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# Radiocarbon dating and chemical imaging of carbon black-based Paleolithic cave art in the Dordogne region (France)

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Affiliations are included on p. 7.

Edited by Mary Stiner, The University of Arizona, Tucson, AZ; received September 29, 2025; accepted January 22, 2026

Paleolithic parietal art in the Dordogne, Southwestern France, was known to present representations solely made with mineral coloring matters. We found a significant number of carbon black-based figures in the galleries of the Font-de-Gaume cave in Les Eyzies, Dordogne, Southern France [I. Reiche, Y. Coquinot, A. Trosseau, A. Maigret, *Sci. Rep.* 13, 22235 (2023)]. Further reflectance imaging spectroscopy allowed a precise non-invasive discrimination between manganese- and carbon-based blacks. Consequently, in the Dordogne region, direct dating of drawn or painted lines was unlocked. Dating parietal representations can prove challenging because of the small amount of matter and the possible contaminations by other carbon sources. The sampling was conducted for radiocarbon dating on two selected figures identified as being made with carbon black: the *Bison* figure HB15 (named by Breuil, today GPCarG-006), located on the left at the level of the *Carrefour* in the public area of the cave, as well as on the *Mask* (human or animal face, GL3D-009) on the right of the remote sector 3 of the lateral gallery. Slightly more recent than expected, the obtained dates are of 13461–13162 calBP for the *Bison*, and of 8993–8590 calBP (left eye), 15981–15121 calBP (upper lip), and 15297–14246 calBP (lower lip) for the *Mask*. Except for one date, these results represent the experimental confirmation of the Paleolithic age of cave art in the Font-de-Gaume cave. This study opens numerous perspectives for a more systematic dating of the parietal representations of the cavern and motivates further research of carbon black-based Paleolithic parietal art in the Dordogne region.

Paleolithic cave art | Font-de-Gaume cave | carbon black-based pigment | <sup>14</sup>C AMS dating | Reflectance imaging spectroscopy

A significant number of carbon black (C black)-based graphical entities was recently discovered in the parietal feature of the main galleries of the Font-de-Gaume cave, Les Eyzies, Dordogne, Southern France (1). Following this discovery, we received special permission to micro-sample two figures, a *Bison* numbered *HB15* by Abbé Henri Breuil (today *GPCarG-006*) at the *Carrefour* (crossing) of the main gallery and a *Mask* (*GL3D-009*) on the right wall of sector 3 in the lateral gallery. The microsamplings, imperceptible to the naked eye, were carried out on January 31st, 2024, and direct accelerator mass spectrometry (AMS) radiocarbon (<sup>14</sup>C) dating on the specimens was conducted thereafter. AMS <sup>14</sup>C dating was required due to the very low amount that can be sampled on cave paintings or parietal drawings, as already shown in other dating studies of Paleolithic sites such as the Chauvet cave, Ardèche, France (2).

The Font-de-Gaume cavern is situated in the Dordogne region, one of the richest areas in Western Europe in terms of decorated Paleolithic caves, which also includes the famous Lascaux cave (3, 4).

It is part of the UNESCO World heritage sites and the age of its ornamentation was estimated to 18,000 to 16,000 y (5) by stylistic observations. Contrary to the general assumption, members of our team recently discovered C black-based figures in this cavity. This discovery is not only significant for the cave but also represents a remarkable find for the entire region (1). Indeed, the caverns in this geographical area were previously known only to exhibit cave art made of engravings as well as drawings or paintings made with iron (Fe) and manganese (Mn) oxide-based coloring matters, which made direct <sup>14</sup>C dating impossible until this study (6, 7).

Numerous realistic mono-, bi-, and polychrome paintings, geometric motives (signs), as well as engravings of different animals constitute the parietal features of the Font-de-Gaume cave (Fig. 1A and SI Appendix, Fig. S1). As of today, nearly eight hundred graphical entities (N 800), including approximately 250 figurative representations (N 250, animals, humans, and masks), 260 geometrical signs (N 260)—including 40

## Significance

We provide the experimental confirmation of the Paleolithic age of cave art in the Font-de-Gaume cave (UNESCO World heritage site). Our team noninvasively imaged carbon black-based figures in the Font-de-Gaume cave thanks to Reflectance Imaging spectroscopy. This finding opened different perspectives for direct radiocarbon dating. Microsamplings were analyzed by means of accelerator mass spectrometry radiocarbon dating enabling accurate dating of minimal samples confirming the Paleolithic age of the cave art. This result represents a scientific breakthrough and a paradigm change with implications for the Paleolithic cave art in the Dordogne region and the broader field of prehistory.

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The authors declare no competing interest.

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of the cave's characteristic tectiforms (N 40)—and countless undetermined graphical palimpsests, have been identified in the ensemble of the galleries of the cavern, which has been partly open to the public since 1902 (8, 9). Font-de-Gaume is also called the “Bison Cave” because of the numerous representations of this animal (N 80) (10). Mammoths (more than N 40), deer (more than N 20), horses (more than N 50), and other animals (ibex rhinoceros, felines, a wolf...), as well as four negative hands have also been inventoried since 1910 (6). Starting in 2020, a research program “Unknown Font-de-Gaume” primarily focusing on the remote parts of the cave has been carried out by an interdisciplinary team supervised by Patrick Paillet (11). Opening up new scientific perspectives, the most comprehensive review of this cave's paintings in their natural and archaeological contexts is currently underway (12).

Naturalistic and other more schematic figures can be distinguished among the existing animal representations. Lifelike animal depictions are exclusively painted with bi- or polychromy, sometimes underlined with black lines. Engravings complete most of these painted figures. The natural tridimensionality of the cave walls was often explored for a more naturalist rendering. The designs were mainly done in black and red, with black to brown and red to yellow hues detected. Naturalistic *Bison* with simple black lines is also present.

Technical and stylistic observations at Font-de-Gaume by Abbé Henri Breuil and later by André Leroi-Gourhan suggested the presence of at least two creation steps in the Paleolithic depictions of this cavern. Similar indications of diachronic ornamentation have also been identified in other cave sites. Different creation steps of parietal decorations were highlighted in the French caves of Lascaux and Rouffignac, in the Dordogne region, and Pech-Merle, in the Lot region (13–21).

The first physico-chemical analyses, performed by Henri Moissan—a French chemist and Nobel prize winner—in 1902, indicated the presence of Fe- and Mn-oxides in coloring matter samples from the naturalistic figures of the Font-de-Gaume décor (22). Our previous *in situ* studies with noninvasive analytical techniques such as portable X-ray fluorescence (pXRF) analyses and micro-Raman spectroscopy confirmed prior findings on the nature of the Fe and Mn-based pigments used in the figurative representations in the naturalistic style (7, 23). Our latest research also revealed that some graphical entities, such as animals exhibiting a more schematic style, were drawn with a C black-based pigment, likely charcoal (1). Charcoal black-based representations were identified and differentiated from other C-based materials thanks to its characteristic broad scattering bands using Raman spectroscopy, like those around 1,400 and 1,600  $\text{cm}^{-1}$  (24). Nonetheless, it should be noted that combustion or smoke black exhibits very similar Raman features. Consequently, we will only speak of C black matter in this article to prevent overinterpretation. In addition, previous false color processed infrared imaging (FCIR) studies displayed a different contrast for black figures performed with a C black matter than those made with Mn-oxides. Combined with the Raman results, FCIR imaging data provide an extrapolation of the identified presence of C black in small areas to larger parts or to the whole figure (1). In this study, the previously developed *in situ* noninvasive methodology was extended with reflectance imaging spectroscopy, RIS, also called hyperspectral imaging. This imaging technique is very powerful as it allows mapping the distribution of chemical compounds (25–29). *In situ* chemical characterization methods confirm independently the reflectance imaging spectroscopy (RIS) data interpretation, making it a strong tool to image noninvasively the prehistoric depictions in the cave.

**Scientific Imaging Results.** In Font-de-Gaume, naturalistic and more schematic representations of animals are superimposed on each other at the level of the central crossing, the so-called *Carrefour*, between the main and the lateral galleries. Reflectance imaging spectroscopy was namely applied to study the panel of the *Carrefour* providing a complete picture of the different representations with their respective chemical compositions.

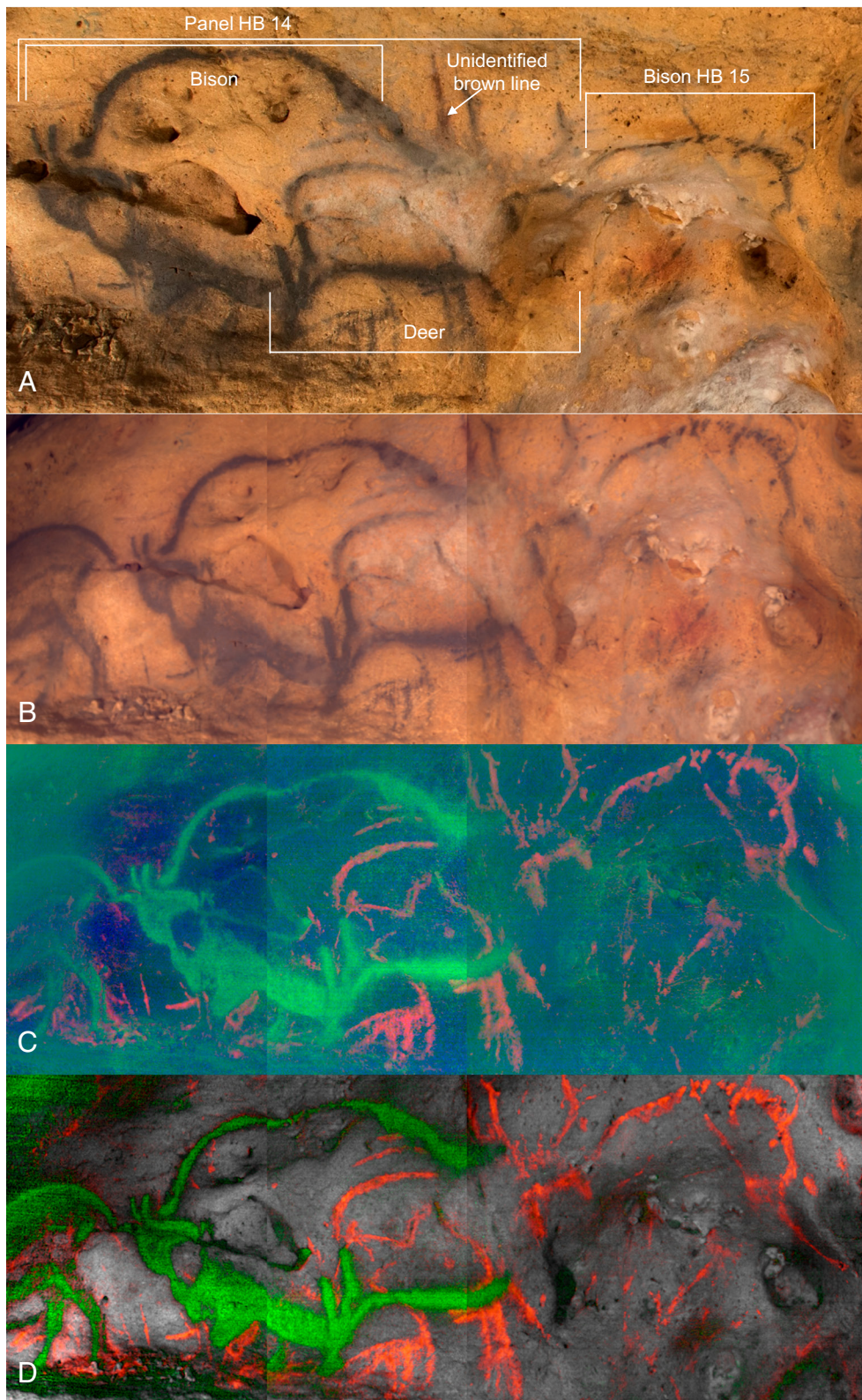
For the acquisition of the RIS data of a Specim IQ (30), a portable hyperspectral camera was used. The limited number of pixels of the Specim IQ requires the stitching of multiple datasets to obtain an overview over a larger area. While an overview image of the discussed area was obtained, slight stitching errors could not be avoided, as seen in Fig. 1 B–D. The acquired data were normalized and stitched datasets were explored by unsupervised machine learning (Principal Component Analysis, PCA and Independent Component Analysis, ICA). The results of an ICA factorization of the area (Fig. 1C) show that the two dark pigments used differ considerably in reflectance, indicating a difference in chemical identity, but the image contains a significant number of artifacts from the inhomogeneous illumination. Further, no spectral information can be directly derived from ICA results. However, based on the ICA results spectra representative for both dark pigments, the rock and the shadowed areas were manually extracted (*SI Appendix*, Fig. S2). Each pixel of the dataset was then expressed as a linear combination of four reference spectra and the obtained distribution images of Mn oxide (green) and C black-based pigments (red) and the underlying rock (white) were combined into an RGB image (Fig. 1D).

This clearly visualizes the presence of at least two kinds of black coloring matters, as previously demonstrated by the spectroscopic pXRF and Raman analyses (1). Further details of the noninvasive chemical characterization of the panels in the main gallery are found in Reiche et al. (1).

Our results show that the *Bison HB15* was entirely drawn with a C black-based matter, likely charcoal, without any other superimposed figure. This depiction, as well as the *Deer* of the panel *HB14*, are stylistically more schematic in comparison to the other naturalistic *Bison* of the panel *HB14* of the *Carrefour* panel. Interestingly, figures made with Mn-oxides and those made with C black are oriented in two opposite directions.

**Figure Selection for Radiocarbon Dating.** This series of figures comprises the naturalistic panel No. *HB14* (Breuil numbering) constituted of the Mn oxide-based *Bison* superimposed with the C black-based *Deer*, to which are added the C black-based *Bison HB15* (*GPCarG-006*) as well as some undetermined schematic remnants. This adjunction of figures made with different coloring matters makes this panel particularly interesting for a combined imaging and  $^{14}\text{C}$  dating study (Fig. 1).

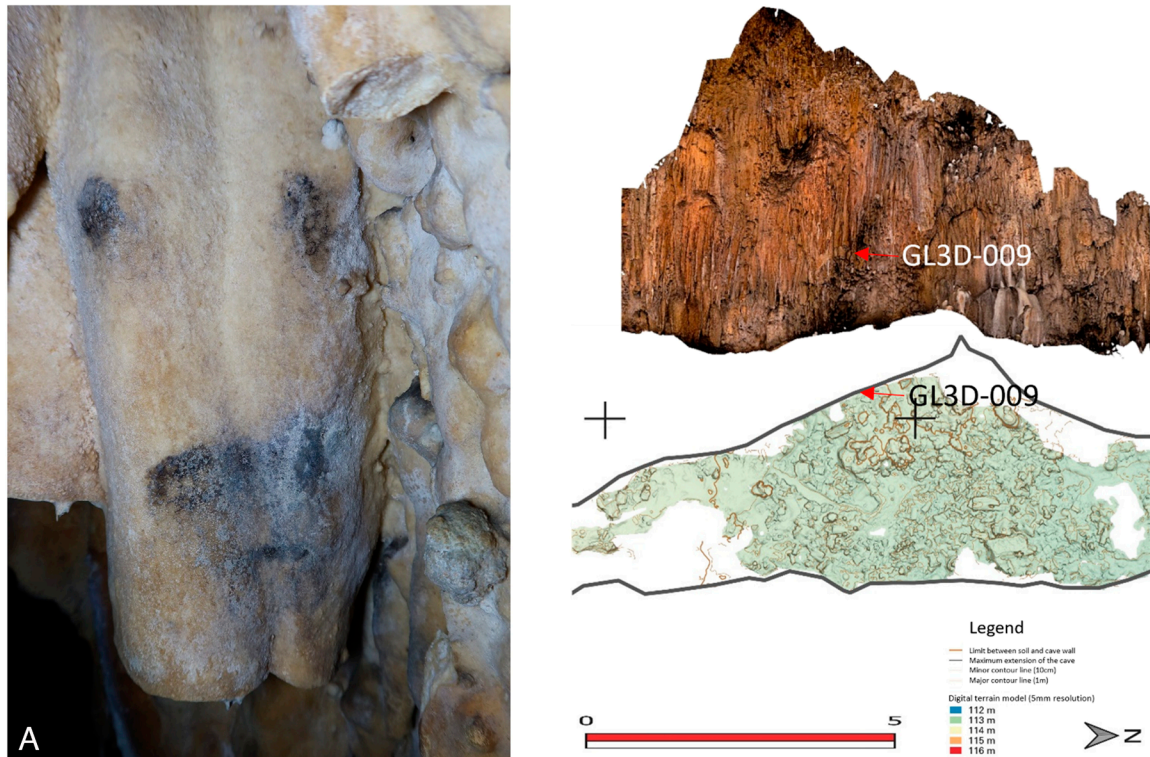
Other than in the main galleries, new figures have been recently discovered in the more remote sectors 2, 3, and 4 of the cave lateral gallery (10). *In situ* Raman spectroscopy gave a spectral response corresponding to C black in the *Mask GL3D-009* in sector 3 of the lateral gallery, even if the characteristic Raman signal was weak due to a high fluorescence background. This *Mask GL3D-009* is situated on the right-hand side of sector 3 of the lateral gallery (Fig. 2A). Manganese oxides were not found, but possible traces of combustion black were detected (Fig. 2B). However, this first analysis would require further *in situ* investigations, although access with analytical instruments is difficult due to the narrowness of the gallery. Nevertheless, the undeniable presence of C black in this depiction, priorly unknown in this sector, has made this *Mask* suitable for direct  $^{14}\text{C}$  dating.



**Fig. 1.** (A) Visible (VIS) photograph of the selected areas at the *Carrefour* including the panels no. *HB14*, a naturalistic *Deer* and *Bison*, and *HB15* (*GPCarG-006*), a more schematic *Bison* © Anne Maigret, C2RMF/CMN, modified by Ina Reiche, Lab-BC. (B) RGB image of the representations of the *Carrefour* at Font-de-Gaume cave calculated from RIS data, illustrating minor stitching artifacts and general distortion. (C) Overlay of ICA components representing the C black-based pigments (red) and Mn oxide-based ones (green) of the *Panel HB14* composed of a *Bison* and a *Deer* as well as the *Bison HB15*. (D) Corresponding RIS processed image indicating a different contrast between figures made with a C black-based black (in red, *Deer HB14* and *Bison HB15*) and made with Mn-oxides (in green, *Bison HB14*). The stitching and coregistration of multiple RIS data cubes left some minor distortion and artifacts. The brown color of the left line next to the antler of the *Deer HB14* in the VIS image can be explained by the presence of red iron oxides. Iron oxides cannot be represented here as the cave wall contains them in small amounts as well. © Matthias Alfeld, TU Delft. Image credit: Reprinted from ref. 1.

We asked for sampling two C black-based figures: the *Bison HB15* and the *Mask GL3D-009* for AMS  $^{14}\text{C}$  dating. The exceptional permissions for sampling allowed a pilot and feasibility study for dating the representations of the Font-de-Gaume cave. The selected figures in this pilot study come from a public and a remote area of the cave representing different conditions in terms of creation and possible contaminations induced by visitors.

**AMS  $^{14}\text{C}$  Results.** Four diminutive subsamples of black pigment from the right *Mask GL3D-009* in the lateral gallery and the *Bison HB15* (*GPCarG-006*) at the *Carrefour* were dated by means of AMS  $^{14}\text{C}$  dating (Fig. 3). Precise sampling locations are given in Table 1 with the  $^{14}\text{C}$  results. The samples were weighted before treatment and masses indicated in Table 1. These masses correspond to the mass of C and that of other materials such as



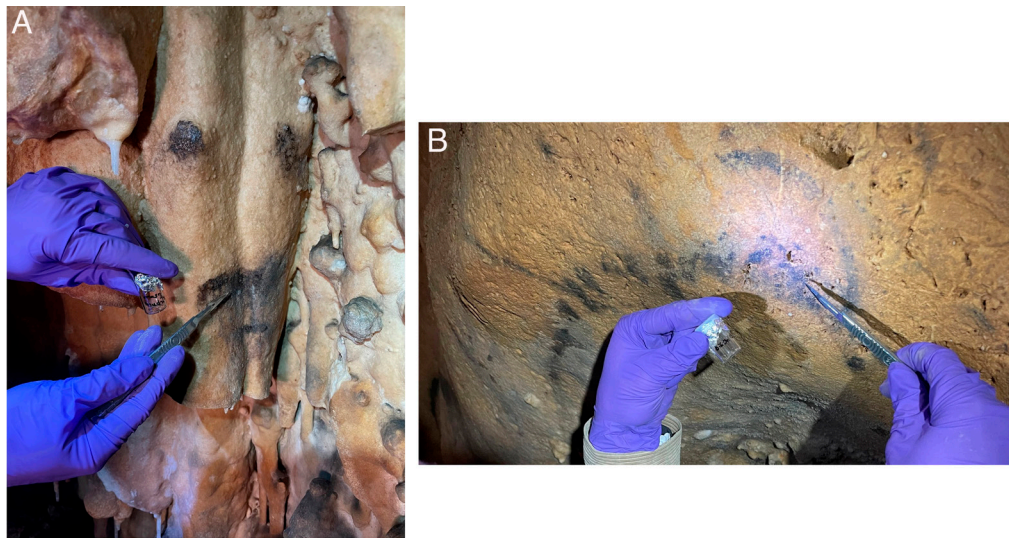
**Fig. 2.** (A) Left: Visible photograph of the *Mask GL3D-009* (© CMN) sampled for radiocarbon dating, and right: its position within sector 3 of the lateral gallery. (B) In situ Raman spectra of two black points performed on this *Mask* indicating the presence of carbon by the characteristic Raman bands at 1,385 and 1,585  $\text{cm}^{-1}$ .

small grains of the cave walls. The samples were washed with HCl to remove these calcium carbonate-based materials. After the treatment, only C black remains in the tube. The samples were not weighted again because of their small size. The risk was to lose the sample during transfer between the different tubes and vials.  $\delta^{13}\text{C}$  values were measured by AMS along with the  $^{14}\text{C}$  dating. The obtained  $\delta^{13}\text{C}$  values were between  $-20$  and  $-30$  ‰, in agreement with the expected values for charcoal. The humic fraction was expected to be too small to be dated.

The  $^{14}\text{C}$  ages obtained for the *Mask GL3D-009* range from  $7,910 \pm 70$  BP for the specimen taken from the left eye to

$12,980 \pm 150$  BP and  $12,570 \pm 130$  BP for the samples taken from the upper lip and lower lip, respectively. The uncertainties of more than 100 y are caused by the extremely low mass of carbon (0.04 and 0.06 mg). The  $^{14}\text{C}$  age obtained for the *Bison HB15 (GPCarG-006)* is  $11,420 \pm 80$  BP.

The  $^{14}\text{C}$  dates were calibrated using the IntCal20, the Northern Hemisphere Atmospheric calibration curve (31) in OxCal v.4.4 (32) (Fig. 4). The calibrated dates for the *Mask GL3D-009* are 8993–8590 calBP (left eye), 15981–15121 calBP (upper lip), and 15297–14246 calBP (lower lip). The calibrated date for the *Bison HB15 (GPCarG-006)* is 13461–13162 calBP.



**Fig. 3.** Figures dated by  $^{14}\text{C}$  and precise location of the samples: (A) *Mask GL3D-009* and (B) *Bison HB15 (GPCarG-006)* © CMN.

## Discussion

In the Dordogne region, France, prehistoric figures dating back to the Paleolithic era were dated successfully. The radiocarbon results confirm the Paleolithic age of two C black-based cave figures of Font-de-Gaume, except for the left eye of the *Mask*. It is important to point out, no figure made with C black had been found in the Dordogne prior to our studies. This is surprising considering the fact that C black, likely charcoal, was the most direct and obvious material used for drawing in caves in Paleolithic times, as it was omnipresent and easy to obtain. There was no obvious reason why it was not used by our prehistoric ancestors. This assumption is corroborated by the fact that most depictions in the Chauvet cave, Ardèche, France, dating to the Aurignacian period, were made with charcoal and could be dated using radiocarbon methodology (2).

The calibrated radiocarbon dates obtained are of 13461–13162 calBP for the *Bison HB15* and of 8993–8590 calBP (left eye), 15981–15121 calBP (upper lip), and 15297–14246 calBP (lower lip) for the *Mask*, corresponding to the Azilian and late Magdalenian periods, respectively. These results are slightly younger than the currently accepted date of the Font-de-Gaume ornamentation, rather placing them in the Middle Magdalenian period.

Possible explanations for the dates of both parietal representations differ because of the different locations of the figures in the cave.

The date range 8993–8590 calBP obtained for the eye of the *Mask GL3D-009* is clearly later than expected. This can be related to a later retouching, mixing modern carbon with the original prehistoric C black pigment. If this is the case and depending on

the time and the quantity of added material, the resulting obtained date can range from the date of the completion of the original figure to the date of retouching. Even though access to the extremely narrow cavities of sector 3 of the lateral galleries is difficult, modern graffiti, dating back to the 19th century/beginning of the 20th c., was found next to the masks, signaling how visitors entered deeply into these remote areas through time. Therefore, it cannot be ruled out that humans explored this area at different periods and, intentionally or not, modified this part of the figure after its creation.

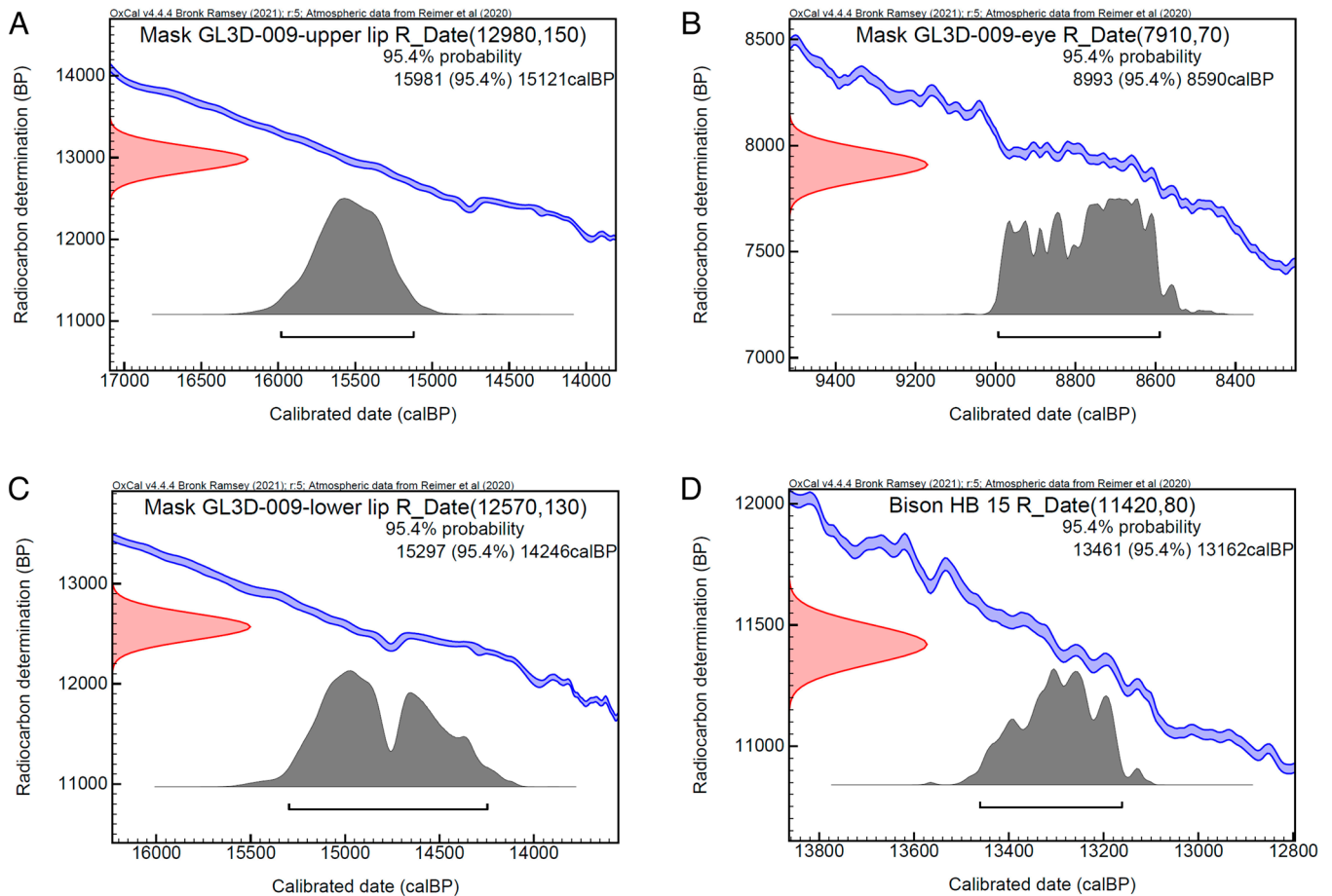
The two other date ranges (15981–15121 calBP and 15297–14246 calBP) obtained on the lips of the *Mask* are close to each other. They correspond to the late Magdalenian period and are close to the stylistic attribution.

A date range of 13461–13162 calBP was determined for the *Bison HB15*. This date range, corresponding to the Azilian period (Pleistocene–Holocene transition), is younger than expected, with very few other examples of figurative art of this transition epoch known.

This relatively late date for *Bison HB15* could be the result of a contamination by more recent C. An increase of only 5% of modern C would be sufficient to make this sample resulting 1,000 y younger. This assumption cannot be completely discounted as *Bison HB15* is located in the most frequented part of the cave, the *Carrefour*, where many past and present visitors have passed through. A picture taken before a restoration treatment of the *Bison HB15* shows an important presence of a C-containing material, removed around 1980 (*SI Appendix, Fig. S1*). The *Bison HB15* does not seem directly touched by the graffiti but is located very close by. As a result, the date distribution determined for *Bison*

**Table 1. Sample description and AMS  $^{14}\text{C}$  dating results obtained on the two graphical entities of Font-de-Gaume cave**

Figure name	Sampling location	LMC14 laboratory number (SacA)	Sample mass (mg)	Carbon mass after cleaning, chemical treatment, and combustion (mg)	$^{14}\text{C}$ age BP	$^{14}\text{C}$ calibrated dates calBP
<i>Mask GL3D-009</i>	Left eye	72,771	16.5	0.11	7,910 ± 70	8993–8590
<i>Mask GL3D-009</i>	Upper lip	72,772	1.3	0.04	12,980 ± 150	15981–15121
<i>Mask GL3D-009</i>	Lower lip	72,773	3.5	0.06	12,570 ± 130	15297–14246
<i>Bison HB15</i>	Head, between the horns	72,774	18.1	0.18	11,420 ± 80	13461–13162



**Fig. 4.**  $^{14}\text{C}$  calibrated dates for the three samples taken from the *Mask GL3D-009* (A–C) and one sample from the *Bison HB15* (GPCarG-006) (D).

*HB15* may have been slightly affected, making it difficult to conclude between an Azilian or Magdalenian attribution.

Two archaeological sites with layers corresponding to the Pleistocene–Holocene transition are reported: the rock shelter *Abri Murat*, in Rocamadour (Lot) (33) and the *Rocher de l'Impératrice*, a small rock-shelter located near *Plougastel-Daoulas* at the Western extremity of Brittany, France (34). Magdalenian/Azilian mobile objects with depictions transitioning from naturalistic to schematic representations were found. The more schematic style found in Azilian depictions finds agreement with that of the Font-de-Gaume *Bison HB15*. The *Mask* is also very schematic, with its style likely corresponding to the late Magdalenian. This might indicate that the more naturalistic animal representations are older than the schematic C-based figures. But we cannot give a definite answer here now because—in principle—it was assumed that the more schematic style was more ancient than the naturalistic style.

Nevertheless, our study represents a milestone for prehistory in the Dordogne, providing direct evidence of Paleolithic cave art in this region that is consistent with stylistic and contextual studies of these famous Paleolithic cave sites.

## Materials and Methods

**Photographic Imaging.** Photography under visible light (VIS) was performed with the use of two halogens, obtaining images in high definition (Nikon, 24 MPixel) of the figures for a detailed study of coloring matters at the scale of the panels and figures, and the identification of the areas to be analyzed successively (Fig. 1A). The locations for subsequent chemical analyses can be judiciously chosen, reducing the number of point analyses required per figure and allowing the extrapolation

of the results of the physico-chemical analyses to the whole figure or at least the remaining visible part of it (1).

**Reflectance Imaging Spectroscopy (RIS) and Data Treatment.** For the acquisition of the RIS data of a Specim IQ (30) portable hyperspectral camera was used. This internal pushbroom scanner allows for the acquisition of hyperspectral data cubes of  $512 \times 512$  pixels with 204 channels, covering the range from 400 nm to 1,000 nm. The walls were illuminated with two ARRILITE 70 Plus 240 V/800 W halogen lamps (ARRI AG, Munich, Germany). Each dataset was acquired twice and in every second, under identical illumination, a ColorChecker Passport Photo (2019 edition) was used as a white reference.

The acquisition of the RIS data were challenging as the cramped space inside the cave and the curved surface of the rock made a homogeneous illumination impossible. Thus, despite our best effort and the use of a white reference in each acquired dataset, slight variations in illumination are found in all datasets. Further, the limited number of pixels of the Specim IQ requires the stitching of multiple datasets to obtain an overview over a larger area, which is complicated by the slight pincushion distortion introduced by the lens of the Specim IQ.

These two effects give rise to the stitching errors and slight distortion observed in (Fig. 1B–D). The acquired data were normalized with in-house written scripts, and datasets belonging to the same scene were stitched with DataHandlerP (Version 1.2, <https://sourceforge.net/p/datahandlerp>). These stitched datasets were explored by unsupervised machine learning (Principal and Independent Component Analysis, PCA and ICA, resp.).

The results of an ICA factorization of the area discussed are shown in Fig. 1C. The results show that the two dark pigments used are clearly different, but the image contains a significant number of artifacts from the inhomogeneous illumination. Further, no spectral information can be directly derived from it.

In order to obtain a more legible representation of the data, an approach was followed that was previously used for the visualization of faint traces of antique polychromy on Greek architecture (25).

Based on the ICA results spectra representative for both pigments, the rock and the shadowed areas were manually extracted as shown in the *SI Appendix, Fig. S2*. Each pixel of the dataset was then expressed as a linear combination of these four reference spectra and the obtained distribution images of Mn and C-based pigments and the underlying rock were combined into the RGB image shown in *Fig. 1D*.

**Experimental Conditions of Portable Micro-Raman Spectroscopy.** The mobile Raman measuring device used was developed by Jobin-Yvon HORIBA and consists of components that can be easily moved during a measurement campaign. The device is equipped with a "Superhead SH 532" measuring head with a 50× Olympus "long working distance" objective and an Edge filter. In situ Raman measurements require an arrangement with high flexibility and high stability at the same time. The head is mounted on a stable tripod with one translation axis (forward and backward) and three rotational axes. Long working distances—focal distance of 5 mm—guarantee the safety of the cave wall and its depictions. The measuring head is connected to an air-cooled Nd:YAG laser operating at 532 nm, providing a maximum power of ca. 100 mW to the spectrograph via a 5 m long, flexible fiber optic fiber. The Raman device is mounted with the HE 532 spectrometers from Jobin-Yvon HORIBA. A Peltier-cooled CCD detector (fixed grating 1,800 lines/mm; fixed wavenumber from 150 to 3,200  $\text{cm}^{-1}$ ; spectral resolution of ca. 3  $\text{cm}^{-1}$ ) was used for the identification of the C-based coloring matter. The integration time during measurements ranged between 1 s and 6 s with 10 to 30 accumulations. The laser power on the sample was controlled by decreasing the power of the laser with a potentiometer. A laser power between 0.4 and 5 mW was used to ensure no risk of pigment transformation. The analyzed area of coloring matter with the 50× objective is of ca. 10 × 10  $\mu\text{m}^2$  (*SI Appendix, Fig. S5*).

**Raman Spectrum Treatment Procedure.** The spectra were evaluated with the LabSpec 5<sup>®</sup> software to obtain the characteristic Raman shift. Two types of treatment have been applied to Raman spectra. The first, applied systematically to all spectra, is the mathematical correction of artifacts due to the Edge filter. Edge filters display a nonlinear transmission response, leading to distinctive ripple patterns in the spectra. To correct this, a simple mathematical procedure can be implemented. It involves recording the spectrum of white light with and then without the Edge filter. The ratio between these two spectra forms the correction factor. Then, it is necessary to multiply this correction factor by the raw spectrum of the sample showing the oscillations. An additional baseline subtraction step ensures that only vibrational bands are present. However, this correction requires access to the Edge filter to record the spectrum of the white light without it; and unfortunately, this is not always the case with portable Raman spectrometers.

The second treatment is not systematically applied of all the spectra. It consists in the baseline subtraction for all spectra or for the ROI 800 to 2,000  $\text{cm}^{-1}$ .

Different C-based references were studied as described in ref. 1 and make it possible to distinguish charcoal from other C-based compounds.

### Procedure for Sampling and AMS Radiocarbon (<sup>14</sup>C) Dating.

**Microsampling for AMS <sup>14</sup>C dating.** Permissions were granted from French authorities and especially the *Centre des Monuments Nationaux* to sample very small amounts of black matter from the right *Mask GL3D-009* in the lateral gallery and the *Bison HB15 (GPCarG-006)* at the Carrefour for radiocarbon dating using <sup>14</sup>C AMS. The sampling, sample preparation, and the dating procedure method were optimized to be as least-invasive and invisible as possible and allow robust dating with minute amounts of C-based material—from a few tens or two hundred micrograms. Four diminutive subsamples of black pigment were taken from the two figures as shown in *Fig. 3*. The sampling spots are invisible by the naked eye.

Sampling was carried out using clean single-use scalpels. Samples were first collected in individual aluminum foils, then stored in glass vials that had been previously chemically and thermally decontaminated (*SI Appendix, Fig. S6*).

**Sample treatment for AMS <sup>14</sup>C dating.** Samples SacA 72771 (*Mask GL3D-009*, left eye) and SacA 72774 (*Bison HB15*, head) underwent ABA (acid–base–acid) pretreatment at room temperature, as follows: HCl (0.5 M, 1 h)/NaOH (0.1 M, 1 h)/HCl (0.5 M, 1 h). Due to their very low mass, the samples SacA 72772 (*Mask GL3D-009*, upper lip) and SacA 72773 (*Mask GL3D-009*, lower lip) were only HCl washed. Between each treatment, the samples were rinsed with deionized water (Millipore® reverse osmosis water, COT < 5 ppb) until a neutral pH was reached. After drying, the samples were combusted in the presence of CuO and Ag at 850 °C for 5 h. The resulting CO<sub>2</sub> was purified and cryogenically collected into a tube through a vacuum line. Graphite targets were produced by reduction of CO<sub>2</sub> by hydrogen over an iron catalyst, following the reaction described by Vogel et al. (35).

Samples were accelerator mass spectrometry (AMS) <sup>14</sup>C dated using the ARTEMIS facility at the LMC14 laboratory (36). A specific procedure for very low mass samples was applied, using standards of similar mass for normalization and control (37, 38).

**Data, Materials, and Software Availability.** Study data are included in the article and/or *SI Appendix*.

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