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Advances and limitations of ^{14}C dating in the field of heritage sciences

Avancées et limites de la datation par le radiocarbone dans le domaine des sciences du patrimoine

***Abstract**. In heritage sciences, the ability to obtain information about the origin and dating of cultural heritage objects is fundamental for placing an object into its historical context. Radiocarbon (^{14}C) dating can help to identify the period during which a work of art was created by dating its constitutive materials. Such information can, however, only be obtained by removing a sample from the object, which is critical since art is irreplaceable and demands that the sampling be kept to a minimum. In this context, we propose a novel dating approach, which targets the natural organic binder of the pictorial layer as a new ^{14}C candidate. In combination with spectroscopic techniques to ensure suitable sample selection, both canvas and paint samples were dated from three oil paintings. While not authenticating the paintings for belonging to a given artist, the ^{14}C results from the baroque and neoclassical objects tend to align themselves with the purported attribution. The third object, attributed to the beginning of the 20th century's modern expressionism movements, showcases the challenges in dating the natural organic binder owing to the presence of paraffin wax. The presented case studies showcase, how ^{14}C dating of the natural organic binder may complement or offer alternate routes of study in assessing an object's historical context. Moreover, the importance of material studies in the sampling step is enlightened as a prerequisite to access reliable ^{14}C ages.*

***Keywords**. Radiocarbon, micro-samples, paintings, oil on canvas, organic binder, analytical chemistry, FTIR spectroscopy.*

***Résumé.** Dans les sciences du patrimoine, la capacité d'obtenir des informations sur l'origine et la datation des objets du patrimoine culturel est fondamentale pour les replacer dans leur contexte historique. La datation par le radiocarbone (carbone 14, noté ^{14}C) peut aider à identifier la période pendant laquelle une œuvre d'art a été créée en datant ses matériaux constitutifs. Une telle information ne peut cependant être obtenue qu'en prélevant un échantillon de l'objet, ce qui est critique car une œuvre d'art est unique et exige que l'échantillonnage soit réduit au minimum. Dans ce contexte, nous proposons une nouvelle approche de datation qui cible le liant organique naturel de la couche picturale. Étayés par les données d'analyses spectroscopiques, permettant une sélection d'échantillons appropriée, des prélèvements de toile et de matière picturale ont été datés sur trois peintures à l'huile. Même si les résultats de datation ne permettent pas d'attribuer les peintures à un artiste donné, ils peuvent cependant confirmer une période de création. Le troisième objet, lié aux débuts des divers mouvements expressionnistes modernes du XXe siècle, met en lumière les enjeux de datation du liant organique naturel du fait de la présence de cire de paraffine. Les études de cas présentées montrent comment la datation par le ^{14}C du liant organique naturel peut compléter ou offrir d'autres voies d'étude pour évaluer le contexte historique d'un objet. Les études de matériaux lors de l'échantillonnage sont également un prérequis indispensable pour accéder à des âges radiocarbone fiables.*

***Mots-clés.** Radiocarbone, microéchantillons, peintures, huile sur toile, liant organique, chimie analytique, spectroscopie FTIR.*

Introduction

Since its discovery in the 1940's, radiocarbon dating has been used to roll back the pages of history by constructing chronologies spanning the last 50'000 years. What started as a discovery in chemistry rapidly exceeded disciplinary boundaries, eventually catching the society's interest with the identification of art forgery cases[1]. The recent progress in

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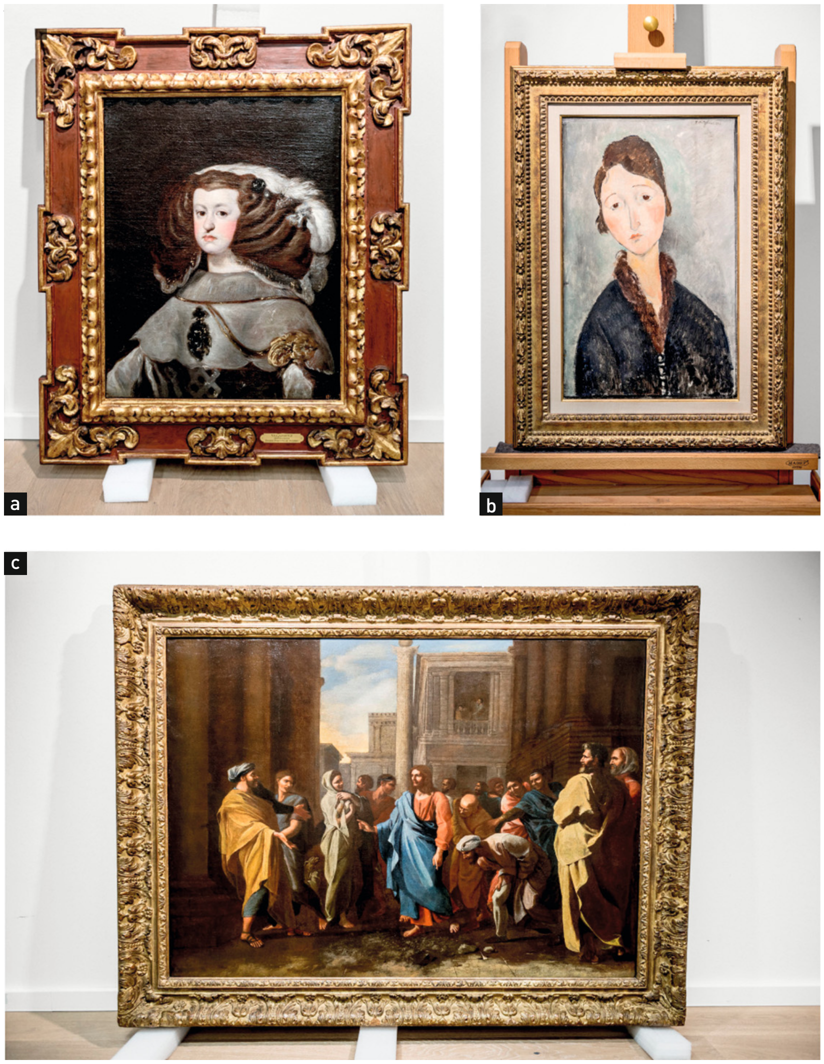

Fig. 1 a-c. Analyzed paintings belonging to John Kreuger's private collection. a. *Queen Maria Anna*, unsigned, attributed to Diego Velázquez (1599-1660), 56 x 72 cm; b. *Ritratto di Giovane Donna*, unsigned, attributed to Amedeo Modigliani (1884-1920), 38 x 61 cm; c. *Christ and the woman taken in adultery*, unsigned, attributed to Nicolas Poussin (1594-1665), 153 x 98 cm. © ETH-Zürich/D. Winkler.

expanding the ^{14}C field to art research was linked to technological development resulting in a substantial decrease in the amount of material necessary for acquiring a ^{14}C age. Generally, the code of ethics in cultural heritage sciences requires "minimal interventions" in the context of sampling. When permitted, ^{14}C dating is generally focused on the materials used as supports. While the radiocarbon date, i.e. the year of plant harvest, and the date signed on the work often match, offsets ranging from 2 to 5 years may also be observed[2]. However, recycling older supports to pretend an older appearance is a known modus operandi by forgers[3]. The possibility to detect post-1950 forged paintings based on the elevated ^{14}C content of the organic binder was already inferred in the 1970's but, at that time, required sampling of several hundred milligrams of material[4]. With the new era of accelerator mass spectrometry (AMS) instruments, the expansion of ^{14}C dating to art research was foreseen as the sample requirements were compared to the sample size routinely taken for material analysis[5]. Although Stulik and Donahue predicted in the late 90s the possibility to date the binding media in paint layers in the near future, it required almost two decades of technical development for this idea to be revisited. The advent of gas ion sources at the end of the 20th century coupled to AMS technology allowed an overall downscaling by six orders of magnitude, i.e. from grams to micrograms of carbon. Within oil paintings, using microsamples of paint, not only the natural organic binder was identified as carrying the potential to provide dating information[6], but also the lead white pigment[7]. These results show great promise for developing more differentiated strategies to be applied to a wider range of art objects allowing the ^{14}C dating technique to move away from dating the substrate only.

In the present study, the applicability of ^{14}C dating to both the canvas and the paint binder in three oil on canvas paintings will be discussed. Being unsigned and undated, the artworks bear no legitimate authorship. The central question is how well do the material ^{14}C ages compare with the period of activity of the attributed artists. Through these three case studies, a new insight to the origin of the objects is pursued while also highlighting the potential and limitations of ^{14}C dating artworks.

Objects of study

The artworks under study belong to a private art collector, who was interested in supporting new research routes for ^{14}C dating artworks and therefore offered to test the applicability and limitations of the ^{14}C method on some objects of his collection. Among the works of art made available was *Queen Maria Anna*, oil on canvas (56 x 72 cm), attributed to Diego Rodríguez de Silva y Velázquez (1599-1660), *Christ and the woman taken in adultery*, oil on canvas (153 x 98 cm), credited to Nicolas Poussin (1594-1665), and *Ritratto di Giovane Donna*, oil on canvas (38 x 61 cm), credited to be a work of Amedeo Modigliani (1884-1920) (fig. 1 a-c).

Table 1. Summary of the paint sample characterization including method, collected data and interpretation

Description	Method	Laboratory data	Interpretation
AM canvas	FTIR [cm^{-1}]	3343, 2896, 1650, 1432, 1365, 1311, 1164, 1111, 1064, 897	Cellulose
AM white	FTIR [cm^{-1}]	2920, 2850, 1739, 1515, 1240, 1166	Oil, lead stearate, saturated hydrocarbon
		3359, 1407, 1045, 839, 682	Basic lead white
	Raman [cm^{-1}]	1050	Lead white
	SEM/EDS	Pb, C, O	Lead white
		Al, Si, O	Kaolin
		Al, Si, O, S, Na	Ultramarine
DV canvas	FTIR [cm^{-1}]	3350, 2899, 1643, 1428, 1370, 1317, 1159, 1104, 1058, 897	Cellulose
DV brown	FTIR [cm^{-1}]	2925, 2852, 1708,	Oil (partially hydrolysed), small amount of saturated hydrocarbon
		1600, 1314	Oxalate
		1650, 1547	Protein
		1411, 876	Calcium carbonate
		3697, 3620, 1115, 1038, 1007, 913	Kaolin
		1160	Quartz
		2010, 1038	Bone black
	Raman [cm^{-1}]	253, 287, 344	Vermillion
		224, 295, 411	Iron oxide (Hematite)
NP yellow	FTIR [cm^{-1}]	2920, 2851, 1739, 1515, 1166	Oil, lead stearate, saturated hydrocarbon
		1406, 1043, 667	Lead white
		2920, 2850, 1514	Lead stearate
	Raman [cm^{-1}]	195, 128	Lead tin yellow
	SEM/EDS	Pb, Sn, O	Lead tin yellow
		Fe, O	Iron oxide
		Pb, C, O	Lead white

Sample selection, material characterization, preparation and AMS measurements

Sampling was conducted with the help of Dr. Jägers, who had previously examined and reported on the paintings' material and techniques. His analyses focused on the identification of the pigments and painting media present. Preliminary macroscopic observation revealed that all three paintings were varnished and in a very good state of preservation. Under UV light the retouches were easily made visible. Both the Velázquez and Modigliani artworks were sampled on the edge of the canvas, yielding primed pieces of canvas, i.e. textile substrate with preparatory paint layer. In contrast, as the Poussin object was relined, no canvas was sampled but only some paint material belonging to the pictorial layer.

The canvas fiber composition was characterized by Fourier-transform infrared spectroscopy (FTIR) and polarized light microscopy[8], where both the warp and weft thread were individually analyzed. The suitability of the sampled paint material, i.e. presence of inorganic pigments and absence of any carbon source other than the binder, followed an already established technical workflow[9]. In order to conduct a meaningful sampling of art objects, a broad understanding of the materials present is necessary. ^{14}C dating thus benefits from complementary analytical techniques, such as FTIR and Raman spectroscopy and, when necessary Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS[10]). The pigment characterization results are summarized in Table 1.

The canvas cuttings were first mechanically separated from the paint ground, cleaned by soxhlet[11] before the standard acid-base-acid (ABA) protocol. The paint samples were immersed in acetone for 15 minutes, then treated with 0.5 M HCl at 70°C for 2 hours.

All ^{14}C measurements were carried out on the Mini Carbon Dating System MICADAS[12]. Canvas and paint

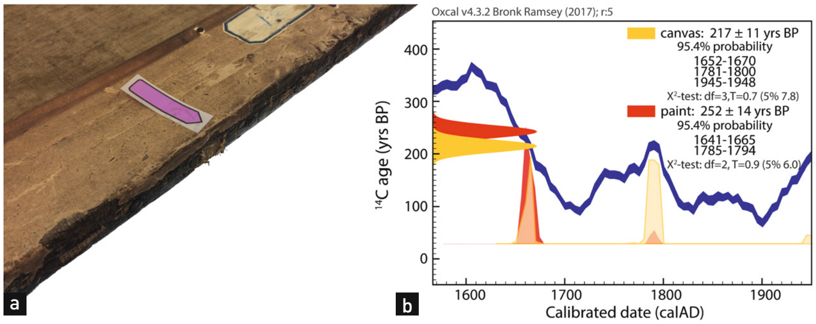

Fig. 2 a-b. Overview of the sampling location on the reverse of *Queen Maria Anna* portrait, where the purple arrow indicates the sample location (a), the agreement between canvas and binder dating is illustrated in the calibration plot (b). © L. Hendriks.

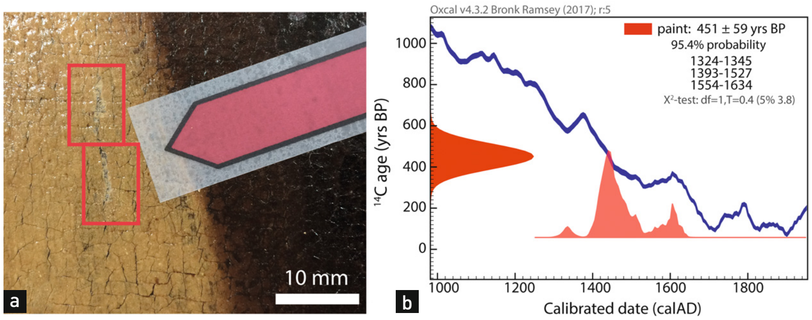

Fig. 3 a-b. The close-up photography (a) and calibration plot (b) are related to the *Christ and the woman taken in adultery* painting, illustrating the sampling of the yellow robe belonging to the figure on the far right of the picture and the respective dating results. © L. Hendriks.

material from the preparatory ground layer were measured as graphite (1 mg C), while the paint material collected from the pictorial layer (<300 µg) was measured as gas target via the coupling of an elemental analyser (EA) to the gas interface[13].

Results and discussion

Dating precision limited by the shape of the radiocarbon calibration curve

A precise dating of baroque, neoclassicism or modern art is often not possible due to the particular shape of the calibration curve between 1700 to 1950. As illustrated in the case of the *Queen Maria Anna* painting, calibration of the individual ^{14}C ages from the canvas result in a time window spanning the 16th to 19th century. Fortunately, the sampling location being at the edge of the canvas (fig. 2 a) allowed sampling of a large piece of material (50 mg) which enabled the measurement of several graphite replicates (n=4). The combined result of the uncalibrated measurements afforded a mean value of 217 ± 11 years before present (BP). The subsequent calibration of the measured canvas ^{14}C ages to the corresponding fibers' year of harvest, displayed in fig. 2 b, spans two time-windows, one covering the third quarter of the 17th century, while the other the last quarter of the 18th century.

The preparatory red ground layer was identified as a mixture of iron oxide, bone black[14], silicate and vermilion mixed in an oil tempera binding medium. The dating of the later yielded a mean value of 252 ± 14 yrs BP (n=3). Upon calibration, the data suggests that the organic material was harvested at the same time period as the canvas fiber material (fig. 2 b). While the first time-window correlates with the time frame of Diego Velázquez' activity (1599-1660), both time-windows are equally probable and the likelihood of a later production at the end of the 18th century cannot be excluded. Yet, the agreement between the canvas and organic binder ^{14}C age is compelling in proving the contemporary origin of both materials. The organic binder is a powerful dating proxy, which allows to dismiss any modern 20-21th century creation by possible canvas recycling[15]. This example puts forward the difficulties associated with dating specific artistic movements, owing to the multiple variations in the calibration curve between the period 1700-1950, also known as the Stradivarius Gap as a reminder of the limitations of the method[16].

Relined canvas preventing the dating of its support

In the event of a relined canvas, targeting the dating of the pictorial layer is a possible asset in providing a historical context as presented in the *Christ and the woman taken in adultery* painting. Following a homogenous ageing craquelé, two minutes paint samples were collected from the yellow robe of the figure on the far right of the picture (↑ 114.5 cm →15.3 cm). This particular sample location was chosen owing to identification of lead tin yellow type I, which is a lead tin oxide (Pb_2SnO_4), as well as lead white and iron oxide within an oily binder, and missing varnish in certain points. The sampled material amounted to 124 and 300 µg material, producing 28 and 11 µg C respectively (fig. 3 a).

After data processing[17], the two micro paint samples were dated 474 ± 69 yrs BP and 393 ± 109 yrs BP. In figure 3 b, the two individual ^{14}C measurements were combined, hereby yielding a mean value of 451 ± 59 yr BP. Upon calibration, the seeds, from which the oil was extracted, were harvested between the mid-14th to mid-17th century. These results correlate with the history of use of lead tin yellow. Its first appearance is reported as early as the 13th century, intensively used between the 15th to 17th century, before disappearing during the 18th century[18]. While the time-window does not contradict an attribution to Nicolas Poussin (1594-1665), it is still broad. This could be improved with better counting statistics, which would require more carbon and hence a larger sample. Nonetheless, it allows to exclude a modern creation during the 19th-21th century.

Modern art and the increased use of synthetic material

Dating of modern art objects is challenging, not only because of the particular shape of the calibration curve, but also due to the increasing use of synthetic material in both the canvas[19] and paint materials, questioning the suitability of the chosen material. As outlined in the *Ritratto di Giovane Donna* example, a good practice prior ^{14}C analysis is to first confirm the natural origin of the canvas fibers or binding media in the paint layer. Following a close match with the IR reference spectrum of cellulose[20], the canvas fibers were identified as cellulose based and further as a mixture of hemp, cotton, and linen with the help of the modified Herzog test[21] (fig. 4 b). Multiple replicates of the canvas (n=7) were ^{14}C dated, where the calibrated mean value 102 ± 10 yrs BP results in two intervals from 1694 to 1725, 1811 to 1871 and 1876 to 1917. Although, the latter is consistent with Modigliani's lifetime, complementary information brought through material analysis is needed to dismiss one or the other interval.

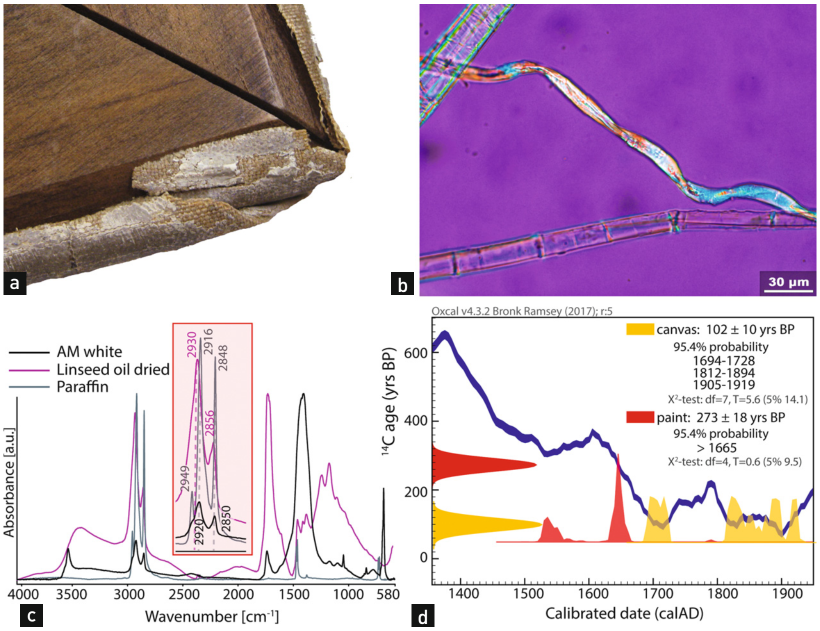

Fig. 4 a-d. Investigation of the object attributed to Amedeo Modigliani. a Sampled area of grounded canvas on the rear of the paintings; b. Polarized light microscopy image of the canvas threads, where the twisted fiber is cotton and the two others belong to the bast fibre type which were further differentiated as hemp and linen using the modified Herzog test (Haugan, Holst, 2013); c. FTIR spectra of the paint material (black) compared against those of aged linseed oil (pink) and paraffin (grey). A more detailed view focusing on the spectral region between 3200-2700 cm^{-1} is displayed (red box), where the band positions of the two CH_2 stretching oscillations in all three materials is indicated. The AM paint bands are the same as in paraffin and shifted compared to the oil bands; d. Calibration results of the canvas and paint. © L. Hendriks.

The additional dating of the binder was pursued since a large piece of canvas, covered with white ground material was sampled. The paint's composition was determined as bearing inorganic compounds (lead white, kaolin and traces of ultramarine) in an oil binder. As illustrated in figure 4 d, in comparison to the canvas, the paint is a hundred years older. Different sources of error were postulated, such as contamination, incomplete removal of the carbonate, but repeated measurements all conveyed the same result. The systematic observed offset hints to the presence of some synthetic material devoid of ^{14}C. A deeper look into the FTIR spectra (fig. 4 c) reveals a signal shift of the two νCH_2 signals relative to the characteristic oil bands (2930, 2856 cm^{-1}), which is specific to alkane chains. This can often be observed in paintings of classical modernism (1900-1939)[22] and is related to additives in the early commercial tube paints[23]. The additional shoulder at 2926 cm^{-1} further hints to a very thick wax coating. Thus, it is possible that a paraffin wax coating is the reason for the observed bias between canvas and binder ^{14}C ages. To confirm this hypothesis, a separation was pursued using direct temperature resolved mass spectrometry analysis (DTMS[24]). The analyzed paint sample displays retention peaks characteristic of the respective methylated ester form of fatty acids, which are related to the drying oil, but also higher linear alkane chains specific to synthetic waxes, which are undoubtedly the source of the ^{14}C contamination.

These results highlight, that although a paint sample is deemed suitable for ^{14}C dating, a critical evaluation of the resulting ^{14}C ages is imperative. Indeed, initially not identified, a second carbon source other than the organic binder biases the results. The contaminant was only later exposed with the help of complementary analytical methods, hereby emphasizing the necessity for a thorough and detailed characterization of all paint components prior to any ^{14}C measurements. FTIR is a powerful technique to fingerprint organic compounds, but reaches its limitations when confronted to mixtures with multiple components. With respect to the ^{14}C sample preparation, the isolation and analysis of the different carbon sources would be of extreme value, however no such protocol has yet been proposed and may be suggested as future routes of study.

Conclusion

In their pioneering work, Stulik and Donahue (1992) were convinced by the future role to be played by ^{14}C dating in art research: "(…) we believe that the methodology developed for radiocarbon dating of binding media in paint layers will bring a new dimension to current and future art historical and art conservation research". The interest in dating artworks it not solely linked to unmasking forgeries and answering authentication questions, where the dating of the natural organic binder eludes the issue of counterfeited artwork made with older painting supports, but also as part of art technological and provenance research.

By testing the applicability of dating the natural organic binder on an eclectic selection of artworks, this study shall contribute to a better understanding of how ^{14}C dating may be applied in the context of heritage science. While ^{14}C dating is without any doubt a powerful tool to help answering time related issues, it may not always play a decisive role as the precision and accuracy of the final calibrated calendar age is dependent of the sample's size, composition and the features of the calibration curve. While previous sampling limitations may now be reconsidered, ^{14}C dating requires the solid support of complementary analytical techniques to account for the complex nature of many artworks and ensure a reliable diagnosis of the procedure. With the understanding that each artwork is unique and represents inherent difficulties, it is crucial that all exogenous carbon sources are identified in order to treat the sample accordingly prior to ^{14}C analysis. Therefore, the need for close collaboration between scientists, conservators and art historians is imperative in the hope of developing an adapted and comprehensive ^{14}C dating strategy for future work in heritage science, as well as for interpretation of the data.

Acknowledgements

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Notes

1. Caforio *et al.*, 2014; Hendriks *et al.*, 2016.
2. Brock *et al.*, 2019.
3. Hendriks *et al.*, 2019a.
4. Keisch, Miller, 1972.
5. Stulik, Donahue, 1992.
6. Hendriks *et al.*, 2018, 2019b.
7. Similarly, to *in-situ* formed calcium carbonate in the dating of lime mortars, lead white incorporates the ^{14}C signature of the atmosphere during its production process, which is then stored in the pigment carbonate anion (Beck *et al.*, 2018, 2020; Hendriks *et al.*, 2019a, 2020; Messager *et al.*, 2020; Quarta *et al.*, 2020; Reiche *et al.*, 2021; Sá *et al.*, 2021).
8. The canvas fibers were dispersed in Meltmount TM resin (refractive index 1.62) and observed on a BH-2 light microscope (Olympus Europa Holding GmbH, Hamburg, Germany) with and without polarizer and red plate. The longitudinal thread features and fibrillar orientation behavior with respect to transmitted plane polarized light and cross-polarized light were observed and compared with known reference samples.
9. Hendriks *et al.*, 2018.
10. FTIR spectra of the samples pressed in a diamond cell were acquired on a Perkin Elmer system 2000 (Perkin Elmer, MA, USA) in transmission mode within a spectral range of 4000-580 cm^{-1} and accumulation of 32 scans per spectrum at a resolution of 4 cm^{-1}. Raman spectroscopy was performed on a Renishaw InVia dispersive Raman system, equipped with a Leica DM microscope and a 785 nm (diode-type), Renishaw HP NIR785 (300 mW) laser source (Renishaw, Gloucestershire, UK). The spectra were recorded using a laser power of 0.01-1 mW on sample, microscope objectives of 50x (NA 0.55) and 100x (NA 0.90) magnification, and a measurement time between 30 and 200 s. The energy dispersive spectroscopy analysis (EDS) were conducted on a Scanning electron microscope ZEISS EVO MA 10 (Oberkochen, Germany) equipped with EDS Thermo Noran System 7.
11. Bruhn *et al.*, 2001.
12. A compact accelerated mass spectrometer (AMS) system developed at the Laboratory of Ion Beam Analysis of ETH Zurich (Synal *et al.*, 2007) allows for the analysis of both graphite and gaseous samples. The calibration software OxCal v.4.3 (Bronk Ramsey, 1995) was used to convert the measured radiocarbon ages to calendar ages with the IntCal13 atmospheric calibration curve (Reimer *et al.*, 2013). In the event of replicates, a weighted mean was calculated using the R_Combine function in Oxcal. An automatic chi-square test allows to assess whether the association between the variables is statistically significant.
13. Ruff *et al.*, 2010.
14. A word of caution is to be added regarding the presence of bone black (see Table 1). This inorganic black pigment contains varying amounts of calcium phosphate, calcium carbonate and carbon, depending on the bone charring process. Here, no interference in the measured ^{14}C age of the organic binder was observed, despite this second carbon source. However, the burnt matter may not be contemporary to the organic binder, as shown in the work of Sá *et al.*, 2021, and thus calls for cautious evaluation of the data.
15. Hendriks *et al.*, 2019b.
16. Jull, 1998.
17. See constant contamination correction procedure as described in Welte *et al.*, 2018.
18. Eastaugh, 2008; Roy, 1993.
19. At the end of the 20th century, canvases were no longer solely produced from natural material but also from synthetic fibres, which being derived from petroleum-based materials are devoid of ^{14}C. Although this practice was rather limited, a canvas from the 20th century could potentially contain synthetic material, as illustrated by the work of Oriola *et al.*, 2014, who in a survey of 12 Dalí paintings identified the presence of synthetic fibres in two of the objects.
20. Garside, Wyeth, 2003.
21. Haugan, Holst, 2013.
22. Zumbühl, Gross, 2009.
23. Eibner (1909) writes about the development of oil colors, where he explains that the admixing of additives like wax, stearin, paraffin or ceresin to the oil came into use in order to create a stiffer medium in which the settling of the pigments was prevented as far as possible. At the same time, the buttery consistency required today was achieved.
24. The sample was methylated with MethPrepII and analyzed using a DSQ II mass spectrometer (Thermo Electron Corporation, Waltham, Massachusetts, U.S.)

with low electron volt ionization (16 eV), equipped with a Rh/Pt filament and undergoing 10 °C/s heating steps and covering a mass range of 45-1050 m/z.

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