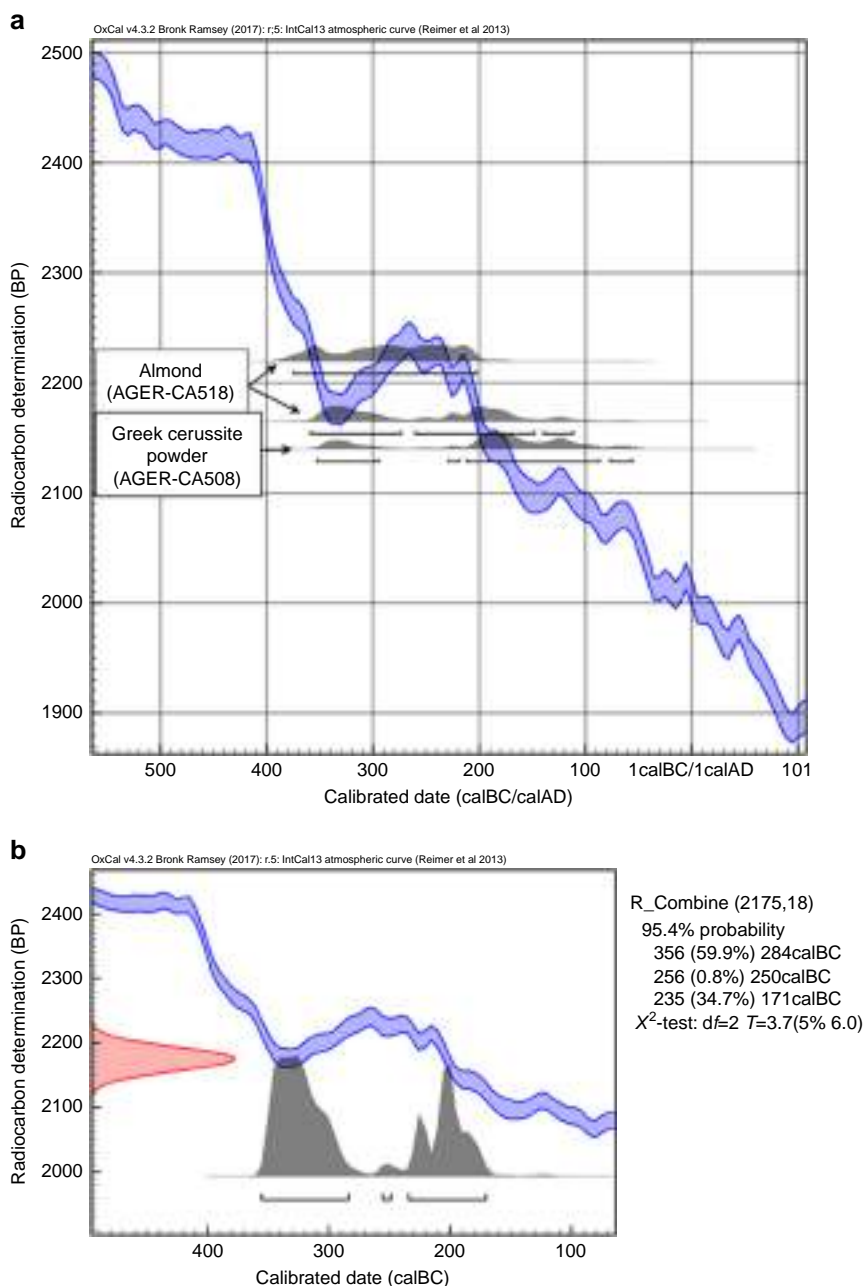


Fig. 2 Radiocarbon dating of a Greek cerussite make-up powder. **(a)** The calibrated radiocarbon date (353–57 calBC) of the Greek cerussite powder (AGER-CA508 - SacA48856) found in the tomb of a child in Eretria (Greece) is compared to two previous radiocarbon dates (359–112 calBC and 375–203 calBC) measured on an almond seed (AGER-CA 518 - 1A214/SacA22810 and 2A214/Sac22811)⁴⁰ of the same tomb²¹. Calibrated dates, represented by age probability distributions in gray, are calculated using the IntCal13 atmospheric calibration indicated in blue (see Methods), **(b)** The statistical combination of the three dates is represented in red before calibration (2175 ± 18 BP) and in gray after calibration (356–171 calBC, see details in the key); A χ^2 test value of $T=3.7 (<6)$ shows the consistency of the dates

anglesite. White powder was thus difficult to obtain and it became necessary to search for pure white compounds.

Phosgenite is a solid white powder. Its presence is observed in the cosmetics as pure or mixed with galena and cerussite. Very few occurrences of natural phosgenite are reported. Contrary to lead carbonates and lead sulfates, phosgenite is, like all minerals of lead and chlorine, soluble and does not accumulate in the oxidized zones of lead deposits³¹. To obtain large quantities of pale powder, the production of an artificial white was thus required. The first evidence that phosgenite was chemically synthesized by ancient Egyptians was reported twenty years ago¹⁵.

This statement was based on the small abundance of these minerals in nature, on ancient recipes and on their replication in modern laboratories. Here, by using radiocarbon, we provide an absolute method to directly identify a synthetic process for phosgenite. Dioscorides in the second half of the first century AD reported a recipe involving lead oxide, salt, and white soda to produce a white compound^{19, 32} (the corresponding chemical compounds are indicated in brackets):

“[...] , mix with 80 Attic drachmai [1 drachme = 3.4 g] of litharge (PbO), one litra of mined salt (NaCl) and pound. Letting some time pass, add 47 holcai [1 holce = 3.4 g] of very white soda

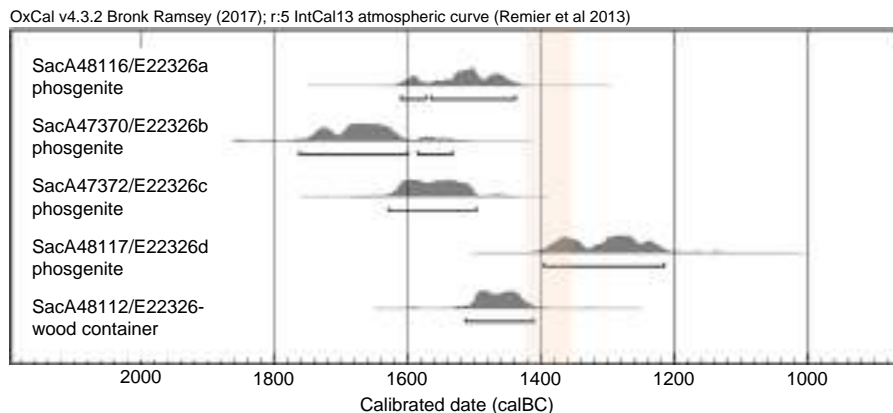


Fig. 3 Calibrated radiocarbon dates of Egyptian make-up. Four phosgenite powders and their wooden container are dated from 1763 to 1216 calBC. This large range can be due to the fact that the four powder samples may not have been manufactured from the same batch since they are preserved in four distinct channels of the container. As the cartouches of Amenhotep III and his wife Queen Tiye are engraved in the wood, the dates ascribed to the Amenhotep III's reign (accession dates from 1423 to 1386 and end of reign from 1385 to 1348 calBC^{22, 23}) are indicated by shaded region

(also translated as natron) (Na_2CO_3) dissolved in water and again pound it until the litharge becomes quite white [...]. That which was washed seems to be good for eye medications, for unseemly scars and for faces full of wrinkles and blemishes”.

Successful replication of this recipe showed that phosgenite is obtained after many repetitive operations^{15, 33}. The first step in the recipe is to form laurionite by stirring PbO (litharge) with NaCl (salt): $\text{PbO} + \text{NaCl} + \text{H}_2\text{O} \rightarrow \text{Pb}(\text{OH})\text{Cl} + \text{NaOH}$. When carbon dioxide is added in the solution, the chemistry of lead oxychloride is altered and phosgenite forms³⁴: $2\text{Pb}(\text{OH})\text{Cl}_{(s)} + \text{CO}_{2(g)} \rightarrow \text{Pb}_2\text{Cl}_2\text{CO}_{3(s)} + \text{H}_2\text{O}$. The $\text{CO}_{2(g)}$ provides the radioactive isotope ^{14}C used for dating the cosmetics. According to our results, the carbon dioxide used to manufacture phosgenite is of atmospheric origin. In the recipe, $\text{CO}_{2(g)}$ is produced by the dissolution of natron in water. The term of natron is vague and can refer to many phases of sodium carbonates (Na_2CO_3 and its hydrated forms or NaHCO_3 (bicarbonate))³⁵. Natural sodium carbonates from the Wadi El Natrum depression were known by the ancient Egyptians³⁴. They are formed during the drying up of salt lakes in summer. Sodium carbonates can be formed at the surface by absorption of carbon dioxide from the atmosphere or in the brine by combination of HCO_3^{2-} with Na³⁵. Over the years the lake builds up a stratigraphy of deposits which are complicated by partial dissolution during the winter when the water rises again. The resulting radiocarbon content of such materials is therefore likely to be complex. However, due to the seasonality of the phenomenon, natron may have been collected annually, limiting in time the incorporation of radiocarbon. The other way of incorporating ^{14}C in phosgenite is during the synthesis as NaOH produced by the chemical reaction is prone to absorb atmospheric CO_2 . The precise source of CO_2 is still an open question, but we can assert that ^{14}C was fixed in the carbonate of the phosgenite through the incorporation of atmospheric carbon dioxide. Furthermore as the quantity of ^{14}C is very close to that of the contemporaneous atmosphere measured in the wood of the container, we demonstrate that this phenomenon took place at the same period. The absorption of CO_2 in sufficient quantity to produce grams of powders reveals an intentional manufacture. We thus confirm that the Egyptian phosgenite was chemically synthesized and that this synthesis was achieved between 1760 and 1200 calBC. Through this innovative process, artificial phosgenite powder was “mass-produced” and used pure to obtain white and cream colors on the Egyptian make-up palette. Artificial phosgenite was also blended with natural galena

and cerussite to lighten the color. In this way, Egyptians of the 18th dynasty not only took advantage of natural resources of lead ore for their cosmetics industry but were also capable of developing targeted chemistry.

More than one millennium later, in Greece, another situation emerged. To satisfy the demand for white cosmetics, the Ancient Greeks artificially produced cerussite, as we now demonstrate. A recipe for “psimythium” is reported by Theophrastus, born around 372 B.C. at Eresos on the island of Lesbos¹⁸:

“Lead (Pb) about the size of a brick is placed in jars over vinegar (CH_3COOH), and when this acquires a thick mass, which it generally does in ten days, then the jars are opened and a kind of mold is scraped off the lead, and this is done again until it is all used up. The part that is scraped off is ground in a mortar and decanted frequently, and what is finally left at the bottom is psimythium (PbCO_3 and $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$)”.

This preparation was also reported by Dioscorides¹⁹ and Pliny the Elder²⁰ in the 1st century AD. In this process, lead is exposed to acetic acid vapors (“placed over vinegar”) and corrodes. Corrosion products consisting of white flakes (“a kind of mold”) form at the surface and are collected. Vinegar vapor converts the lead to white lead acetate³⁶. CO_2 is required at this stage to produce plumbonacrite ($\text{PbCO}_3 \cdot 3\text{Pb}(\text{OH})_2 \cdot \text{PbO}$), hydrocerussite and then cerussite. A supply of CO_2 is not mentioned in the recipe, but our results indicate that carbon dioxide of atmospheric or organic origin was the main reactant to produce the carbonate. CO_2 probably came from organic impurities in the vinegar or could be supplied by the fermentation of additional, but not reported, organic matter. Later recipes mention dung or horse manure to produce CO_2 ^{37, 38}. As for the artificial phosgenite, ^{14}C was fixed in the carbonate and decayed over time. Its measurement provides direct evidence that the Greeks synthesized artificial cerussite to produce white make-up in the 4th century BC. Despite its toxicity, psimythium was preferred to other white pigments such as chalk, kaolin, or plaster because of its excellent concealing effects³⁹.

We have demonstrated, using radiocarbon measurement, that natural and artificial cerussite can be unequivocally differentiated. This procedure can be extended to all other carbonates, as we also show for phosgenite. We confirm that ancient Egyptians and Greeks were capable of chemically synthesizing lead carbonate make-up and we provide a time scale showing that phosgenite was artificially produced one millennium before cerussite. During the Egyptian Kingdom cerussite was a natural mineral extracted from the galena mines.

Table 2 Radiocarbon dates of Egyptian cosmetics composed of various lead compounds

| Louvre Museum sample label | Period | Composition ^{13, 15, 24} | Expected age (years) | Radiocarbon date ± 30 (years BP) | Calibrated date (95.4%) (calBC) |
|--------------------------------|--------------------------------------|---|----------------------|----------------------------------|---------------------------------|
| AF 6772 | Middle or new kingdom | Mixture of galena, <i>cerussite</i> , and laurionite | −2106/−1069 | 9410 | 8793-8575 |
| E 25257 | Early dynastic Period | Mixture of galena, <i>cerussite</i> , and anglesite | −3100/−2700 | 8270 | 7481-7142 |
| E 21562 | New Kingdom | Mixture of galena, laurionite, <i>cerussite</i> , and <i>phosgenite</i> | −1550/−1069 | 5775 | 4720-4528 |
| E 23092 | 18th dynasty | Mixture of galena, <i>cerussite</i> , <i>phosgenite</i> , anglesite, and laurionite | −1550/−1425 | 5780 | 4714-4544 |
| AE000245 | Early dynastic Period | Powder not analyzed | −3100/−2700 | 4810 | 3652-3525 |
| E 11048c cosmetics | Before or during Tutankhamun's reign | Mixture of galena, <i>cerussite</i> , and <i>phosgenite</i> | ≈1400-1300 calBC | 4745 | 3637-3380 |
| E 11048 ^e cosmetics | | Mixture of galena, <i>cerussite</i> , and <i>phosgenite</i> | | 4970 | 3893-3661 |
| E 11048c container | | Reed | | 3065 | 1412-1234 |
| E 11048 ^e container | | Reed | | 3130 | 1495-1300 |

As galena (PbS), laurionite (PbCl(OH)), and anglesite (PbSO₄) do not contain carbon, the radiocarbon measurements concern phosgenite (Pb₂Cl₂CO₃) and cerussite (PbCO₃) exclusively (in italic in the table). Radiocarbon dates of two cosmetics containers in reed are reported for comparison. See Supplementary Tables 1, 3, 4 for more details.

In conclusion, we provide an absolute method to directly date lead carbonates. We extend the range of inorganic materials datable by the radiocarbon method. We anticipate that our methodology will be applied to lead white, which is the most important pigment in art history, paving the way for a new tool for the authentication of ancient paintings.

Methods

Selection and collection of the samples. We selected samples of cosmetics according to their archeological context and chemical composition (Supplementary Table 1). Powder of 20–50 mg were taken directly from their wood, reed or alabaster containers held in the Louvre museum, Paris, France (Département des Antiquités égyptiennes and Département des Antiquités grecques, étrusques et romaines). In order to avoid any contamination, we used sterile tools and receptacles. The selected objects are associated to identified Egyptian or Greek tombs and some containers are decorated with clear inscriptions. The wood cylinder of the white phosgenite make-up (E 22326) is engraved with the cartouches of Amenhotep III and his wife Queen Tiye. Two reed cases (E 11048c, E 11048e) were found during the excavations of Lady Touti's tomb at Medinet el-Gorab (Fayoum). Her death dates back to the 18th dynasty, just before or during Tutankhamun's reign. The small pyxide containing a pale pink powder (AGER-CA508) comes from a tomb discovered in Eretria (Greece) dated by coin identification from ca 330 to ca 266 BC²¹. An almond seed from the same tomb was previously radiocarbon dated between 360 and 196 calBC⁴⁰. We collected samples of powders which were chemically analyzed in previous studies by scanning electron microscopy and quantitative X-ray diffraction^{12–15, 24}. Pure phosgenite (E 22326a/b/c/d), pure cerussite (AGER-CA508), and different mixtures of phosgenite, cerussite, laurionite, and galena (AF 6772, E 11048c/e, E 21562, E 23092, and E 25256/eb) were identified and selected.

Preparation of modern replications of cerussite according to the historical process. Modern samples of cerussite were reproduced by a pigment supplier according to the historical process^{18–20}. Pieces of lead were placed over a vessel filled with vinegar. Lead was exposed to acetic acid vapors in the presence of horse manure (sample MH) or sugar and yeast dissolved in water (sample MM). White flakes of lead carbonate were produced, collected and milled to obtain a fine pigment. For both samples, the pMC values (Supplementary Table 5) are in accordance with modern radiocarbon contents.

Sample preparation. We prepared samples for radiocarbon analysis using a purposely-designed protocol. To avoid any contamination during the sample preparation process, glassware and tools were thoroughly cleaned. First, glassware was boiled at 100 °C with lab detergent, washed with water, then placed overnight in a 10% HCl bath and washed again with deionized water. Each piece of glassware was covered with aluminum foil and baked at 450 °C for 5 h to remove any remaining organic contaminants. Stainless steel tools were hand washed with TFD4 (detergent, foam for the decontamination of radioactivity), rinsed with deionized water, cleaned again in ethanol in an ultrasonic bath and finally dried in a 60 °C oven.

Samples of cosmetics were first observed under the microscope to remove possible macro-contaminants. However, due to the small size of the samples, we did not apply the standard acid-base-acid method which is usually used to remove micro-contaminants. To control this procedure, modern cerussite samples were treated in the same way. For all the samples, we succeeded in extracting carbon from the lead carbonates. We obtained carbon contents of 0.2 to 1 mg. Samples were directly thermally decomposed in a sealed tube at 400 °C for 2 h on a vacuum line (5×10^{-6} mbar). Lead carbonate decomposes, producing lead oxide, carbon dioxide and water. CO₂ was separated from H₂O using a dry ice/alcohol trap (−78 °C) and the pressure of each CO₂ sample was measured to determine the carbon content. We produced graphite targets by reducing CO₂ with hydrogen over iron catalyst⁴¹. Before the reaction, the iron powder (Merck, particle size 10 μm) was degassed for 1 h at 600 °C under vacuum. Hydrogen was introduced in the reduction line with an H₂/CO₂ ratio of approximately 2.5. Iron was heated at 600 °C while the water was trapped at −78 °C. The pressure in the reaction lines was monitored and the reduction ended when the slope of the pressure became below 0.3% in 3 to 4 h. For some samples, due to the presence of Cl (from phosgenite) and/or S (from galena), we had to apply a Sulfix treatment to achieve the carbon formation reaction¹⁶.

The wood and reed materials of the cosmetics containers were prepared using the standard acid-base-acid method (0.5 M HCl at 80 °C, 1 h/ 0.1 M NaOH at 80 °C, 1 h/ 0.5 M HCl at 80 °C, 1 h)¹⁶ and then dried under vacuum overnight (60 °C-0.1 mbar). CO₂ was obtained by combustion (5 h, 850 °C) in a sealed tube with an excess of CuO (400–500 mg) and a 1-cm Ag wire. CO₂ was separated from H₂O using a dry ice/alcohol trap (−78 °C) and the pressure of each CO₂ sample was measured to determine the carbon content.

Radiocarbon measurements. Carbon isotopes were measured by AMS on the LMC14/ARTEMIS facility¹⁷. We used the NEC9SDH-2 Pelletron coupled to a 134-position MC-SNICS cesium sputter ion source. Normalization of the measurements was done with the oxalic acid II (1 Ox-II per 10 unknown samples). International intercomparison sample (FIRI H) and blanks (C1) were measured with the samples. ¹⁴C ages were calculated using the Mook and van der Plicht⁴² recommendations. Calibration of the radiocarbon dates was against the IntCal13 atmospheric calibration curve⁴³ using OxCal v4.2⁴⁴ (Supplementary Tables 2–5).

Data availability. Data that support the findings of this study are available within the article and its Supplementary Information files and from the corresponding author upon request.

Received: 13 March 2018 Accepted: 21 May 2018

© The Author(s) 2018

References

- Labeysie, J. & Delibrias, G. Dating of old mortars by the carbon-14 method. *Nature* **201**, 742 (1964).

2. Ringbom, Å., Lindroos, A., Heinemeier, J. & Sonck-Koota, P. 19 years of mortar dating: learning from experience. *Radiocarbon* **56**, 619–635 (2014).
3. Hayen, R. et al. Mortar dating methodology: assessing recurrent issues and needs for further research. *Radiocarbon* **59**, 1859–1871 (2017).
4. Delqué-Kolic, E., Leroy, S., Pagès, G. & Leboyer, J. Iron bar trade between the Mediterranean and Gaul in the Roman period: C-14 dating of products from shipwrecks discovered off the coast of Saintes-Maries-de-la-mer (Bouches-Du-Rhone, France). *Radiocarbon* **59**, 531–544 (2017).
5. Leroy, S. et al. Consolidation or initial design? Radiocarbon dating of ancient iron alloys sheds light on the reinforcements of French Gothic Cathedrals. *J. Archaeol. Sci.* **53**, 190–201 (2015).
6. Leroy, S., Hendrickson, M., Delqué-Kolic, E., Vega, E. & Dillmann, P. First direct dating for the construction and modification of the baphuon temple mountain in Angkor, Cambodia. *PLoS ONE* **10**, e0141052 (2015).
7. Stols-Witlox, M. *Historical recipes for preparatory layers for oil paintings in manuals, manuscripts and handbooks in North West Europe, 1550-1900: analysis and reconstructions 1400-1900*. PhD thesis, Univ. of Amsterdam, 5 September 2014.
8. Lucas, A. Cosmetics, perfumes and incense in ancient Egypt. *J. Egypt Archaeol.* **16**, 41–53 (1930).
9. Leblanc, C., Shimy, M. A. H. & Goyon J.-C. Eds., *Parfums, onguents et cosmétiques dans l'Égypte ancienne: actes des rencontres pluridisciplinaires tenues au Conseil National de la Culture, Le Caire 27-29 avril 2002* (Centre français de culture et de coopération du Caire, Cairo, 2003).
10. Bardiès-Fronty, I., Bimbenet-Privat, M. & Walter, P. (eds), *Le bain et le miroir. Soins du corps et cosmétiques de l'Antiquité à la Renaissance* (Gallimard, Paris, 2009).
11. Diamandopoulos, A., Kolonas, L. & Grapsa-Kotrotsou, M. Use of lead cosmetics in Bronze-Age Greece. *Lancet* **344**, 754–755 (1994).
12. Martinetto P., Anne M., Dooryhée E. & Walter P. in *Radiation in Art and Archaeology* (eds Creagh, D. & Bardley, R.) 297–316 (Elsevier, Amsterdam, 2000).
13. Martinetto, P. et al. Synchrotron X-ray micro-beam studies of ancient Egyptian make-up. *Nucl. Instrum. Methods Phys. Res. B* **181**, 744–748 (2001).
14. Welcomme, E., Walter, P., Van Elslande, E. & Tsoucaris, G. Investigation of white pigments used as make-up during the Greco-Roman period. *Appl. Phys. A* **83**, 551–556 (2006).
15. Walter, P. et al. Making make-up in Ancient Egypt. *Nature* **397**, 483–484 (1999).
16. Dumoulin, J.-P. et al. Status report on sample preparation protocols developed at the LMC14 Laboratory, Saclay, France: from sample collection to ¹⁴C AMS measurement. *Radiocarbon* **59**, 713–726 (2017).
17. Moreau, C. et al. Research and development of the artemis ¹⁴C AMS facility: status report. *Radiocarbon* **55**, 331–337 (2013).
18. Caley, E. R., Richards J. F. (eds), *Heophrastus On Stones: Introduction, Greek Text, English Translation, and Commentary* (Ohio State University Press, Columbus, Ohio, 1956).
19. Pedanius Dioscorides. *De Materia Medica*. Translated and edited by Lily Y. Beck. 3rd, revised edn (Olms Verlag AG, Hildesheim, Germany, 2017).
20. Bostock, J. & Riley, H.T., *Pliny the Elder. The Natural History*. (Taylor and Francis, Red Lion Court, Fleet Street, London, 1855).
21. Hasselin Rous, I. & Huguenot, C. Offrandes hellénistiques en miniature: le mobilier d'une tombe d'enfant d'Érétie conservé au musée du Louvre. *Rev. Archéol.* **63**, 3–64 (2017).
22. Bronk Ramsey, C. et al. Radiocarbon-based chronology for dynastic Egypt. *Science* **328**, 1554–1557 (2010).
23. Quiles, A. et al. Bayesian modelling of an absolute chronology for Egypt's 18th Dynasty by astrophysical and radiocarbon methods. *J. Archaeol. Sci.* **40**, 423–432 (2013).
24. Martinetto, P., *Etude cristallographique des préparations cosmétiques de l'Égypte Ancienne: apports du rayonnement synchrotron à l'analyse quantitative et microstructurale des matériaux archéologiques*. PhD thesis, Univ. of Grenoble. (2000).
25. Dee, M. et al. Synchronising radiocarbon dating and the Egyptian historical chronology by improved sample selection. *Antiquity* **86**, 868–883 (2012).
26. Keim, M. F. & Markl, G. Weathering of galena: mineralogical processes, hydrogeochemical fluid path modeling, and estimation of the growth rate of pyromorphite. *Am. Mineral.* **100**, 1584–1594 (2015).
27. Stos-Gale, Z. A. & Gale, N. H. Sources of galena, lead and silver in Predynastic Egypt. *Rev. d'Archéométrie* **5**, 285–95 (1981).
28. Castel, G. & Soukiassian, G. Les mines de galène pharaoniques du Gebel el-Zeit (Égypte). *Bull. Soc. Fr. d'Égyptol.* **112**, 37–53 (1988).
29. Castel, G., Pouit, G. & Soukiassian, G. Pharaonic galena mines of Gebel Zeit, Egypt, in the Miocene of the Red Sea. *Chron. Rech. Min.* **492**, 19–32 (1988).
30. Shortland, A. J., Nicholson, P. T. & Jackson, C. M. Lead isotopic analysis of eighteenth-dynasty Egyptian eyepaints and lead antimonate colourants. *Archaeometry* **42**, 153–157 (2000).
31. Emmons, W. H. The enrichment of ore deposits. *U.S. Geol. Surv. Bull.* **625**, 3–530 (1917).
32. Tsoucaris, G., Walter, P., Martinetto, P. & Lévêque, J.-L. Les cosmétiques au temps de l'Égypte pharaonique. *La Jaun. Et. la Rouge* **56**, 46–48 (2001).
33. Tapsoba, I., Arbault, S., Walter, P. & Amatore, C. Finding out Egyptian gods' secret using analytical chemistry: biomedical properties of Egyptian black makeup revealed by amperometry at single cells. *Anal. Chem.* **15**, 457–460 (2010).
34. Edwards, R., Gillard, D. P., Williams, A. & Pollard, A. M. Studies of secondary mineral formation in the PbO-H₂O-HCl system. *Mineral. Mag.* **56**, 53–65 (1992).
35. Shortland, A. J. Evaporites of the Wadi Natrun: seasonal and annual variation and its implication for ancient exploitation. *Archaeometry* **46**, 497–516 (2004).
36. Niklasson, A., Johansson, L.-G. & Svensson, J.-E. The influence of relative humidity and temperature on the acetic acid vapour-induced atmospheric corrosion of lead. *Corros. Sci.* **50**, 3031–3037 (2008).
37. Stols-Witlox, M. in *Studying Old Master Paintings - Technology and Practice* (ed. Spring, M.) 284–294 (Archetype Publications, London, 2011).
38. Gonzalez, V. et al. Revealing the origin and history of lead-white pigments by their photoluminescence properties. *Anal. Chem.* **89**, 2909–2918 (2017).
39. Walter P. et al. in *Le bain et le miroir. Soins du corps et cosmétiques de l'Antiquité à la Renaissance*. (eds Bardiès-Fronty, I., Bimbenet-Privat, M. & Walter, P.) 42–44 (Gallimard, Paris, 2009).
40. Gandolfo, N., and Richardin, P. *Radiocarbon dating of an almond of the Eretria city (CA518), Louvre museum, C2RMF*, Report No. 21072, 24 march 2011.
41. Vogel, J. S., Southon, J. R., Nelson, D. E. & Brown, T. A. Performance of catalytically condensed carbon for use in accelerator mass spectrometry. *Nucl. Instrum. Methods. Phys. Res. B* **5**, 289–293 (1984).
42. Mook, W. G. I & van der Plicht, J. Reporting ¹⁴C Activities and Concentrations. *Radiocarbon* **41**, 227–239 (1999).
43. Reimer, P. J. et al. IntCal13 and Marine13 radiocarbon age calibration curves 0–50,000 years cal BP. *Radiocarbon* **55**, 1869–1887 (2013).
44. Bronk Ramsey, C., Scott, M. & van der Plicht, J. Calibration for Archaeological and Environmental Terrestrial Samples in the Time Range 26-50 ka cal BP. *Radiocarbon* **55**, 2021–2027 (2013).

Acknowledgements

We acknowledge Isabelle Pallot-Frossard and Brigitte Bourgeois (C2RMF) for their administrative support for sample collection permission at the Louvre museum. This is LSCE contribution number 6442.

Author contributions

L.B. conceived the study and wrote the paper. L.B., I.C., E.D.-K, C.M., and J.-P.D. designed the experiments. L.B., I.C., and C.M. selected and collected the samples. I.C. and M.P. prepared the samples and C.M. measured radiocarbon. L.B., E.D.-K, C.M. and J.-P.D. analyzed the data. H.G. and V.J. gave access to the Louvre museum collection, gave assistance for sampling and provided archeological information.

Additional information

Supplementary information accompanies this paper at <https://doi.org/10.1038/s42004-018-0034-y>.

Competing interests: The authors declare no competing interests.

Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions/>

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2018