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RADIOCARBON AMS DATES FOR PALEOLITHIC CAVE PAINTINGS

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ABSTRACT. Advances in radiocarbon dating by accelerator mass spectrometry (AMS) have made it possible to date prehistoric cave paintings by sampling the pigment itself instead of relying on dates derived from miscellaneous prehistoric remains recovered in the vicinity of the paintings. The work at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) concentrated on prehistoric charcoal cave paintings from southern France and northern Spain. In most caves, pigment samples were collected from several paintings, and in some instances the sample size allowed for multiple independent measurements on the same figure, so that the coherence of the calculated dates could be tested. Before being dated, each specimen was subjected to a thermal treatment preceded by an acid and basic treatment of intensity commensurate with the sample size.

Nine bison drawings from three caves in the Cantabrian region of Spain—two from Covaciella, three from Altamira, and four from El Castillo—were sampled and dated. The 27 dates fell between 13,000 and 14,500 BP, allowing us to attribute the drawings to the Magdalenian period. The 24 dates for 13 drawings in the Cosquer cave indicated two distinct periods of painting activity—one around 28,000 BP and the other around 19,000 BP. The Chauvet cave paintings turned out to be the oldest recorded to date, as five dates fell between 32,000 and 31,000 BP. After discussing the sample preparation protocol in more detail, we will discuss the ages obtained and compare them with other chronological data.

INTRODUCTION

For over a decade, tandem accelerators at several laboratories have obtained radiocarbon dates for parietal art by dating the pigment. Whereas blood residues (Loy et al. 1990), beeswax (Nelson et al. 1995), or plant resins (Hedges et al. 1988) used in the paintings have been dated, it is wood charcoal used in the production of some of the black paintings that has received the most attention (Russ et al. 1990; Valladas et al. 1992; Igler et al. 1994). Since 1992 we have used the Gif sur Yvette tandem accelerator to date charcoal scrapings from prehistoric cave drawings. The protocol followed in our sample preparation will be discussed briefly, since the details have already been published (Valladas et al. 1999). We will concentrate on the dates spanning a period of almost 20,000 years, which we obtained for prehistoric charcoal drawings in several Spanish and French caves.

PROCEDURE

To protect the visual integrity of the drawings the pigment was scraped within rock cracks or from the thickest layers, otherwise the same figure was sampled in several places. Unless the painting was done in manganese dioxide, the samples of black pigment, weighing 10–100 mg, contained wood charcoal, sometimes accompanied by calcite grains from the rock face. In some instances the wood could be identified as belonging to the species *pinus*. Figure 1 shows how the scrapings were treated to eliminate contamination by extraneous carbon (Valladas et al. 1999). The conventional acid and basic treatment of charcoal was more or less rigorous according to the sample size. The residue from

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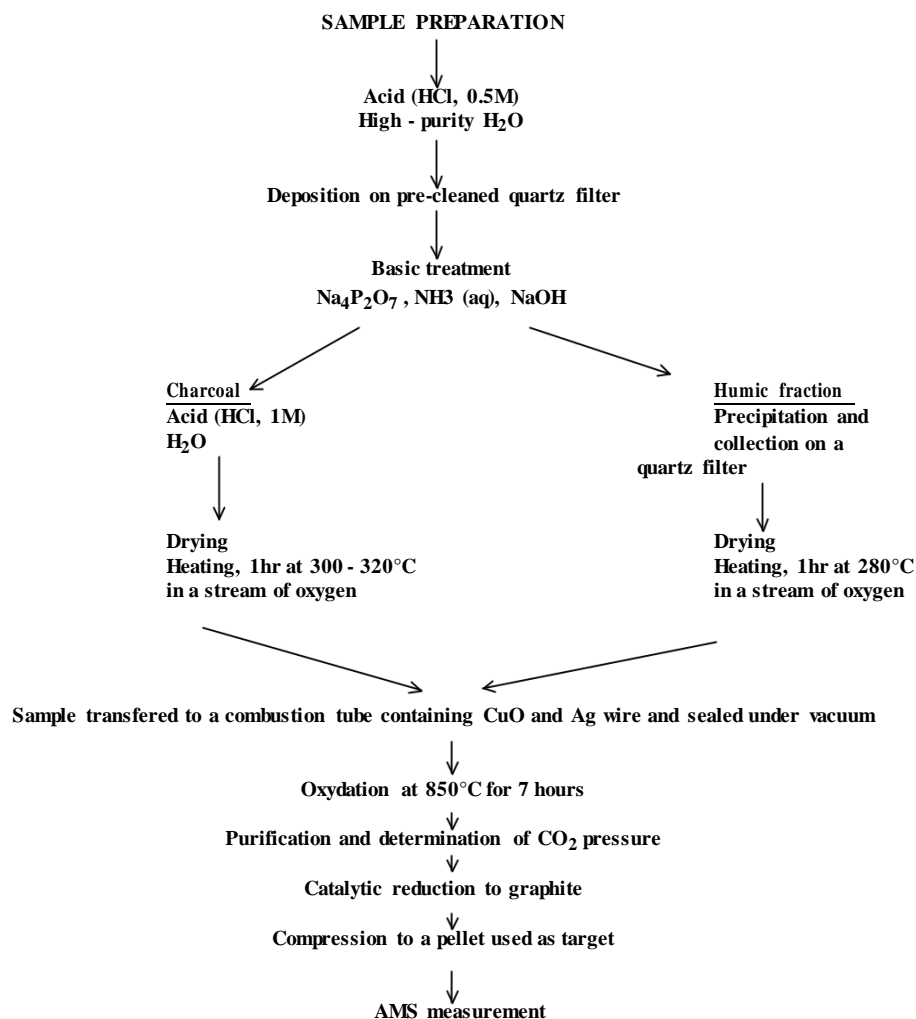


Figure 1 Experimental procedure. The basic treatment is gentle at first, increasing in intensity according to the vulnerability of the sample. We begin with a dilute solution of sodium pyrophosphate whose concentration is increased progressively. Aqueous ammonia of gradually increased concentration is used next, followed by sodium hydroxide treatment in cases of alkali-resistant pigments. As a rule, the treatment stops when the filtrate becomes highly colored. The coloration suggests that not only the outer grain layers have been stripped but that a good fraction of the original charcoal has passed into solution. If the treatment were not interrupted in time, no charcoal might remain for dating. The remaining charcoal grains are washed again with aqueous HCl.

the initial acid bath was retained on a pre-cleaned quartz-frit filter and subjected to subsequent basic and acid washings (see Figure 1 legend). After chemical treatment, the purified charcoal or humic acids collected on the quartz filler were heated in a stream of oxygen for about an hour between 280 and 320 °C to remove some additional organic contaminants.

Whatever remained was oxidized to CO₂ then reduced to graphite and compressed into pellets for the accelerator (Arnold et al. 1987). The purification process eliminated about 90% of the original mass, leaving us with pellets usually containing from one-half to 1 mg of carbon (Tables 1 and 2, column 3).

Table 1 Radiocarbon dates for prehistoric paintings at three Spanish caves: Covaciella, Altamira, and El Castillo. Humic acid data are written in italics.

Cave and sample	Lab code	Dateable carbon (mg)	Date (BP)	Error (yr) 1 σ	Calibrated age (2 σ) ^a
<i>Covaciella</i>					
Bison 25 ^b	GifA 95281	1.4	14,060	140	17,453–16,309
	GifA 95370	0.3	<i>13,700</i>	<i>140</i>	<i>17,019–15,906</i>
Bison 26 ^b	GifA 95364	2.34	14,260	130	17,681–16,545
	<i>GifA 95362</i>	<i>0.3</i>	<i>14,260</i>	<i>180</i>	<i>17,750–16,476</i>
<i>Altamira</i>					
Bison XXXIII ^c	GifA 91181	1.49	14,330	190	17,849–16,539
	GifA 96071	1.7	14,820	130	18,361–17,166
	<i>GifA 91330</i>	<i>0.53</i>	<i>14,250</i>	<i>180</i>	<i>17,738–16,465</i>
Bison XXXVI ^c	GifA 91179	0.7	13,940	170	17,350–16,133
	GifA 96060	2.17	14,800	150	18,361–17,120
	<i>GifA 91254</i>	<i>1.38</i>	<i>14,710</i>	<i>200</i>	<i>18,323–16,948</i>
Bison XLIV ^c	GifA 91178	0.87	13,570	190	16,939–15,681
	GifA 96067	0.54	13,130	120	16,314–14,682
	<i>GifA 91249</i>	<i>0.663</i>	<i>14,410</i>	<i>200</i>	<i>17,960–16,613</i>
Magdalenian bone	GifA 90047		14,520	260	18,195–16,634
Engraved bone	GifA 90057		14,480	250	18,129–16,607
<i>El Castillo</i>					
Bison 18a ^c	GifA 96079	1.02	12,620	110	15,689–14,196
	GifA 91004	0.82	13,060	200	16,351–14,448
	GifA 96068	1.05	13,520	130	16,791–15,713
Bison 18b ^d	GifA 91172	0.69	12,910	180	16,140–14,362
Bison 18c ^d	GifA 95136	1.4	10,510	100	12,926–11,953
	GifA 95146	1.4	11,270	80	13,772–13,010
	GifA 96077	2.05	10,720	100	12,992–12,359
	GifA 96078	1.13	10,740	100	13,000–12,373
	<i>GifA 95375</i>	<i>0.33</i>	<i>12,390</i>	<i>190</i>	<i>15,563–13,845</i>
Bison 19 ^d	GifA 95227	1.16	13,520	120	16,779–15,726
	GifA 95226	1.36	13,570	130	16,851–15,771
	GifA 98152	1.36	13,710	140	17,031–15,917
	GifA 98151	0.97	14,090	150	17,502–16,329
	<i>GifA 98159</i>	<i>0.34</i>	<i>13,510</i>	<i>190</i>	<i>16,867–15,612</i>
Engraved bone ^d	OxA 970		10,310	120	12,821–11,444
Bone harpoon ^{de}	OxA 972		12,390	130	15,527–13,874
Bone spearhead ^e	OxA 971		16,850	220	20,889–19,284

^aStuiver et al. (1998)

^bFortea Perez (1996)

^cAlcade del Rio et al. (1911)

^dGowlett et al. (1987)

Table 2 Radiocarbon dates for prehistoric paintings at two French caves, Cosquer and Chauvet. Humic acid dates are written in italics.

Cave and sample	Lab code	Dateable		Error (yr) 1 σ
		carbon (mg)	Date (BP)	
<i>Cosquer^a</i>				
Horse 1	GifA 92416	1.56	18,840	250
	GifA 92417	0.94	18,820	310
	<i>GifA 92422</i>	<i>1.23</i>	<i>18,760</i>	<i>220</i>
Feline	GifA 92418	1.52	19,200	240
Bison 1	GifA 92419	0.64	18,010	200
	GifA 92492	1.22	18,530	190
	<i>GifA 92423</i>	<i>0.26</i>	<i>16,390</i>	<i>260</i>
Megaceros 1	GifA 95135	1.25	19,340	200
	<i>GifA 95365</i>	<i>0.12</i>	<i>13,460</i>	<i>330</i>
Horse 7	GifA 98186	0.84	19,720	210
	<i>GifA 98196</i>	<i>0.29</i>	<i>19,740</i>	<i>340</i>
Deer	GifA 98188	0.25	19,290	340
Star mark	GifA 96075	0.87	17,800	160
Horse 5	GifA 96072	0.84	24,730	300
Hand 12	GifA 95358	0.63	24,840	340
	<i>GifA 95372</i>	<i>0.26</i>	<i>23,150</i>	<i>620</i>
Bison 2	GifA 96069	1.79	26,250	350
	GifA 95195	2.04	27,350	430
	<i>GifA 95308</i>	<i>0.23</i>	<i>23,080</i>	<i>640</i>
Hand 1	GifA 92409	0.86	27,110	430
	GifA 92491	1.59	27,110	400
	<i>GifA 92424</i>	<i>0.44</i>	<i>26,180</i>	<i>370</i>
Hand 19	GifA 96073	1.30	27,740	410
Oval mark	GifA 96074	2.12	28,370	440
Soil charcoal	Ly-5558		18,440	440
Soil charcoal	GifA 92348	2.39	20,370	260
Soil charcoal	GifA 92349	2.17	26,360	440
Soil charcoal	GifA 92350	2.06	27,870	470
<i>Chauvet^b</i>				
Right rhinoceros	GifA 95132	1.40	32,410	720
	GifA 95133	1.22	30,790	600
Left rhinoceros	GifA 95126	0.80	30,940	610
Bison	GifA 95128	0.83	30,340	570
	<i>GifA 95155</i>	<i>0.42</i>	<i>30,800</i>	<i>1,500</i>
Torch scraping 1	GifA 95129	2.30	26,980	410
	GifA 95130	1.76	26,980	420
	<i>GifA 95158</i>	<i>0.308</i>	<i>25,700</i>	<i>850</i>
Torch scraping 2	GifA 95127	1.22	26,120	400
Soil charcoal	Ly-6878	5.000	29,000	400
	Ly-118/Oxa	2.500	24,770	780
	Ly-6879	2.000	22,800	400

^aFor pictures of the dated paintings see Clottes and Courtin (1994) and ^bClottes et al. (1995).

Whenever enough material was available, multiple datings were done on the same drawing to test the reproducibility and coherence of the results, and the humic acid fraction obtained during the basic treatment was also dated to see to what degree the initial pigment sample might have been contaminated (Batten et al. 1986). As will be seen in the next section, the purified charcoal and the humic acid fraction usually yielded similar results. While good agreement between the two sets of dates generally increases one's confidence in the reliability of the dates, one can never exclude a remote possibility that both fractions may have been contaminated somehow. When the two fractions diverge, the humic acid fraction, which one expects to contain more contaminants, tends to give a lower figure. In such cases the age of the purified charcoal is more trustworthy.

The described preparation procedure was previously tested from the Solutrean level of the *Abri des Peyrugues* on a piece of charcoal that was broken into several pieces. Some pieces were subjected to very strong chemical treatment, others were treated in the same way as the pigment samples, still others subjected to chemical but not thermal treatment. These results show that 1) the strong and weak treatments of the same charcoal gave similar results, and 2) the thermal treatment did eliminate some additional contamination by more recent carbon, since the samples thus treated gave slightly older ages. The results confirmed also the good reproducibility of our protocol (Valladas et al. 1999).

The extent of contamination by modern carbon during sample preparation was determined by subjecting several >100,000-yr-old charcoals to the same treatment as our pigment samples. This contamination estimated at 0.50 ± 0.13 pMC, was used to make a suitable correction to the calculated pigment ages.

RESULTS

Spanish Caves

We will first discuss the dates obtained for a number of bison painted in three Spanish caves—Cova-ciella, Altamira, and El Castillo—during the Magdalenian.

Covaciella cave was discovered in 1994 in eastern Asturias at the edge of the Cantabrian region (Fortea-Perez 1996). On the western part of the main panel one finds aligned a female (n°25) and a male bison (n°26) painted in black. These two bison, which are only a few centimeters apart, were sampled within a year of the cave's discovery.

Table 1 lists the dating results. One can see that the purified charcoal obtained from the two bison paintings have virtually the same age, $14,060 \pm 140$ and $14,260 \pm 130$ BP, respectively. The humic acid (italicized in the table) and purified charcoal fractions of the bison gave ages similar enough to suggest minimal sample contamination.

We have no dates for the associated archaeological material because excavation work has not been completed.

Altamira cave. (Santillana del Maar) in the province of Cantabria has been studied since the 19th century (Bernaldo de Quiros 1994; Moure et al. 1996). On its painted ceiling, about 20 bison are depicted in red and black or only in black (Figure 2). Two adjacent polychrome bison (XXXIII and XXXVI; Breuil and Obermaier 1935) were sampled as well as a black bison (XLIV). Each pigment scraping was divided in two, and each subsample was treated and dated separately (Table 1). The two purified charcoal fractions of bison XXXIII gave comparable ages: $14,330 \pm 190$ BP and $14,820 \pm 130$ BP, ages close to the $14,250 \pm 180$ BP obtained on humic acid fractions (italicized in Table 1). On the other hand, for the other two bison (XXXVI and XLIV) the purified charcoal ages

were more widely scattered, ranging from 13,100 to 14,800 BP, and in some instances younger than the corresponding humic acid fractions (14,710 and 14,410 BP for bison XXXVI and XLIV, respectively). At the moment, we have no simple explanation for these younger dates. The rock-face conditions at Altamira make contamination by old water-borne carbon highly improbable. The same cannot be said for contamination by modern carbon, since the cave has been extensively visited for over a century. The fragility of the collected pigment obliged us to resort to a relatively weak basic treatment, so some younger carbon might have survived. In our opinion, if one assumes that all bison were painted at about the same time and that the design was not retouched at a later date, the older dates (14,330 and 14,800 BP) are most reliable. In favor of this argument is the fact that bone specimens from the Magdalenian strata were dated to the same age range (see Table 1). Engraved on one of the dated fragments was a deer similar to the deer painted on the ceiling.

El Castillo cave. (Puente Viesgo), also in Cantabria, is located not far from Altamira (Moure et al. 1996). The prehistoric paintings are currently being studied by F Bernaldo de Quiros, V Cabrera-Valdés, A Moure, and C Sainz. The four bison sampled are situated in the same panel of the cave (Figure 3): three of them are bicolored (No 18a and 18b, and 18c; Alcade del Rio et al. 1911): one (18a) has an additional negative hand print and two extra animals, the other (18b) is accompanied by four human hand imprints; the remaining bison (No 19; Alcade del Rio et al. 1911) is exclusively in black. Three dates were obtained for bison 18a, one for 18b, and four dates for each of the other two bison. Only two humic acid fractions obtained on No 19 and 18c were large enough for dating. Bison 18a yielded rather unusual results. A pigment sample from the abdomen was dated to $12,620 \pm 110$ BP, whereas a scraping from one hind leg gave the dates of $13,060 \pm 200$ and $13,520 \pm 130$ BP, respectively.

The reason for such a discrepancy is uncertain at the moment. There is no indication that this particular painting was retouched at a later date. As in the case of Altamira cave, one can assume that some of the El Castillo paintings have been contaminated by modern carbon because of their location near the path used today by the numerous visitors to the cave. So, it appears to us that the oldest dates obtained for this bison should be the most relevant. Taking this hypothesis into consideration, we obtained ages ranging between about 13,000 and 13,700 BP for bison 18a, 18b, and 19, which are roughly compatible within 2σ . It would be interesting in the future to get additional dates for bison 18b to check the result obtained so far ($12,910 \pm 180$ BP), which appears slightly younger than the highest ages obtained for bison 18a and 19. As a matter of fact, it is possible that the age obtained for bison 18b was underestimated due to the presence in the charcoal of a small contamination by modern carbon. If it is the case, the time interval for the paintings of these three bison could be made even shorter.

In the case of the fourth bison (18c) purified charcoal gave four dates between 10,500 and 11,300 BP, whereas the humic acid fraction yielded a slightly older date of $12,390 \pm 190$ BP. As for bison XXXVI and XLIV of Altamira, we cannot exclude that these particular samples were more contaminated than the others from the site and that our treatment proved to be inadequate. In that case, the oldest date obtained on the humic fraction ($12,390 \pm 190$ BP) should be the most relevant for this painting. If so, this bison might have been painted more recently than the three others and have been contemporaneous with a bone harpoon from layer 6 of the same site, which yielded a similar age of $12,390 \pm 130$ BP (Gowlett et al. 1987).

The calibrated ^{14}C dates of the Spanish paintings and of archaeological remains from corresponding sites are compared in Table 1 (Stuiver et al. 1998). At Altamira, most of the paintings and remains found on the ground fall between 18,000 and 16,500 BP. The Covaciella bison fall within the same

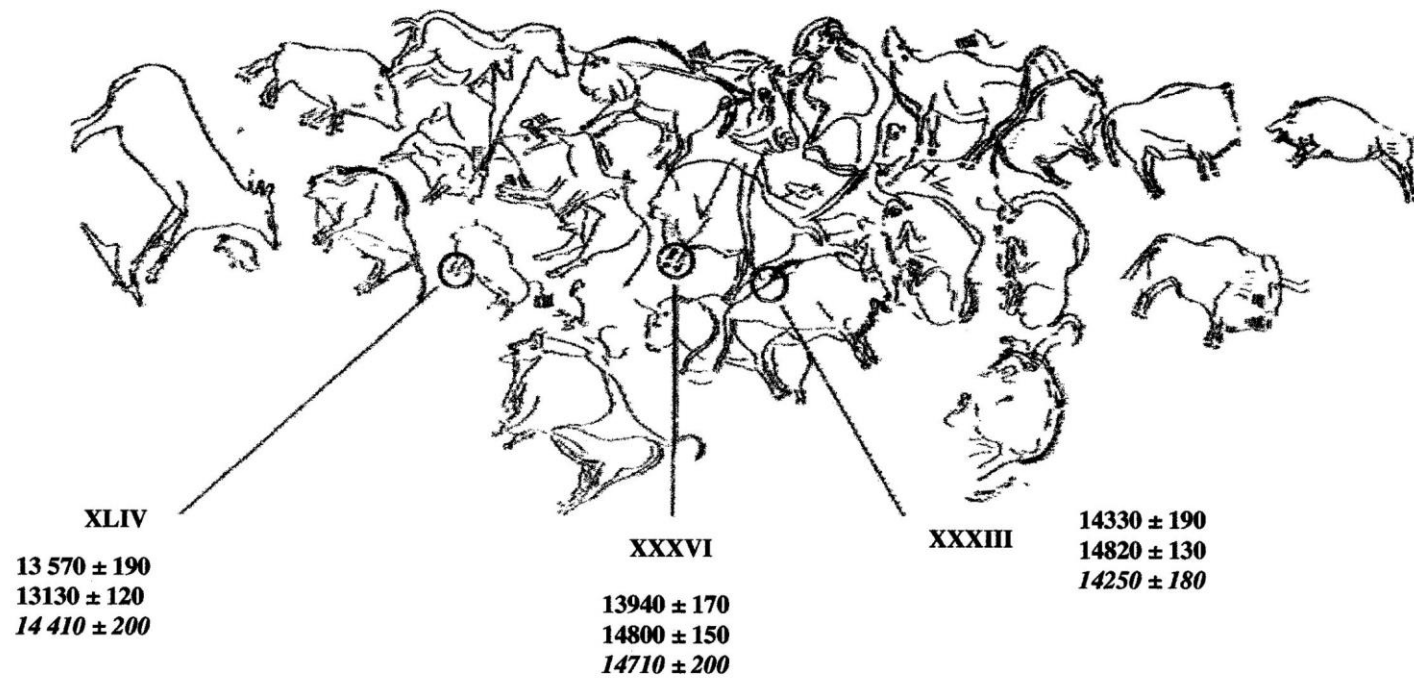


Figure 2 Images from the Altamira painted ceiling (Breuil and Obermaier 1935). The locations of the three dated bison are indicated along with the dates obtained on purified charcoals and humic fractions (in italics).

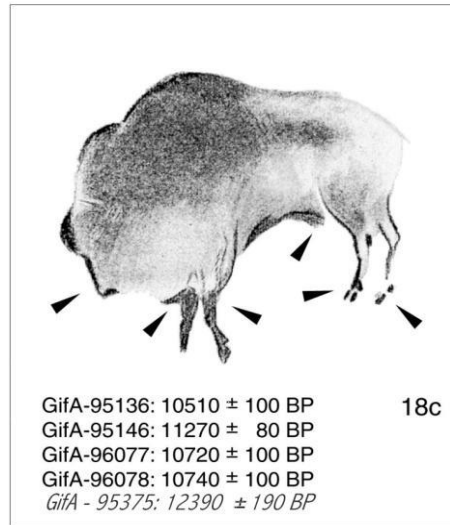
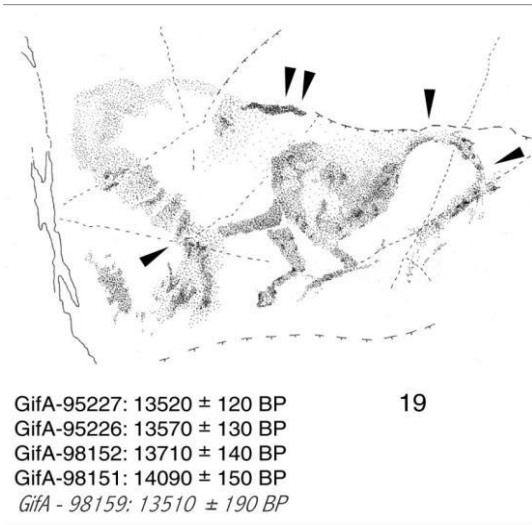


Figure 3 El Castillo panel with the four bison. The locations of the four dated bison are indicated along with the dates obtained on purified charcoals and on humic fractions (in italics).

age range, and so were probably painted at about the same time. The El Castillo bison appear to be somewhat more recent, since at least three date to between 16,500 and 14,400 BP, and the fourth is even younger.

French Caves

We will now discuss the dates obtained at two recently discovered caves in France. In 1991 scuba divers discovered near Marseilles the Cosquer cave, whose entrance is now 40 m below sea level. The cave is richly decorated with rock paintings and carvings (Clottes et al. 1992, 1997). About 24 dates were obtained for 13 charcoal drawings: three horses, two bison, a feline, a stag, and a giant deer, as well as three negative hands and two geometric signs (Clottes and Courtin 1994). Table two shows the dating results. As usual, the humic acid fractions yielded similar or slightly lower ages than the purified charcoal. Some pigment scrapings were divided in two and the two halves were treated and dated separately, yielding usually compatible ages at the 1- σ level. The paintings can be grouped into two time periods about 10,000 years apart. The first group consisting of negative hands, a bison, and an oval sign, were dated to between 28,000 and 27,000 BP, during the Gravetian period. Except for one horse, the other animals and the star-like sign were dated to between 19,700 and 18,500 BP, during the Solutrean period. Taking into account the amplitude of the errors, it is not possible to conclude if each of the two painting phases lasted a brief period of time or stretched over centuries. However, one of the hands and a horse had an age of about 25,000 BP. Only after additional dates have been obtained will we know whether these two dates represent an intermediate period of cave decoration or if they are the result of more extensive contamination.

The time span that separates the two bison (1 and 2) that are similar and depicted on the same wall is rather surprising. This fact can be interpreted in at least two ways: either the stylistic conventions were maintained over extremely long time periods, or the older one was not created using fresh charcoal. To help us choose between these alternatives additional dates will be needed. It is noteworthy that charcoal fragments collected on ground surface also fall within two distinct time intervals: 18–20 and 26–28 ka BP, respectively (see Table 2).

If the Cosquer dates surprised some prehistorians, the surprise was nothing compared to the impact of dates obtained several years later for the parietal art at Chauvet cave discovered in Ardeche in December 1994. It is currently being studied by a multidisciplinary team under the direction of Jean Clottes (Clottes et al. 1995). So far, about a dozen dates have been obtained for two rhinoceroses, a bison, and two torch rubbings.

Most humic-acid fractions yielded dates in good agreement with those obtained on purified charcoal. The animal representations were dated to between about 32,000 and 30,500 BP, within the Aurignacian period (Table 2). The torch scrapings were about 27,000 years old, a date not surprising if one notes that in one case the torch was scraped against a layer of calcite deposited on top of a drawing! Included in Table 1 are ages obtained for charcoal collected on the surface of the ground. The ages ranged from 30 to 20 ka BP, suggesting that the cave must have been visited on several occasions before it was sealed off by a rock-fall. Dates from additional samplings are being processed and will be published in the near future.

CONCLUSION

Even if the direct dating of cave paintings is still in its infancy, the few dates reported so far have convinced art historians of the need to revise prior ideas about the evolution of prehistoric art. The

findings at Chauvet cave, in particular, indicate that theories assuming a linear progression from simple to more complex composition have to be discarded.

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