

## IN SEARCH OF LOST TIME. DATING METHODS FOR PREHISTORIC ART: the Example of Aurignacian Sites

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### **Abstract**

*The need for an accurate chronological framework is particularly important for the early phases of the Upper Paleolithic, which correspond to the first works of art attributed to Aurignacian groups. Carbon-14 is the only method used for the direct dating of organic pigments, but indirect methods are used to date subsequent deposits on rock art (thermoluminescence, OSL, Uranium/thorium, etc.). All these methods are based on hypotheses and present interpretative difficulties, which form the basis of the discussion presented in this article.*

### **Keywords**

*Rock art, absolute dating, radiocarbon, thermoluminescence, optically stimulated luminescence, Uranium/Thorium series, oxalates.*

## **Introduction**

The accuracy of the radiocarbon dating method decreases as the age of the sample increases. The earlier the age, the higher the uncertainty, due to additional causes of error. Moreover, the ages obtained by carbon-14 do not correspond to exact calendar years and thus require correction. The effects of this correction become very significant and inaccurate beyond 30 ka. It is for this reason that the period corresponding to the advent of anatomically modern humans (*Homo sapiens sapiens*) in Europe and the transition from Neanderthal Man to modern Man remains relatively poorly secured on an absolute time scale, opening the way to all sorts of speculation and controversy. As long as it is based on dates with an accuracy of one to two thousand years and which fluctuate according to calibration curves and the technical progress of laboratories, our reasoning remains hypothetical. In such a fluctuant context, it would be illusory to place the earliest artistic parietal and portable representations from the Swabian Jura, the southwest of France, the Rhone Valley, Romania or Veneto on a relative timescale.

In this article on absolute dating methods, we will briefly recall the scientific principles on which the different methods are based, in order to allot more scope to the causes of error that blur our overall vision, but also to recent technological progress which offers an optimistic outlook for the future of our discipline. Most of this paper will deal with carbon-14 as it is the only direct dating method applicable to parietal art (although it is limited to charcoal drawings).

In order to date red paintings and engravings, indirect methods allow us to estimate the age of the deposits that form after the completion of the art works. These techniques are thermoluminescence (TL) and the uranium / thorium series, applicable to calcite deposits in caves, the dating of calcium oxalate coating and amorphous silica patinas that form on rocks exposed to daylight

and lastly, optically stimulated luminescence (OSL), a technique used to date the sediments related to parietal art. In most cases, these methods provide a minimum age, a *terminus ante quem* that can be far removed from the archeological reality, as deposits can form quite late on and in an intermittent way. But other causes of error can increase uncertainty, some of which can even contribute to yielding abnormally high ages.

## 1 - Carbon-14

### A - Principle

In the upper atmosphere, high energy cosmic rays transform nitrogen atoms ( $^{14}\text{N}$ ) into  $^{14}\text{C}$ , a radioactive element that disintegrates into  $^{14}\text{N}$  with first-order kinetics characterized by a half-life period of 5 568 years (period of time required for half of the initial  $^{14}\text{C}$  to disappear). The concentration of  $^{14}\text{C}$  in the atmosphere and the oceans as carbon dioxide then remains almost stationary. This  $^{14}\text{CO}_2$  passes directly into the metabolic cycle of animals and plants, so that the proportion of  $^{14}\text{C}$  is constant in all living creatures and begins to decrease from their time of death, when there is no further exchange with the environment. Libby (1949) inferred from this that it was possible to determine the date of the death of the organism by measuring the residual proportion of  $^{14}\text{C}$ .

### B - Technique

For many years, the proportion of residual  $^{14}\text{C}$  was measured by counting the number of disintegrations after the transformation of carbon into gas (*gas proportional counter*) or into liquid (*liquid scintillation counter*), which required considerable quantities of organic matter (10 g. of charcoal for example). More recently, the mass spectrometry accelerator technique (AMS) results in the direct measurement of the  $^{14}\text{C}/^{12}\text{C}$  ratio on samples of a few milligrams, thereby making it possible to directly date charcoal drawings.

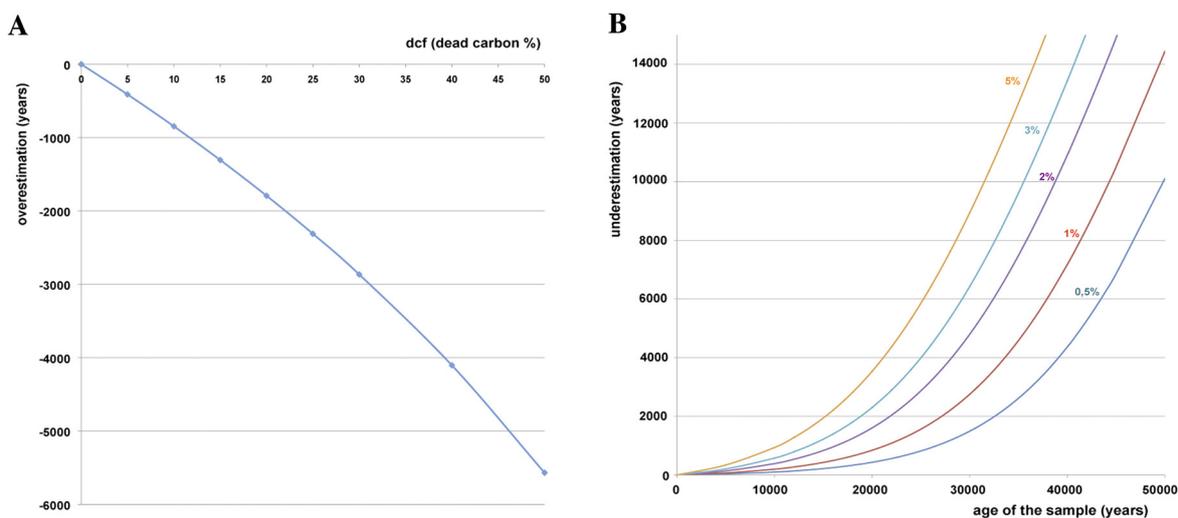
### C - Causes of error

There are many but they are of disparate importance.

- 1) The half-life period used by Libby (and used since by convention) turned out to be erroneous. It is now calculated at 5 730 years (and not 5 568 years), which represents an age underestimation of about 3%. Calibration curves correct this error (see calibration below).
- 2) Measurements of  $^{14}\text{C}$  concentration are flawed by statistical error and the age is given as an average value  $m$  and a standard-deviation  $\sigma$ . There is a 68% chance that the age is in the  $[m-\sigma, m+\sigma]$  interval and a 95% chance that it is in the  $[m-2\sigma, m+2\sigma]$  interval. Throughout the years, techniques have improved and standard-deviations have decreased, but it is important not to confuse the *accuracy* of the measurements expressed by  $\sigma$  with the *uncertainty* surrounding the real age of the dated object.<sup>1</sup>

1. Several measurements carried out on the same object sometimes present a low standard-deviation, but the averages can be very different. For example, the same bison from the cave of Castillo (Cantabria) yielded two ages of  $12\,620 \pm 110$  BP (GifA-96079) and  $13\,520 \pm 130$  BP (GifA-96068). These measurements are quite accurate, but the age of the painting is very uncertain, since the difference between these two averages is 900 years (or seven times the value of  $\sigma$ !).

- 3) The main cause of error does not stem from the measurements, but from sample purification. A physico-chemical pretreatment in the laboratory is required to eliminate any potential organic contaminants. Yet, laboratories use different procedures and these have evolved throughout time. We must thus focus on these procedures as they can yield considerably different results, especially for samples with an age of more than 30 ka. But we must first of all discern two types of impurities; those that increase the age and those that result in younger dates ([figure 1](#)).



**Figure 1** - Influence of impurities on radiocarbon dating. A: Ageing by dead carbon (containing no more  $^{14}\text{C}$ ); B: Rejuvenation by recent carbon according to the impurity percentage.

If the dated sample contains an impurity of an infinitely early age (which no longer contains  $^{14}\text{C}$ , what we refer to as “dead carbon”, for example from carbonates of geological origin), then the age is older, but this is independent from the age of the sample and the effects are limited (less than 900 years for 10% of dead carbon; [figure 1<sup>A</sup>](#)).

On the other hand, impurities containing recent carbon are a particularly serious source of error, especially for older samples. A sample with a real age of 40 000 years, only containing 1% of recent carbon, would yield an apparent age of 32 800 years, which corresponds to a rejuvenation of 7 200 years! ([figure 1<sup>B</sup>](#)).

Therefore the main cause of error in radiocarbon dating is the presence of recent carbon leading to more recent dates. In comparison, the ageing of samples through the presence of “dead carbon” is almost negligible.<sup>2</sup> Note that for paintings exposed to air, contamination by organic matter of

2. This double observation can be applied to the well-known, but still unresolved case of the black dots superposed on yellow aurochs in Candamo Cave (Asturias, Spain) (Fortea, 2002). Two dates yielded ages of  $32\,310 \pm 690$  BP (GifA-96138) and  $33\,910 \pm 840$  BP (GifA-98201). Later, two dates conducted by another laboratory yielded  $15\,870 \pm 90$  BP (GX-278-42) and  $15\,160 \pm 90$  BP (GX-278-41). The gap between these two series gave rise to controversy (Pettitt, Bahn, 2003). Two hypotheses can be envisaged: 1) if the “real” age is  $\approx 16$  ka, an apparent age of  $\approx 33$  ka would imply that the sample contained 87% of dead carbon, which is totally improbable! 2) if the “real” age is  $\approx 33$  ka, an apparent age of  $\approx 16$  ka would imply that the sample contained 12% of recent carbon, which is also very unlikely. The only remaining possibility is that the two series correspond to totally unconnected parietal events, but no satisfactory explanation has yet been proposed. A third series of recently published dates (Corchón *et al.*, 2014) gave dates for these same dots varying from  $18\,020 \pm 230$  BP (GifA-11450/SacA-26192) to  $22\,620 \pm 260$  BP (GifA-12092/SacA-28706) with  $\delta^{13}\text{C}$  varying between -20.6 and -34‰, which could indicate carbon matter of different origins.

indeterminate age must also be taken into account. Calcium oxalate deposits can be mixed in with pigments and skew the results as their age can vary from the age of the paintings to the present-day (see below the paragraph on oxalates). It is thus essential to ensure that oxalates have been eliminated (Bonneau *et al.*, 2011).

The significance of these contaminations explains why all current research is aimed at improving pretreatment procedures. In sum, the classical method of charcoal preparation, called ABA (three steps consisting of an acid treatment, then basic, then acid again) has now been replaced by a variant known as ABOx-SC (an oxidation stage and step combustion are added to the acid and basic treatment). In nearly all cases, the ABOx-SC procedure yields dates 3 000 to 5 000 years older than the ABA procedure, which shows that the elimination of impurities containing recent carbon has greatly improved (table 1).

Site	Cultural attribution	Material	<sup>14</sup> C BP (ABA)	<sup>14</sup> C BP (ABOx-SC)	<sup>14</sup> C cal BP (Intcal13) (95,4 %)	Reference
Fumane	Proto-Aurignacian	charcoal	30 650 ± 260 (OxA-11347)	35 640 ± 220 (OxA-17569)	[40860-39700]	Higham <i>et al.</i> , 2009
	Proto-Aurignacian	charcoal	31 830 ± 260 (OxA-11360)	35 180 ± 220 (OxA-17570)	[40320-39140]	Higham <i>et al.</i> , 2009
	Proto-Aurignacian	charcoal	32 530 ± 240 (OxA-19411)	34 940 ± 280 (OxA-19412)	[40040-38880]	Higham <i>et al.</i> , 2009
	Proto-Aurignacian	charcoal	33 380 ± 210 (OxA-19525)	35 850 ± 310 (OxA-19584)	[41230-39780]	Higham <i>et al.</i> , 2009
	Mousterian	charcoal	33 700 ± 600 (OxA-6463)	40 150 ± 350 (OxA-17980)	[44470-43110]	Higham <i>et al.</i> , 2009
Mochi (Grimaldi)	Proto-Aurignacian	charcoal	34 870 ± 800 (OxA-3592)	36 350 ± 260 (OxA-19569)	[41550-40380]	Douka <i>et al.</i> , 2012

**Table 1** - <sup>14</sup>C dating of charcoal from Proto-Aurignacian sites. Comparison of pretreatment protocols by the ABA and ABOx-SC method.

For bone dating, a new method of collagen extraction and purification has also been developed. An ultrafiltration technique isolates collagen macromolecules, which often results in much older dates (Higham *et al.*, 2006; table 2). If the samples are “clean”, the different methods give similar results, but if they are very polluted, purification by ultrafiltration can yield ages several thousand years older, which calls into question certain archeological hypotheses, like for example the notion of a Neanderthal “refuge” south of the Ebre (Wood *et al.*, 2013; Higham *et al.*, 2014).

Site	Cultural attribution	Material	<sup>14</sup> C BP (ion-exchange resin)	<sup>14</sup> C BP (ultrafiltration)	<sup>14</sup> C cal BP (Intcal13)	Reference
Geissenklösterle	Early Aurignacian	Bones (collagen)	30100 ± 550 (OxA-6256)	35 050 ± 600 (OxA-21659)	[41030-38470]	Higham <i>et al.</i> , 2006
Arrillor	Mousterian (level Imc)	Bones (collagen)	37100 ± 1000 (OxA-6106)	44 900 ± 2100 (OxA-21986)		Higham <i>et al.</i> , 2014

**Table 2** - <sup>14</sup>C dating of bones from the Early Aurignacian site of Geissenklösterle and the Mousterian site of Arrillor. Comparison of collagen purification protocols on ion-exchange resin and by ultrafiltration.

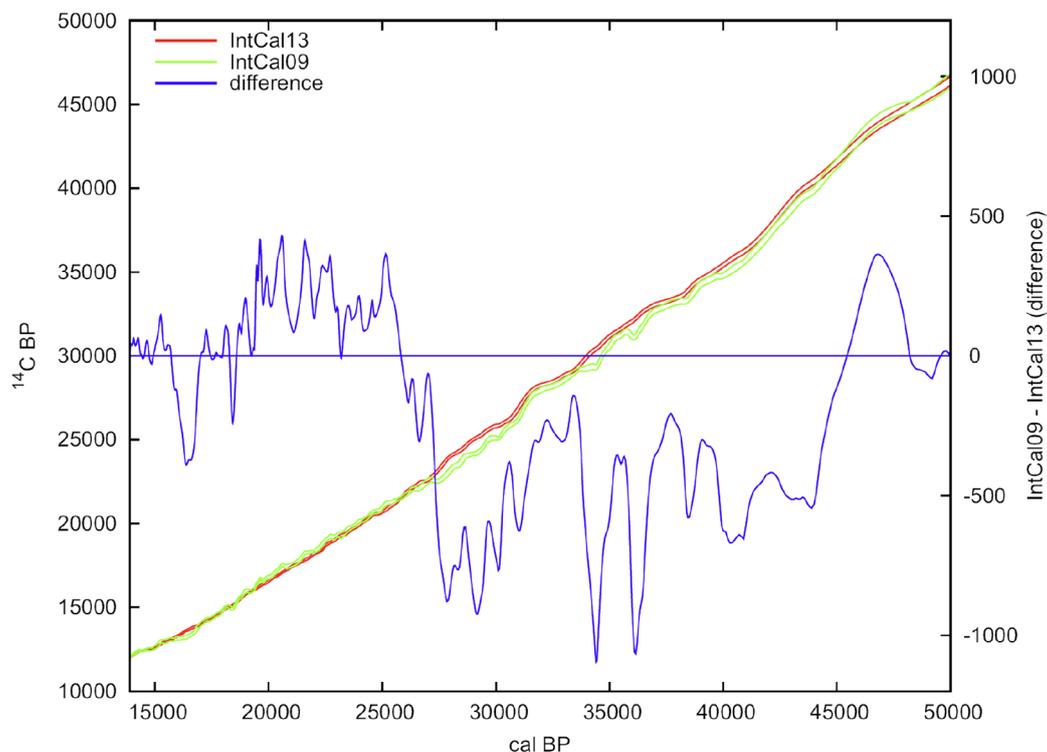
More recently, a dating method of an amino acid extracted from collagen (hydroxyproline) aged the Sungir graves by almost 5 000 years, dating them to 30 000 BP (Marom *et al.*, 2012; Nalawade-Chavan *et al.*, 2014). Note that the new dates obtained for the initial phase of the Aurignacian are now more consistent and the Neandertal-*Homo sapiens* transition is currently placed at beyond 40 000 BP in calendar years (see calibration below).

Another area in which laboratories have made great progress is with the maximum measurable age, which has gone back by more than 10 000 years. Today, 50 000 year-old samples can be dated with acceptable levels of accuracy (Higham *et al.*, 2006; Cottreau *et al.*, 2007).

## D - Calibration

Libby's hypothesis stating that the rate of formation of  $^{14}\text{C}$  in the upper atmosphere has always been constant turned out to be erroneous, as variations in the earth's magnetic field and solar activity lead to variations in  $^{14}\text{C}$  concentration. At certain periods, this was very different from the current value, resulting in a first cause of error. A second cause of error is due to what we call the reservoir effect of oceans. The  $\text{CO}_2$  dissolved in the oceans tends to become concentrated in the depths where there is very little exchange with atmospheric  $\text{CO}_2$ . Consequently, the proportion of  $^{14}\text{CO}_2$  tends to decrease with depth. During cold periods, the thermohaline circulation decreases, which results in the rate of  $^{14}\text{C}$  in living organisms and an overestimation of their age (plateau effect).

The calibration of radiocarbon ages is carried out through correlation with other methods yielding calendar ages, such as dendrochronology (until 10 000 BP), marine or lacustrine varves or dating of corals or speleothems with uranium series. The calibration curves vary according to research progress and are regularly revised (CalPal-2007, IntCal09, Intcal13; [figure 2](#)). It is thus



**Figure 2** - Intcal 13 calibration curves (northern hemisphere) and Intcal 09 between 15 and 50 ka cal BP (after Reimer *et al.*, 2013).

imperative to always indicate the  $^{14}\text{C}$  age with its standard-deviation  $\sigma$ , calibrated age brackets with a probability of 95% ( $2\sigma$ ) giving the calibration curve used, as these present non-negligible differences. For example:

$$36\,000 \pm 500 \text{ }^{14}\text{C BP} = [39660-42380] \text{ (calPal-2007-HULU) 95\%}$$

$$[40150-42040] \text{ (Intcal-09) 95\%}$$

$$[39610-41640] \text{ (Intcal-13) 95\%}$$

## E - Interlab comparison

Some intractable opponents of the early age of Chauvet Cave have questioned the fact that the dates were obtained by a single laboratory (Pettitt, Bahn, 2003), even though the six direct dates on pigment used for the paintings are remarkably consistent and compatible with a single episode in the cave, with an average date of  $30\,890 \pm 250$  BP (probability > 95%). In reply to this objection, three large pieces of charcoal retrieved from the Megaloceros Gallery were cut up and sent to four different laboratories (LSCE-Gif sur-Yvette, Oxford, Groningen and Poznan). The results are perfectly consistent, both in relation to each other and in relation to the age of the black paintings (Cuzange *et al.*, 2007).

Charcoal no. 1 :  $32\,151 \pm 83$  BP (average of 8 measurements)  
 Charcoal no. 2 :  $31\,857 \pm 79$  BP (average of 9 measurements)  
 Charcoal no. 3 :  $31\,755 \pm 105$  BP (average of 7 measurements)

Unfortunately, this experiment did not silence the antagonists, who were taken off guard and advanced improbable hypotheses to continue to refute the age of the paintings from Chauvet Cave (Combiér, Jouve, 2012).

## 2 - Thermoluminescence (TL)

### A - Principle

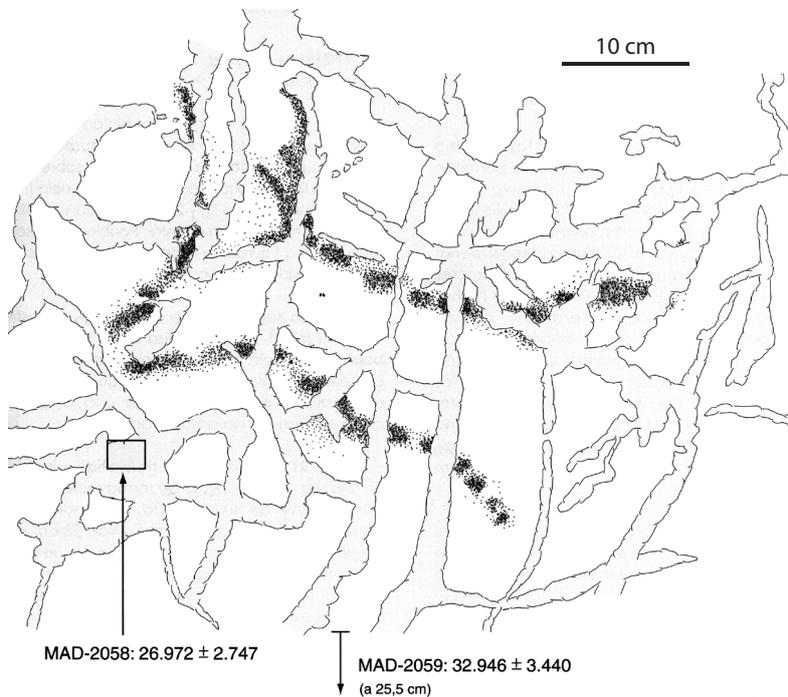
When solid matter such as flint or calcite is bombarded by cosmic rays, electrons are trapped in high energy levels. When this matter is heated to  $275^\circ\text{C}$ , the trapped electrons revert to their fundamental level by emitting radiation (luminescence peak). The technique consists in subjecting the sample to additional known irradiation doses, in order to calculate the paleodose (which is to say the irradiation that the sample was exposed to during the period of time since it was last heated (for flint), or since its formation (for calcite). The main difficulty consists in measuring the dose of annual radiation (this is the main cause of error).

The method is widely used for dating burnt flints found during excavations and generally gives quite consistent results with radiocarbon dating.<sup>3</sup> Conversely, TL has not often been used to date calcite deposits on prehistoric paintings.

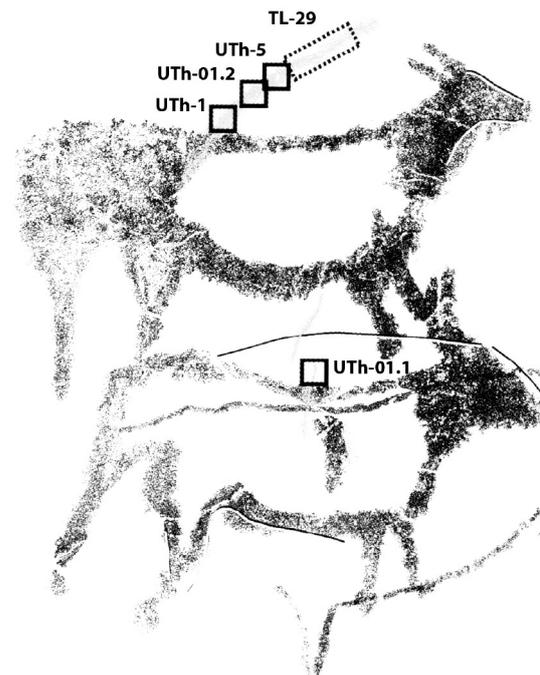
3. For example, TL dating of six burnt flints from layer III of Geissenklösterle (early Aurignacian) yielded an average age of  $40.2 \pm 1.5$  ka (Richter *et al.*, 2000), whereas reindeer bone from the same layer dated by  $^{14}\text{C}$  recently gave ages of  $36\,650 \pm 750$  and  $36\,850 \pm 800$  by ultrafiltration, which corresponds to an age of about 41.2 ka in calibrated ages (Intcal13) (Higham *et al.*, 2012).

### B - Applications to rock art

TL dating of calcite deposits was used in the Paleolithic caves of Pendra and La Garma (Cantabria). In Pendra Cave, the simultaneous dating of the calcite underlying and overlying the paintings provided a timeframe for the probable age of the paintings. In this way a red deer protome yielded a minimum age of  $26\,972 \pm 2\,747$  years, which is the approximate equivalent of  $22 \pm 2$  ka  $^{14}\text{C}$  BP (figure 3) and would place the technique of punctuated painting used in this cave in the recent Gravettian (González Sainz, San Miguel Llamosas, 2001). In La Garma Cave, a calcite cord with the lower end covering the outline of a red ibex gave a TL age of  $34\,175 \pm 3\,850$  years (or about 29 000 in equivalent  $^{14}\text{C}$  years) (González Sainz, 2003), but the sample came from higher up on the cave wall so it is possible that the calcite flow began at an earlier stage (figure 4). These experiences show the potential of the method but archeological reasoning must always be backed up by in-depth knowledge of local hydrogeological conditions.



**Figure 3** - Deer from Pendra Cave (Cantabria) with localization of samples taken for dating by thermoluminescence and dates obtained (after González Sainz, San Miguel Llamosas, 2001).



**Figure 4** - La Garma Cave (Cantabria). Localization of samples and dates obtained by TL and U/Th (after González Sainz, 2003, modified).

TL-29 :  $34\,175 \pm 3\,850$   
 UTh-5 :  $26\,800 \pm 480$   
 UTh-01.2 :  $28\,800 \pm 1\,850$   
 UTh-1 :  $26\,100 \pm 960$   
 UTh-01.1 :  $37\,000 \pm 1\,100$

### 3 - Optically Stimulated Luminescence (OSL)

#### A - Principle

The principle is similar to TL and this method is applied to materials such as quartz grains and feldspar. In this case, light and not heat is used to stimulate luminescence. What is dated here is the last previous exposure to solar light. This is based on the assumption that this exposure completely wipes out the history of the crystal, as otherwise ages would be overestimated. However, when OSL-<sup>14</sup>C correlations are possible, results are generally satisfactory.<sup>4</sup>

#### B - Applications to rock art

OSL applications to rock art are relatively infrequent, as it is only an indirect method for dating sediments assumed to be related to cave art. The dating of the sediments from two decorated rock shelters in Tassili can be cited as an example, although the link between the dated levels and the paintings was not backed up by a geomorphological study (Mercier *et al.*, 2012), and, in particular, the dating of engravings from Qurta in Egypt (Huyge *et al.*, 2011). Four dates between 10 and 17 ka were obtained for sediments clearly covering the engravings. In spite of the wide time bracket (probably due to post-depositional reworking), it confirms that these are Pleistocene engravings. These limits appear to be acceptable, as a <sup>14</sup>C date of around 14 ka cal BP was obtained on small animal bones from the same sediments.

### 4 - Uranium /Thorium Series

#### A - Principle

When calcite precipitates to the surface of a limestone wall, it traps a small quantity of uranium transported by infiltration water (but no thorium which is not soluble in water). Uranium <sup>234</sup>U then disintegrates into thorium <sup>230</sup>Th. Assuming that calcite acts as a closed system with no exchange with the outside environment, the imbalance between these two elements, that is the <sup>230</sup>Th/<sup>234</sup>U activity ratio, should allow us to determine the date when the calcite precipitated (assuming that no thorium was initially present, which must be confirmed, as detrital thorium contributions are sometimes possible). The dating method by U/Th series yields satisfactory results for massive speleothems (stalactites or flowstones), as dating is carried out on small samples taken from the core of the mass. It is even one of the means used to establish <sup>14</sup>C calibration curves (by simultaneously measuring the age of calcite by U/Th dating and <sup>14</sup>C on the same samples, taking account of the “dead carbon” fraction).

#### B - Applications to rock art

In certain hydrogeological conditions, fine layers of calcite can cover a painting or an engraving and the U/Th method can be used to determine the minimum age of the prehistoric artwork. However, this involves specific problems, as the interface of these calcite veils with the surrounding environment remains open to exchange.

4. For an anthropogenic level in the southwest of Australia, an average date of  $28 \pm 2$  ka cal BP was obtained by <sup>14</sup>C and  $25.5 \pm 1.4$  ka by OSL (Turney *et al.*, 2001).

## C - Causes of error

The  $^{230}\text{Th}/^{234}\text{U}$  ratio used to determine the age of the calcite can be skewed for two reasons:

- an error with the numerator ( $^{230}\text{Th}$ ), as solid particles of detrital origin containing thorium (in the form of two isotopes  $^{230}\text{Th}$  and  $^{232}\text{Th}$ ) can be trapped in the calcite when it forms. If the presence of detrital thorium is revealed by an abnormally low  $^{230}\text{Th}$  and  $^{232}\text{Th}$  ratio (<50), a correction is required.
- an error with the denominator ( $^{234}\text{U}$ ). Errors of this kind are very probable when the walls are subjected to strong run off and the calcite layer is thin, as in these conditions, the closed system hypothesis is no longer valid; uranium, which is relatively soluble, can be partially eliminated. Note that even with massive speleothems, an opening of the system can be observed. This occurs in particular when environmental conditions have changed dramatically in comparison to conditions during calcite precipitation (Borsato *et al.*, 2003).

If the proportion of detrital thorium is underestimated and if the lixiviation of uranium is ignored, this leads in both cases to *abnormally early dates*. This situation was encountered in a cave in Borneo where a stalagmitic drapery covering a hand print was dated by both U/Th and  $^{14}\text{C}$ . The  $^{14}\text{C}$  ages are identical at the base of the drapery and near the outer edge ( $9\,000 \pm 1\,000$  cal BP depending on the value adopted for the dead carbon fraction, which indicates that the drapery probably formed over a very short lapse of time). Conversely, the U/Th dates are very variable: 9 800 at the base, which is consistent with the  $^{14}\text{C}$  age and indicates very little leaching, whereas near the outer edge, the unexpected age of 27 000 years shows that a significant fraction of uranium was eliminated and effectively the uranium concentration is twice lower than at the base (Plagnes *et al.*, 2003).

We can learn several lessons from this example. First of all, the age of a prehistoric work of art determined by the U/Th dating of overlying calcite can be greatly over-estimated. This observation thus calls for a degree of elementary caution: when results yield an older date than expected given the archeological data, several precautions must be applied:

- 1) checking the U/Th dates with an independent method (the systematic association of the  $^{14}\text{C}$  method applied to the same calcite samples);
- 2) indicating the concentrations in uranium so that we can assess certain local anomalies;
- 3) proceeding with an in-depth study of the hydrogeological conditions of the cave walls in order to detect former or present-day run off zones, liable to interfere with results.

In the absence of such checks, very early U/Th dates must be viewed with the utmost caution. For example, this is the case for certain dates obtained for Cantabrian cave art (Pike *et al.*, 2012). Out of about fifty published dates, three-quarters of them are not worthy of discussion as they are post-Paleolithic and represent far removed *terminus ante quem* from the archeological context (figure 5). This situation was foreseeable, as in several French caves, speleothem growth was shown to restart towards 16 ka after a long period of interruption spanning most of the Upper Paleolithic (Genty *et al.*, 2004; Genty, 2008). It is thus not surprising that calcite yields ages from the end of the Tardiglacial or the Holocene. Only a small number of extremely early dates (including one of  $41\,400 \pm 570$  years) have seized the attention of authors, who developed a discussion on the archeological significance of these dates without questioning the implications of the measurements. Yet, given the fact that part of the uranium may be dissolved, which is a particularly probable hypothesis for thin layers of calcite in an active cave, and in the absence of information excluding this hypothesis, any discussion of these early dates should be adjourned, as it would be redundant (Clottes, 2012; Bednarik, 2012). It is better to wait patiently for the dates to be confirmed...

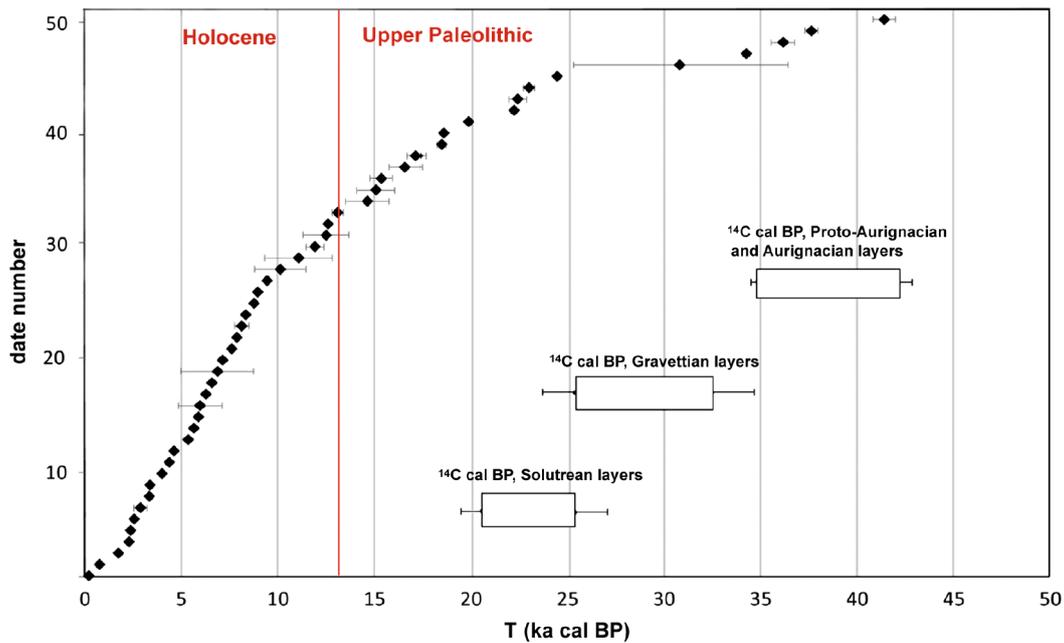


Figure 5 - Dates obtained by U/Th in eleven Cantabrian decorated caves (after Pike *et al.*, 2012, modified).

The same conclusion also applies to the U/Th dates on a panel of red representations from La Garma (figure 4), where concretions on two neighboring caprids, in strictly the same style, yielded dates ranging between 26 100 and 28 800 years for one and  $37\,000 \pm 1\,100$  years for the other (González Sainz, 2003), showing that unexpected phenomena can differentially affect very close zones.

There is one remaining point to discuss. In most cases, samples are taken by scraping the calcite with a scalpel, which is not a good solution as it only gives the age of the outer layer; the layer furthest away from the paintings! In these conditions, it is not surprising that we very often obtain sub-contemporaneous ages for Paleolithic paintings. The ideal solution consists of sampling the whole calcite layer and establishing a microstratigraphy in order to date very fine layers separately. Yet, this is possible today with the MC-ICPMS (multi-collector inductively coupled plasma mass spectrometry) technique. In a cave in Timor, it was possible to date calcite layers about 0.1 mm thick separately using laser ablation (Aubert *et al.*, 2007). In this way, the superficial layer bearing the paintings gave a *terminus post quem* of 6 ka, which is probably a realistic age, given the local archeological data. In the underlying layers, a red pigment layer was bracketted between 24 and 29 ka. Note that if the whole thickness of the calcite had been dated without discernment, it would have yielded an average age of no archeological significance. Another lesson to bear in mind when presenting rock art dates obtained with the U/Th method.

## 5 - Calcium oxalates

### A - Principle

In shelters receiving daylight, the colonization of rock walls by bacteria, fungi and lichens leads to the formation of a biofilm containing oxalic acid. This biofilm forms calcium oxalate crystals (whewellite or weddellite), when it comes into contact with calcium carbonate, and these crystals can be dated by  $^{14}\text{C}$ , giving a minimum age for the paintings.

Blocks bearing oxalate surface coatings have been identified in a site in Kimberley (Australia). As the formation of oxalates ceases during burial, the age should be close to the age of the layer. In effect, the dating of the oxalates yielded  $36\,400 \pm 1\,800$  BP and  $34\,870 \pm 740$  BP, which is consistent with the age of the layer dated by charcoals to  $36\,010 \pm 790$  BP and  $40\,100 \pm 1\,220$  BP, given the important margins of error (Watchman *et al.*, 2005).

## B - Application to rock art

A remarkable example comes from Australia where a micro-stratigraphy was carried out on an oxalate layer with a thickness of 2.1 mm recovered from a wall. Each layer was dated by AMS and the tens of dates obtained all conform with the expected order, with a very wide time range from  $3\,340 \pm 60$  BP to  $28\,100 \pm 400$  BP, from the surface to the host rock (Campbell *et al.*, 1996). Several layers of pigments were identified in the cross-section of the sample, in particular a layer of goethite between 22 800 and 25 800 BP.

Only Holocene examples are known in Europe, notably a Chalcolithic rock art shelter in Spain where underlying and overlying deposits yielded a maximum age of  $4\,675 \pm 35$  BP and a minimum age of  $2\,610 \pm 60$  BP (Ruiz *et al.*, 2012).

## 6 - Amorphous silica

Films of amorphous silica form on sandstone or schistous surfaces exposed to the elements. They trap organic matter that can potentially be dated. This was attempted for the engravings in the Côa Valley (Portugal), but with rather disparate results (Watchman, 1995) and several causes of error have been identified (Dorn, 1997). The main cause is undoubtedly the heterogeneous nature of the trapped organic matter, some of which can be much older and some very recent, resulting in average values of no significance.

## Conclusion

The dating of prehistoric parietal art in general and Aurignacian art in Western Europe in particular, is a challenge both for specialists of physico-chemical dating methods and for archeologists, as our knowledge of the first modern human cultures across the world depends on it. The  $^{14}\text{C}$  method is undoubtedly currently the most reliable method, but it also entails its share of problems. The other methods, most of which are reliable in certain circumstances (dating of burnt flint by thermoluminescence, dating of massive speleothems by the U/Th series method) still present difficulties and at times, inconsistencies when we attempt to apply them to parietal art, mainly due to poor knowledge of disruptive factors affecting calcite deposits in caves. Although these results are not yet totally convincing and should be considered with extreme caution, studies of these methods must continue in order to identify the causes of error, to minimize their effects and to specify the optimal conditions of use and the validity limits for each method.

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