U-Series Dating of Paleolithic Art in 11 Caves in Spain

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Paleolithic cave art is an exceptional archive of early human symbolic behavior, but because obtaining reliable dates has been difficult, its chronology is still poorly understood after more than a century of study. We present uranium-series disequilibrium dates of calcite deposits overlying or underlying art found in 11 caves, including the United Nations Educational, Scientific, and Cultural Organization (UNESCO) World Heritage sites of Altamira, El Castillo, and Tito Bustillo, Spain. The results demonstrate that the tradition of decorating caves extends back at least to the Early Aurignacian period, with minimum ages of 40.8 thousand years for a red disk, 37.3 thousand years for a hand stencil, and 35.6 thousand years for a claviform-like symbol. These minimum ages reveal either that cave art was a part of the cultural repertoire of the first anatomically modern humans in Europe or that perhaps Neandertals also engaged in painting caves.

European Upper Paleolithic cave painting and engraving are among some of the earliest examples of art and human symbolic behavior, although there is considerable uncertainty in when they began and how styles and practices developed. Accurate dating would help determine whether they arrived with the earliest populations of anatomically modern humans by 35 to 40 thousand years ago, were a byproduct of their interaction with Neandertals, or developed later (*1*–*4*). Distinct phases are recognized in the art, based on technique, theme, style, and superimposition (*5*), but it is unclear whether these overlapped or evolved. Engravings and, in many cases, paintings lack organic pigments or binders suitable for accelerator mass spectrometry radiocarbon dating (*6*). Where suitable material exists (e.g., charcoal pigments), only small samples can be dated so as to minimize damage to the art, magnifying the effects of contamination and resulting in larger uncertainties. Discrepancies between multiple ^{14}C determinations on a single painted motif have been common, as are discrepancies between the dates of different chemical (e.g., humic/humin) fractions of the same sample (*7*).

We used uranium-series disequilibrium to date the formation of thin calcite flowstone growths that formed on the surfaces of paintings and engravings in 11 caves in Asturias and Cantabria, northwestern Spain. This approach circumvents the problems related with radiocarbon dating (*6*) and yields minimum ages for the art. In some cases where paint has been applied atop a flowstone or a flowstone has been engraved, maximum ages can also be obtained (*8*). Uranium-series isotopes can be measured in samples as small as 10 mg (*9*, *10*), which makes it possible to acquire samples whose stratigraphic relationship with the art is robust.

Results

We obtained 50 calcite samples that overlay paintings or engravings from the 11 cave sites in Asturias and Cantabria in northwest Spain (Fig. 1). Samples of between 10 and 150 mg were extracted by scraping with a blade or with an electric drill. We sampled calcite covering a variety of art and representing a range of styles. The samples were processed and U-series isotopes measured by using the method of Hoffmann *et al.* (*9*–*11*). Where sampling allowed a second aliquot to be taken, we tested the integrity of the calcite by comparing the dates of the upper layers of the calcite to those closer to the painting. In all cases, the date from the deeper sample was older, supporting the reliability of our method (*11*).

Our U-series ages ranged from 0.164 to 40.8 ky [corresponding to radiocarbon ages of near modern to 35,500 radiocarbon years before the present (^{14}C yr B.P.)]. Figure 2 shows calculated uranium series dates, from calcite on top of paintings, arranged in ascending order (also table S1). A painting cannot be younger than the calcite that formed on top of it, but there is an unknown delay between the execution of the painting and the formation of the calcite, so we present the data as the cumulative proportion, p, of paintings we have dated that cannot be younger than the date, T (Fig. 2 and table S1).

For context in discussing the ages of the paintings, the earliest reported ^{14}C date for the Proto-Aurignacian culture in northern Spain, assumed to represent the arrival of *Homo sapiens*, is from the site of Morin at 36,590 ± 770 ^{14}C yr B.P., yielding (*12*) a 2-σ calibrated age of 40,037 to 42,778 calendar years before the present (cal yr B.P.). This has been thought to be followed by the Aurignacian I at about 40,000 cal yr B.P. and the Aurignacian II culture at about 37,000 cal yr B.P. (*13*). In France and Iberia, the latest Aurignacian dates from 37,000 to 34,500 cal yr B.P. (*14*). In Cantabria, the latest Aurignacian is possibly represented at Cuco and dated to 30,020 ± 160 ^{14}C yr B.P. (34,490 to 35,032 cal yr B.P.) (*15*). The earliest Gravettian levels in northern Spain are around 27,400 ^{14}C yr B.P. at Antoliñako and Almada; the most precise age is from Antoliñako at 27,390 ± 320 ^{14}C yr B.P. or 31,145 to 32,487 cal yr B.P. (*16*). The latest Gravettian is represented by a date of 20,124 ± 340 ^{14}C yr B.P. (23,275 to 24,975 cal yr B.P.), again from Morin (*16*), which is within error of the earliest date on Solutrean levels from La Riera (20,970 ± 620 ^{14}C yr B.P., 23,578 to 26,921 cal yr B.P.). In light of other ages from southwest Europe (*17*, *18*), the

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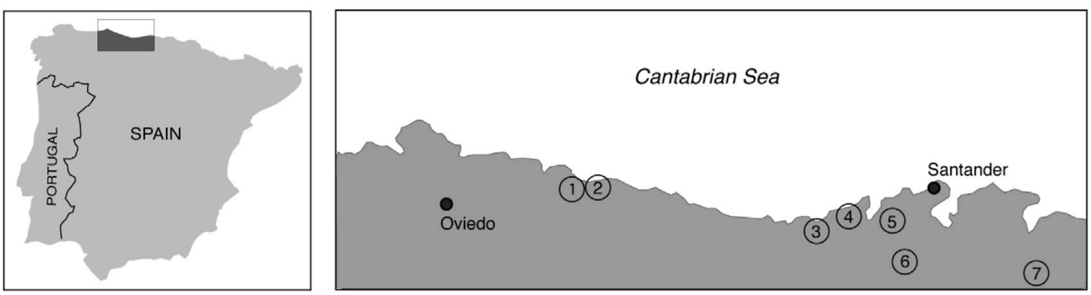

Fig. 1. Locations of the caves sampled: 1, Pedroses; 2, Tito Bustillo; 3, Las Aguas; 4, Altamira; 5, Santiàn and El Pendo; 6, El Castillo, La Pasiega, and Las Chimeneas; 7, Covalanas and La Haza.

latter date is a more reliable indicator of the timing of the Gravettian-Solutrean transition in northern Spain.

Nearly 20% of our dates on cave paintings fall into pre-Magdalenian times (i.e., before 21,000 cal yr B.P.), and of these four are pre-Gravettian. This distribution is not meant to represent relative intensity of artistic activity over time because of sampling bias, including those caused by cave settings and the influence of climate on calcite growth (*19*), but the dates indicate that early painting was not a one-off activity. Below and in Table 1 and Fig. 3, we focus on several of the more interesting (pre-Magdalenian) dates.

Altamira. Altamira cave, on the northern coast of Spain, contains numerous paintings, including of human hands and animals. The chronology of the art has been debated since its discovery, particularly since Breuil developed a scheme based on the superimpositions of several paintings (*20*, *21*). Although there is general agreement that several phases are recognizable in the cave's 10 main decorated zones, these have been suggested to span either a relatively short period of time that corresponds broadly to the cave's known archeology—that is, the Solutrean and the Magdalenian, Leroi-Gourhan's styles III and IV (*22*, *23*)—or considerably longer (*21*). We obtained a minimum age of 22.0 thousand years (ky) for the red dot outline horse on the ceiling of the polychrome chamber (O-53); thus, it is at least Solutrean in age. A second minimum age of 35.6 ky was obtained for the large claviform-like symbol (O-50) in the

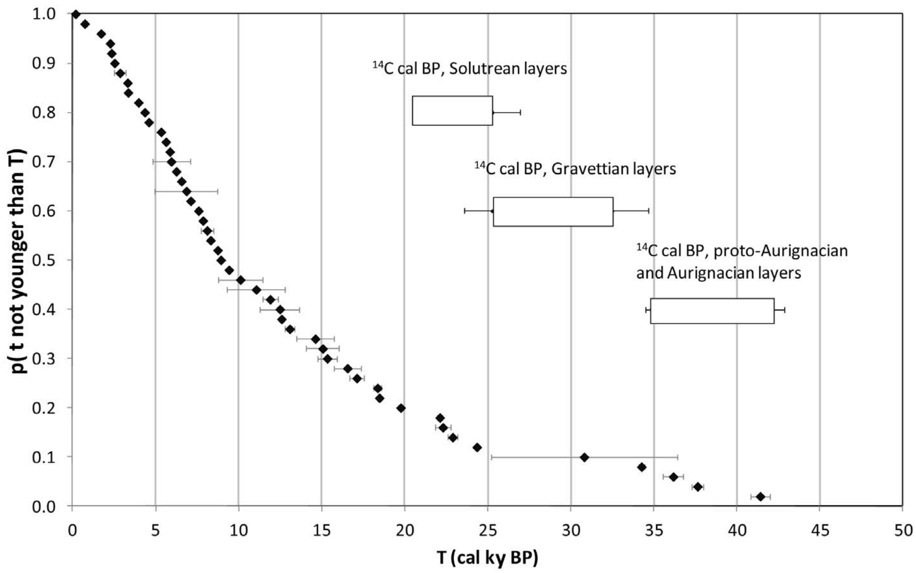

Fig. 2. U-series ages representing minimum ages for the cave art that we have sampled. Also shown is the pre-Magdalanian radiocarbon chronology from excavated cultural horizons in northern Spain (with arbitrary *y*-axis offsets for clarity).

Table 1. Results of U-series disequilibrium dating for samples mentioned in the text. All isotopic ratios are activity ratios; errors are at 2σ. Ages are corrected for detritus by using an assumed $^{232}Th/^{238}U$ activity of 1.250 ± 0.625 and $^{230}Th/^{238}U$ and $^{234}U/^{238}U$ at equilibrium, except age marked with an asterisk, which is corrected by using measured values on insoluble residue $^{230}Th/^{232}Th$ = 0.8561 ± 0.0039, and age marked with a dagger, which is corrected by using measured values on insoluble residue $^{230}Th/^{232}Th$ = 0.9390 ± 0.0077.

Sample BIG-UTh-	Site	Description	$^{230}Th/^{238}U$	$^{234}U/^{238}U$	$^{230}Th/^{232}Th$	Uncorrected age (ky)	Corrected age (ky)
			Minimum ages				
O-53	Altamira	Overlays red spotted outline horse of *Techo de los Polícromos* chamber	0.2884 ± 0.0013	1.5471 ± 0.0026	107.07 ± 0.20	22.26 ± 0.11	22.11 ± 0.13
O-80	El Castillo	Overlays black outline drawing of indeterminate animal of corridor of *Techo de las Manos*	0.7879 ± 0.0047	3.9828 ± 0.0073	30.01 ± 0.15	23.43 ± 0.16	22.88 ± 0.27
O-58	El Castillo	Overlays red stippled negative hand stencil of *Techo de las Manos*	0.5272 ± 0.0020	2.5774 ± 0.0049	222.70 ± 0.49	24.42 ± 0.11	24.34 ± 0.12
O-21	Tito Bustillo	Red pigment associated with anthropomorphic figure of *Galería de los Antropomorfos*	0.6252 ± 0.0031	1.8038 ± 0.0037	2.17 ± 0.01	44.94 ± 0.29	30.8 ± 5.6 29.65 ± 0.55*
O-69	El Castillo	Large red disk of *Galería de los Discos*	0.7512 ± 0.0029	2.7072 ± 0.0051	788.2 ± 5.5	34.28 ± 0.17	34.25 ± 0.17
O-50	Altamira	Large red claviform-like symbol of *Techo de los Polícromos*	0.4933 ± 0.0024	1.6594 ± 0.0030	17.473 ± 0.068	37.60 ± 0.23	36.16 ± 0.61
O-82	El Castillo	Sample overlays red negative hand stencil, and underlies yellow outline bison of *Panel de las Manos*	0.5112 ± 0.0029	1.6970 ± 0.0035	48.81 ± 0.49	38.15 ± 0.27	37.63 ± 0.34
O-83	El Castillo	Overlays large red stippled disk of *Panel de las Manos*	0.3573 ± 0.0022	1.1048 ± 0.0020	28.64 ± 0.29	42.38 ± 0.33	41.40 ± 0.57
			Maximum ages				
O-87	El Castillo	Underlies large red disk of *Galería de los Discos* (same panel as O-69)	0.7969 ± 0.0038	2.7432 ± 0.0051	61.24 ± 0.61	36.11 ± 0.21	35.72 ± 0.26
O-48	Tito Bustillo	Underlies red anthropomorph figure of *Galería de los Antropomorfos* (see also O-21)	0.5281 ± 0.0038	1.6895 ± 0.0042	7.260 ± 0.047	39.85 ± 0.36	36.2 ± 1.5 35.54 ± 0.39†

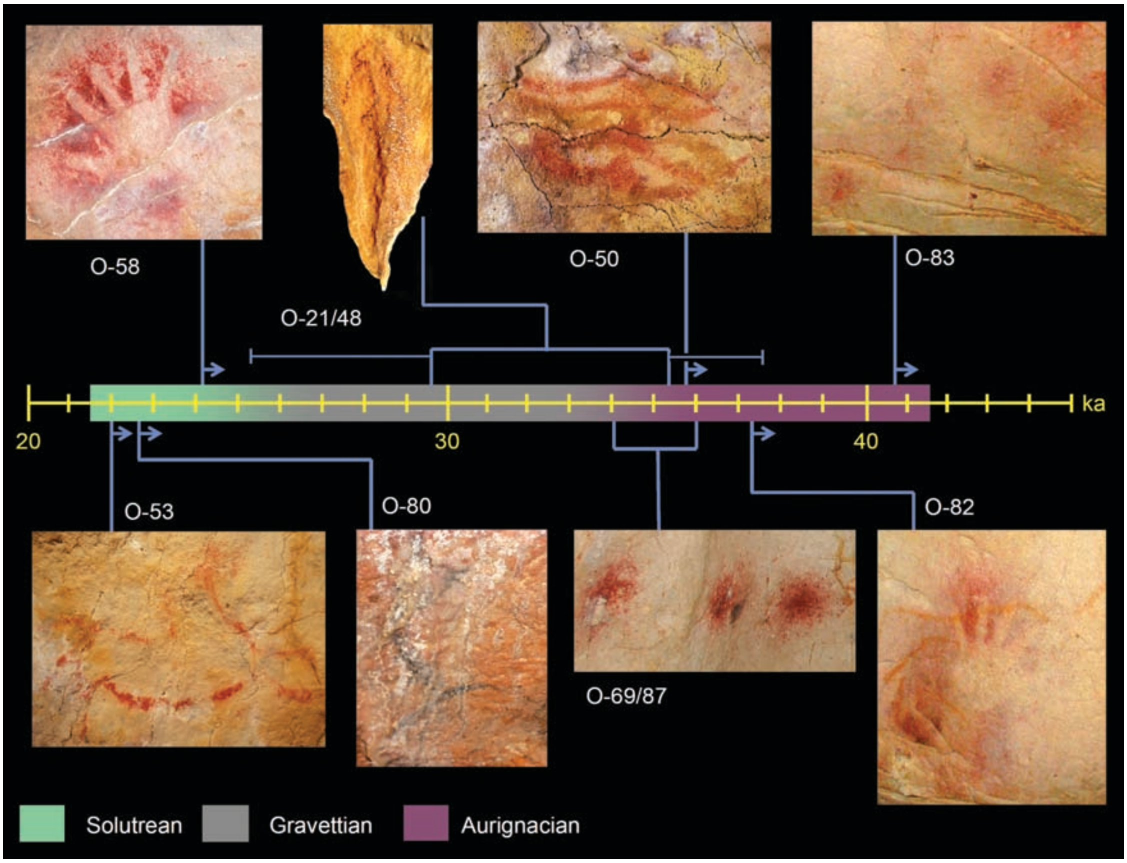

Fig. 3. A time line of the cave art dated. A single arrow represents a minimum age, but, where two dates are indicated, both maximum and minimum ages have been obtained. The error bars for O-21 reflect the variation resulting from the two different methods of detrital correction (*11*). Larger versions of these images showing sample locations are available in the supplementary materials, figs. S2 to S12.

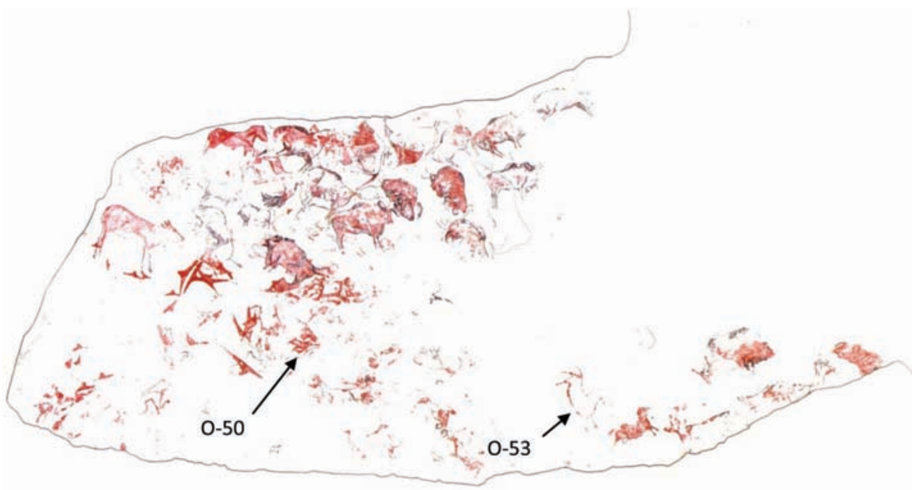

Fig. 4. The *Techo de los Polícromos*, Altamira Cave, showing the red spotted outline horse (sample O-53) and the larger red claviform-like symbol (sample O-50). [Tracing credit: National Museum and Research Centre of Altamira/Pedro Saura]

famous *Techo de los Polícromos* (Fig. 4); thus, it must be considerably older and at least Aurignacian in age. The previous chronological schemes all placed the panel's polychrome images later, in the Magdalenian (*5*). Our date thus indicates earlier use of the cave and support, and may extend, the long chronology. Although a few small claviforms on the same panel are superimposed on the polychromes and thus were painted afterward, our result for the larger version of the sign confirms Breuil's suggestion that red claviforms (or claviform-like symbols) originated before the Solutrean and probably in the Aurignacian and had a long chronological currency (*24*).

El Castillo. The caves of El Castillo, along the Pas river in northern Spain, also contain more than 100 images in multiple chambers. We obtained an age of >22.6 ky (O-80) for the black outline drawing of an indeterminate animal, which demonstrates that it was painted at least during the Solutrean. Traditional chronological schemes attribute most of the black animal figures to Magdalenian times (*25*) as a succession to the earlier red figures. This result suggests an earlier chronology for at least some of the black figures.

We also dated calcite overlying one red disk in the *Corredor de los Puntos* (fig. S7) and underneath another one, providing a minimum age of 34.1 ky (O-69) and a maximum age of 36.0 ky (O-87). Given the homogeneity in technique and location of the various large disks, it seems reasonable to assume they represent a single episode of painting. If so, the dates constrain the paintings to the latest part of the Aurignacian.

Hand stencils (O-58 and -82) are found in numerous caves in France and Spain. They are thought to have been made by blowing pigment onto the hand placed against the cave wall. They are usually assumed to be mainly or exclusively Mid Upper Paleolithic (Gravettian) in age, and, where available, direct radiocarbon measurements support this notion (ages range from ~29,000 to 22,000 ^{14}C yr B.P. for paintings at Gargas, Cosquer, Labattut, Fuente de Salin, and Paglicci) (*26–28*). We dated two hand stencils at El Castillo. One date of >24.2 ka for O-58, close to the Solutrean/Gravettian boundary, is consistent with the stylistic attribution of hand stencils to the Gravettian. But the other date from a hand stencil from the *Panel de las Manos* (O-82) is older,

>37.3 ka, and from the Aurignacian period or earlier. This date considerably increases the antiquity of this motif and implies that depictions of the human hand were among the oldest art known from Europe. One of several large red disks (O-83) nearby, also made by using a blowing technique, has a minimum age of 40.8 ky, supporting this interpretation. Because the disk and hand stencil are in the same panel (Fig. 5), it is possible that the older age of 40.8 ky is the minimum age of the entire composition, including rectangular and oval signs, about 40 hand stencils, and dozens of large disks, indicating intense artistic activity in pre-Gravettian times.

Tito Bustillo. The *Galeria de los Antropomorfos* in the cave of Tito Bustillo (Ribadesella) contains a scarf stalactite, about 3 m above the present ground surface, painted on two sides with two anthropomorphic figures and red pigment along the vertices of the stalactite. We dated calcite on top of this red pigment, providing minimum ages with two different methods of detrital correction (*11*) of 29.6 and 25.2 ky, and a sample drilled into a recent break, providing maximum ages of 35.5 and 37.7 ky, (samples O-21 and -48). These results put the possible age of the painting from the Gravettian (either early or late) to the Late Aurignacian. Excavation in the *Galería de los Antropomorfos* yielded charcoal radiocarbon dated to 32,990 ± 450 ^{14}C yr B.P. (38,729 to 36,665 cal yr B.P.) (*29*) associated with a short-lived and nondomestic human occupation as far back as the Aurignacian, represented by pigment, crushed bones, and deliberately selected flat stones. Our result confirms that this cave hosts a long artistic tradition. These results may imply an old age for early paintings that are partly covered in the *Panel de los Polícromos*, elsewhere in the cave, which is thought to have been painted in the Magdalenian (*7*, *29*).

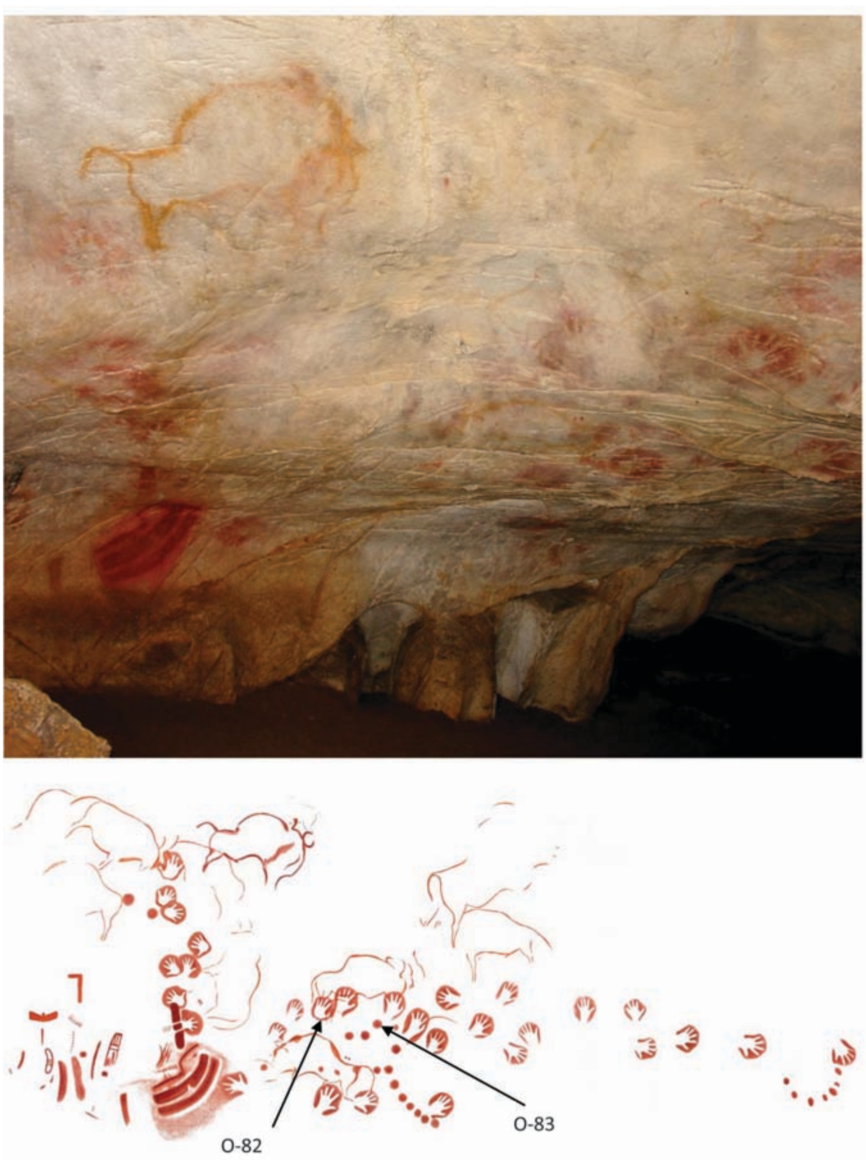

Fig. 5. The *Panel de las Manos*, El Castillo Cave, showing the location of samples O-82 overlaying a negative hand stencil, and O-83 overlaying a large red stippled disk. The tracing is taken from (*35*).

Discussion

Our dates show that artistic activity began at least in the Aurignacian period, in two distinct caves, and in one case at least as far back as 40.8 ka. The large red disk from El Castillo (O-83) currently represents the earliest dated example of European cave art. Its age is ~4000 years earlier than the claimed age of the art at Grotte Chauvet, France. The oldest radiocarbon date there is 32,410 ± 720 ^{14}C yr BP (35,300 to 38,827 cal yr B.P.), although others cluster around 35,000 cal yr B.P. (*30*, *31*).

Pre-Gravettian cave painting should be evident elsewhere in Europe. Blocks presumed to be a former cave wall, with red pigment (one interpreted as an anthropomorphic figure), have been found in Aurignacian layers in Fumane Cave, Italy (*32*), and in several rockshelters of the Vezere River, Dordogne (*33*). The pre-Gravettian signs (large dots, disks, and the claviform-like symbol) and hand stencils that we dated are similar to many found in other caves across Europe, although use of particular symbols may differ regionally (*34*). The apparent lack of further pre-Gravettian examples elsewhere in Europe is more likely the result of targeting charcoal-based black pigments with radiocarbon dating and the resulting ambiguities than a genuine absence of pre-Gravettian images.

Our results are consistent with the notion that there was a gradual increase in technological and graphic complexity over time, as well as a gradual increase in figurative images. Our earliest dates (pre-Gravettian) are for art that is nonfigurative and monochrome (red), supporting the notion that the earliest expression of art in Western Europe was less concerned with animal depictions and characterized by red dots, disks, lines, and hand stencils. If the earliest cave paintings appeared in the region shortly before 40.8 ka, this would, assuming that the Proto-Aurignacian cultural complex was made exclusively by *Homo sapiens*, support the notion that cave art coincided with their arrival in western Europe ~41.5 ka and that the exploration and decorating of caves was part of their cultural package. However, because the 40.8-ky date for the disk is a minimum age, it cannot be ruled out that the earliest paintings were symbolic expressions of the Neandertals, which were present in Cantabrian Spain until at least 42 ka (*13*, *15*).

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Supplementary Materials
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Materials and Methods
Figs. S1 to S12
Table S1
References (*35–39*)

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Spin-Orbit Echo

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Preserving and controlling the quantum information content of spins is a central challenge of spintronics. In solids, the relativistic spin-orbit interaction (SOI) leads to a finite spin lifetime. Here, we show that spin information is preserved by the hidden conserved "twisted spin" and survives elastic disorder scatterings. This twisted spin is an adiabatic invariant with respect to a slow change in the SOI. We predict an echo phenomenon, spin-orbit echo, which indicates the recovery of the spin moment when the SOI is tuned off adiabatically, even after spin relaxation has occurred; this is confirmed by numerical simulations. A concrete experiment in two-dimensional semiconductor quantum wells with Rashba-Dresselhaus SOI is proposed to verify our prediction.

For the manipulation of spin and spin current by electric fields in spintronics, the relativistic spin-orbit interaction (SOI) is essential because it connects the orbital motion and the spin of an electron (*1*). This interaction, however, destroys the rotational symmetry in the spin space and the consequent spin conservation law. In the presence of the SOI, there are several mechanisms to relax the spins by changing their direction at and between impurity scatterings (Fig. 1A) (*2–8*); spins decay with a (phenomenological) spin lifetime τ_s, which is typically on the order of (or less than) 1 ns [(Fig. 1B, (i) to (iv)]. This is a serious issue for applications because the transfer and storage of information for a long time/distance is a crucial requirement for device function.

It has long been recognized that the SOI is closely related to the parallel transport and rotating frame comoving with the electron in the context of Thomas precession (*9*). This naturally leads to the formulation of the SOI in terms of the SU(2) spin gauge field $\hat{A}_\mu$ ($\mu = t, x, y, z$) connecting the neighboring frames in the nonrelativistic approximations to the Dirac equation (*10–12*). Based on this idea, there have been many attempts to find a conserved quantity by generalizing the spin (*11–17*). It has been known (*11*, *12*, *18*) that the electronic spin is only covariantly conserved as $D_0 s_a + \boldsymbol{D}\cdot\boldsymbol{j}_a = 0$, a spin density s_a, and a spin current density $\boldsymbol{j}_a$ (a = x, y, z); i.e., the continuity equation where the usual derivative ∂_μ is replaced by the covariant derivative $D_\mu := (D_0, \mathbf{D})$ holds. This means that the conservation law is satisfied in the comoving spin frame with the electron's motion but not in the laboratory frame. In a notable recent advance related to this concept, experiments were performed in semiconductor quantum wells with Rashba (α) and Dresselhaus (β) SOIs described by $H_{\mathrm{RD}} = \frac{p^2}{2m} + \alpha(p_y\sigma_x - p_x\sigma_y) + \beta(p_x\sigma_x - p_y\sigma_y)$, where H_{RD} is the Rashba-Dresselhaus Hamiltonian, $\boldsymbol{p}$ is the momentum, m is the mass of an electron, σs are the Pauli matrices, and $\hbar = 1$. In this system, the lifetime of a Fourier component of the spin $S_{\boldsymbol{q}}$ for $\boldsymbol{q} = (2\sqrt{2}m\alpha, 2\sqrt{2}m\alpha)$ [persistent spin helix (PSH)] is observed to be enhanced when the condition $\alpha = \beta$ is satisfied (*19*, *20*). In this case, the SU(2) gauge field strength $\hat{F}_{\mu\nu} \propto (\alpha^2 - \beta^2)\sigma_z$ is zero; that is, the SOI vanishes in the rotated spin frame.

We explicitly construct a conserved twisted spin in a generic situation when the electric field is regarded as a background static field (Fig. 1A). Furthermore, we study the adiabatic invariance of this twisted spin and predict a phenomenon called the spin-orbit echo [Fig. 1B, (iv) to (vii)]. The twisted spin preserves the information on the spin, and as the SOI is switched off adiabatically, the spin is recovered to coincide with the conserved twisted spin.

We consider a noninteracting electron system whose Hamiltonian is given by (*10–12*)

$$H = \frac{1}{2m}\left(\boldsymbol{p} - \frac{e}{mc^2}\hat{\boldsymbol{A}}\right)^2 + V(\boldsymbol{x}) \qquad (1)$$

where $\hat{\boldsymbol{A}} = \sum_{i,a} A_i^a \mathbf{e}_i \sigma_a/2$, where $A_i^a := \sum_l \varepsilon^{ial} E^l$ describes the SOI, $\mathbf{e}_i$ is the unit vector, and $V(\boldsymbol{x})$ is a scalar potential that includes the periodic crystal potential and the disorder potential. Here, $-e$ represents the charge of an electron; c is the velocity of

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