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Refining ^{14}C dating of bone >30,000 BP: Establishing an accurate chronology for the Middle to Upper Palaeolithic transition in France.

Proefschrift

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"Love and marriage, they go together like a horse and carriage … You can't have one without the other … Try, try, try to separate them, it's an illusion…" Frank Sinatra "Love and Marriage" 1955

To my daughter Olivia

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Abstract

This thesis aims to improve the chronology of the transition from the Middle to Upper Palaeolithic in France through the radiocarbon dating of bone collagen samples. This requires accurate calibration of the radiocarbon time scale for this time interval, reliable extraction of collagen from prehistoric bones and accurate AMS radiocarbon dating.

The recent developments in radiocarbon calibration beyond 26,000 cal BP, which have resulted in the formulation of an internationally agreed calibration curve spanning back to 50,000 cal BP, are discussed in the introductory section of this thesis.

The methodological section of this thesis presents the results of experiments undertaken to establish an optimal procedure for extracting collagen from bone samples for radiocarbon dating. The main objectives of these experiments were to remove contamination from the organic bone fractions, which generally results in younger ages, and to avoid the incorporation of exogenous carbon in the laboratory through careful cleaning of the equipment. In order to achieve these aims, a suite of bone pretreatment methods were adopted and the resulting collagen extracts were sent for dating to different laboratories. The radiocarbon ages obtained from two test bones cover large ranges, which fall significantly beyond measurement error. This may be due to differences in both pretreatment methods and in the set-ups of different AMS facilities. The research undertaken for the present thesis has allowed the author to establish a protocol of laboratory procedures that produces consistent ages for bone collagen older than 30,000 cal BP

This protocol was implemented at the Max Planck Institute for Evolutionary Anthropology (MPI-EVA) and, in chapter 7 of the thesis, it is adopted to establish a chronological framework for the site of Les Cottés in France. This site has an almost uninterrupted sequence spanning from the Middle to the Upper Palaeolithic, including Mousterian, Châtelperronian and Aurignacian occupations. The AMS radiocarbon determinations obtained from bone collagen samples, pretreated according to the quality criteria developed in this thesis, accurately date not only the different human cultures which succeeded each other at Les Cottés, but also the climatic episodes and oscillations which characterized the Middle to Upper Palaeolithic transition. This case study demonstrates that AMS radiocarbon dating of mammal bone collagen can be reliably used for establishing the chronology of sites older than 30,000 ^{14}C years BP and with well-preserved deposits.

1. Introduction

As observed by Colin Renfrew, radiocarbon has played a revolutionary role in archaeology since the 1950s, first through the invention of scientific dating and second by providing calendar time scales for European prehistory in the Neolithic and Bronze Age periods. More recent examples are the improved constraint of the Eastern Mediterranean Late Bronze Age (Friedrich, et al., 2006), and the redefining of Egyptian chronology (Bruins, 2010, Bruins and Plicht, 2001, Bruins, et al., 2009, Plicht and Bruins, 2001, Ramsey, et al., 2010). However, for the Middle to Upper Palaeolithic (MUP) period in Europe, radiocarbon dating is still controversial. Limited dating evidence and the challenges of radiocarbon dating at the limits of the method mean that there is much room for speculation and controversial conclusions or opinions.

The key questions for this transitional period are if Neanderthals and Modern Humans (MH) overlapped in time, and if so, did they exchange technology, culture or genes, and why did Neanderthals disappear in central Europe at about the time when MH entered this region for the first time?

All these aspects have been widely discussed for several decades and there are numerous strong and divergent opinions. This debate continues mainly because one central element is unresolved, chronology. There are three main aspects which render radiocarbon dating difficult in this time range. This period is close to the limit of the dating range of radiocarbon, so statistical errors can be large. The low remaining ^{14}C activity makes dating materials very vulnerable to contamination *in situ* and in the lab, and, finally, calibration of radiocarbon ages to calendar ages at this antiquity was not possible until a few years ago.

This thesis addresses these crucial points. Radiocarbon calibration is now possible back to 50,000 cal BP (Reimer, et al., 2009) and moreover, claims of fundamental limitations are not justified (paper 1 in this thesis, Talamo et al. 2012). At the core of this thesis are studies undertaken to establish reliable methods for the extraction of good quality collagen from archaeological bone (paper 2 in this thesis, (Talamo and Richards, 2011)). Based on the experience obtained in these studies, an accurate time frame for key sites, showing the full MUP interval, has been created (paper 3 in this thesis, (Talamo, et al., 2012)).

This thesis is structured as follows: In chapter 2, the radiocarbon method is outlined. The present state of the calibration of the radiocarbon time scale is presented focusing on the recent extension and consolidation back to the time interval of the MUP. An overview of measurement techniques is given, with an emphasis on AMS as the main radiocarbon measurement technique in use today. The focus of chapter 3 is how to obtain the most reliable ages from bone samples from MUP sites. Bone from archaeological context is the preferred material to obtain dates, especially when compared to charcoal, but it presents challenges due to its open structure. In the past decade it has become apparent that the traditional pretreatment methods are insufficient for very old bone samples, because they may not be capable of removing modern contamination to a satisfactory level. The quantitative aspect of what the addition of a level of modern contaminant ^{14}C contribution would be is shown and development of new techniques including the use of ultrafiltration is discussed.

In chapter 4 the description of the implementation of the bone pretreatment and sample preparation to produce AMS graphite targets at the Max Planck Institute are outlined. The protocol of lab procedures is presented in detail, including documentation of the production of a database that was created during this thesis.

In chapter 5 (paper 1) the chronology of the Middle to Upper Palaeolithic transition is discussed. Chronology is crucial to the debate about all aspects of technological/cultural contact and exchange between Neanderthals and Anatomically Modern Humans in Europe. Radiocarbon is the backbone of the time frame during this period, even though it is close to the limit of the method because competing dating techniques such as OSL are much less precise or limited in their applicability. However, strong doubts have been raised about the validity of the radiocarbon technique, mainly for the following reasons: 1) Strong fluctuations of atmospheric ^{14}C have been postulated for the interval from 45 to 35 ka BP rendering radiocarbon ages ambiguous. 2) Until recently several different ^{14}C datasets were used for calibration in this time period, leaving room for interpretation of the synchronicity of techno-complexes or the role of climate anomalies in human evolution. In this paper it is shown that these issues are now fully resolved, because the large ^{14}C anomalies are shown to be artefacts beyond plausible physical limits for their magnitude. Previous inconsistencies between ^{14}C radiocarbon datasets have been resolved and a new radiocarbon calibration curve, IntCal09 (Reimer, et al., 2009) has been created.

In chapter 6 (paper 2) the crucial steps needed to obtain good quality collagen from ancient bones are studied in detail. Bone is a commonly used material for radiocarbon dating, yet, at ages close to the limit of the method (>30,000 BP), it is a substantial challenge to remove contamination and produce accurate ages. In this paper the preliminary results are reported of a dating study of two bones older than 30,000 years, which were each treated with a suite of pretreatment procedures, including ultrafiltration (Brown, et al., 1988). Substantial differences in the radiocarbon ages were observed, which are most likely linked to crucial steps in the removal of contamination both from the laboratory and from the bone itself.

In chapter 7 (paper 3) the lessons learned are applied to the site of Les Cottés in south-west France, which is one of the rare sites that possesses a complete and well-defined sequence, covering the Middle to Upper Palaeolithic transition period. We undertook an extensive radiocarbon dating program on mammal bone, which allows us to propose a chronological framework of five distinct phases dating from the Mousterian to the Early Aurignacian at this site.

2. Radiocarbon dating

2.1 History and the present state of radiocarbon calibration

The construction of accurate radiocarbon calibration curves is an ongoing aspect of the radiocarbon method. The most direct archives of radiocarbon activity in the past are tree-rings, because trees incorporate atmospheric CO_2 directly into their tissues. Tree-ring chronologies themselves are constructed and replicated using numerous individual trees, providing extremely precise annual calendar ages. The first internationally agreed calibration curve using tree-rings was published in 1986 dating back to 7300 cal BP (Stuiver, 1986). After various modifications and extensions the current recommended calibration curve is IntCal09 (Reimer, et al., 2009).The tree ring section of the IntCal09 curve, which dates back to 12,550 cal BP, closely represents a true record for the atmospheric radiocarbon fluctuations of the mid-latitude Northern Hemisphere.

Beyond the tree ring data, most radiocarbon samples in 'known-age' records are derived from non-terrestrial archives, such as marine deposits and corals, which are subject to reservoir effects. These reservoir effects are caused by the mixture of sources of ^{14}C of different age in the sample. In the case of marine carbonates, such as corals and foraminifera, the carbon in the tissue comes from the atmosphere, by gas exchange of CO_2 as well as from old carbon upwelling from the deep ocean. As a result of this mixing process organic matter living in the top layer of the ocean exhibits an apparent radiocarbon age, the marine reservoir age that can range several hundred years. To obtain the atmospheric ^{14}C level from marine carbonates the reservoir age must be accounted for. It is important to note that the marine reservoir correction is dependent on location and time, because the upwelling of old carbon and the rate of gas exchange may vary due to local mixing of the ocean and climate.

Another source for ^{14}C calibration is terrestrial carbonate, such as speleothemes (dropstones/stalagmites in caves). The carbonate of speleothemes is formed from CO_2 in topsoil and from carbonate dissolved from limestone (which is ^{14}C free). The ratio of the two contributions depends on several factors such as soil humidity, temperature, and carbonate content. These factors are variable over the earth and consequently the apparent ^{14}C age, called the dead carbon fraction, of newly formed speleothemes can vary between 0 and ca. 2000 years (Hendy, 1970). From this discussion of reservoir ages it is obvious that there is a potential of error when terrestrial carbonates are used for calibration, and in fact this situation occurred until 2009.

In 2006 the tree ring based calibration was extended back to 12,600 cal BP (Schaub, et al., 2008, Schaub, et al., 2007), and there is a floating pine chronology back to circa 14,200 cal BP (Hua, et al., 2009, Kromer, et al., 2004). Beyond this age there are a number of datasets available; here I give a short list of them.

- Cariaco Basin (Hughen, et al., 2006, Hughen, et al., 2004a, Hughen, et al., 1998, Hughen, et al., 1996, Hughen, et al., 2004b) provided sediment cores from an anoxic marine basin off the coast of Venezuela. The Late Glacial section is laminated in annual layers back to 14,500 cal BP. The older section back to 50,000 cal BP is not laminated, and its time scale must be obtained from elsewhere, e.g. by linking ^{18}O fluctuations in Cariaco core foraminifera to corresponding ^{18}O signals in layer-counted Greenland ice cores or to U/Th dated speleothemes in Hulu Cave, China.
- Corals from the Atlantic and Pacific Ocean dated by U/Th (Bard, et al., 1998, Burr, et al., 1998, Cutler, et al., 2004, Fairbanks, et al., 2005).
- Subtropical Atlantic marine sediments from the Iberian Margin (Bard, et al., 2004).
- Bahamian Stalagmite (Beck, et al., 2001).
- Arabian speleothemes from a cave on Socotra Island in the Indian Ocean, south of the Arabian coast. This stalagmite grew between about 42,000 and 55,000 cal BP (Weyhenmeyer, et al., 2003).
- North Atlantic Marine sediment data, of both benthic and planktonic foraminifera from several mid- to high latitude North Atlantic marine cores (Kreveld, et al., 2000, Voelker, et al., 2000)
- Lake Suigetsu in Japan (Kitagawa and van der Plicht, 1998, Staff, et al., 2009) which are laminated lake sediments.
- Lake Lisan (Hajdas, et al., 2003, Hajdas, et al., 2004) limnic carbonates, which require a strong dead carbon correction.

Only U/Th dated datasets (corals, speleothemes) have an independent time scale, and the remaining datasets obtained their age/depth relation by comparison to another archive, e.g. Greenland ice cores. Therefore, differences between those datasets can arise not only from radiocarbon or reservoir errors but also from errors in the absolute time scale. This was the main reason why the IntCal04 working group discouraged the use of calibration curves beyond 26,000 cal BP. However, an average curve of all datasets was calculated and given as NotCal04 (Plicht, et al., 2004), to indicate that it should *not* be used for calibration.

In 2007 radiocarbon calibration saw substantial progress. The European tree-ring chronology was extended by Schaub et al. (2007) back to 12,593 cal BP; in addition, floating sections of wood from Germany, Italy, Switzerland and France now extend well back into the Late Glacial period (Hua, et al., 2009). Moreover, in New Zealand, *Kauri* trees were found with ages that extend beyond the range of radiocarbon and are currently being dated in the age range between 25,000-55,000 BP (Hogg, et al., 2007, Turney, et al., 2007). These finds do not yet provide a continuous tree-ring chronology but they do provide us the possibility to better understand the fluctuation of radiocarbon concentration in the atmosphere in the past.

A major part of the differences between the high-resolution Cariaco dataset and coral data were resolved when the Cariaco age/depth model was changed to be based on the ^{230}Th-dated Hulu Cave speleothemes instead of on Greenland ice cores (Hughen, et al., 2006). The age model was mapped onto the Cariaco Basin ^{14}C series by correlation of associated $\delta^{18}O$ and grey scale variations that define DO events. The new Cariaco Basin ^{14}C record linked to Hulu Cave provides an improved high-resolution marine-based calibration dataset, especially for the age range of 15,000 to 50,000 years (Figure 2.1).

The calendar age errors for the Cariaco-Hulu age model are significantly smaller than previously reported due to high precision U/Th dating of the Hulu cave series. What still remains is the uncertainty in the marine reservoir age. Evidence for only a small variation in reservoir age is provided by the agreement between Cariaco and German pine ^{14}C dates during the last deglaciation and early Holocene (Hughen, et al., 2000). In contrast, a floating tree ring chronology and ^{14}C record that has been tentatively anchored to Cariaco data suggests that the reservoir age may have changed during the

Allerød and transition into the early Younger Dryas (Hua, et al., 2009, Kromer, et al., 2004).

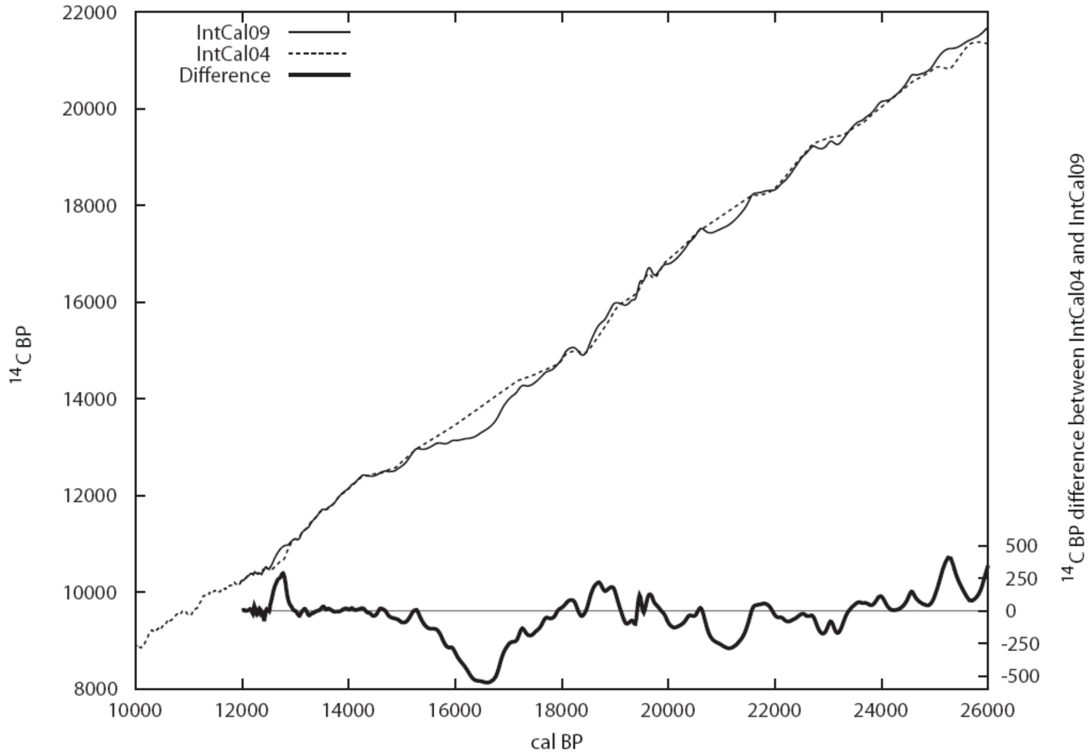
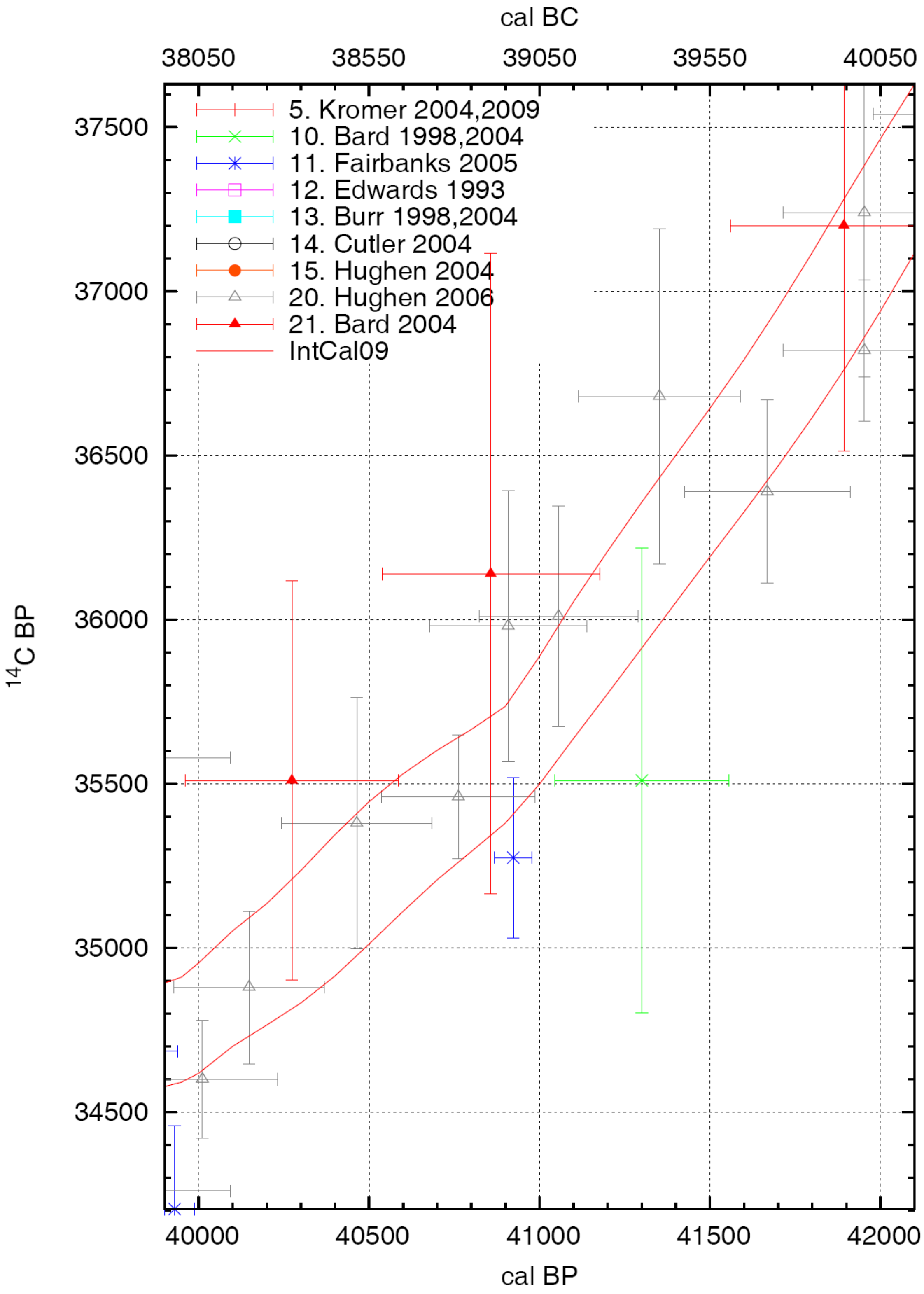
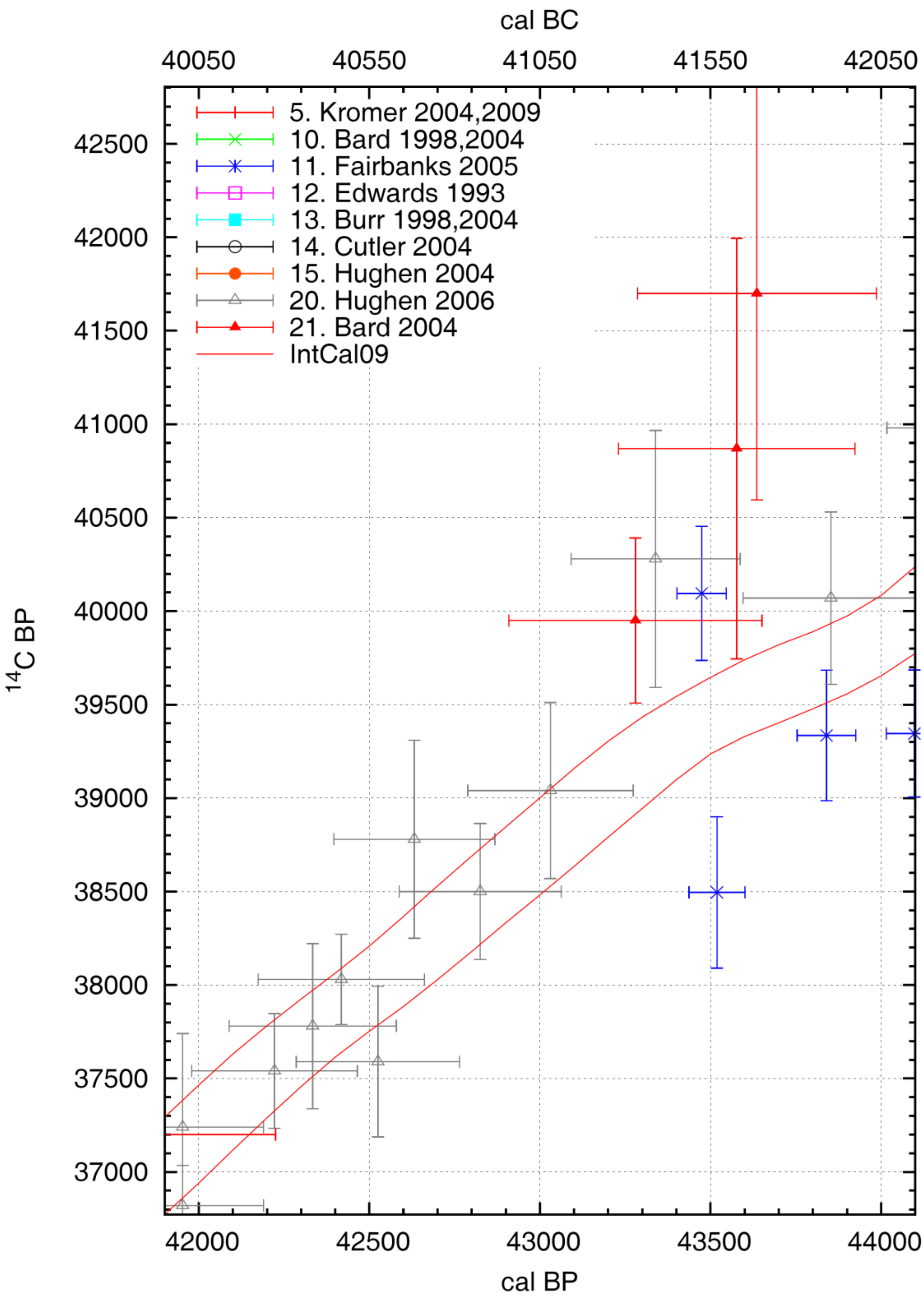


Figure 2.1 Difference between the calibration data curves IntCal04 and IntCal09 in the interval 10,000 to 26,000 cal BP. The shifts are mainly caused by the change of the Cariaco time scale to the Hulu Cave U/Th time scale(Reimer, et al., 2009).

Consequently, the IntCal working group constructed a new calibration curve back to 50,000 cal BP, which was accepted by the radiocarbon community (Reimer, et al., 2009). It is currently considered to be the best available calibration dataset and the interval of interest for this thesis is shown in figure 2.2.

The strong discrepancies between the Bahamian speleothemes ^{14}C dataset (Beck, et al., 2001) for ages older than 35,000 cal BP were resolved when the speleotheme data were corrected for background variations and fluctuations in dead carbon fraction (Beck, et al., 2008, Hoffmann, et al., 2008, Hoffmann, et al., 2010).


cal BC
38050
38550
39050
39550
40050
5. Kromer 2004,2009
10. Bard 1998,2004
11. Fairbanks 2005
12. Edwards 1993
13. Burr 1998,2004
14. Cutler 2004
15. Hughen 2004
20. Hughen 2006
21. Bard 2004
IntCal09
37500
37000
36500
36000
35500
35000
34500
14C BP
40000
40500
41000
41500
42000
cal BP


cal BC
40050
40550
41050
41550
42050
5. Kromer 2004,2009
10. Bard 1998,2004
11. Fairbanks 2005
12. Edwards 1993
13. Burr 1998,2004
14. Cutler 2004
15. Hughen 2004
20. Hughen 2006
21. Bard 2004
IntCal09
42500
42000
41500
41000
40500
40000
39500
39000
38500
38000
37500
37000
14C BP
42000
42500
43000
43500
44000
cal BP

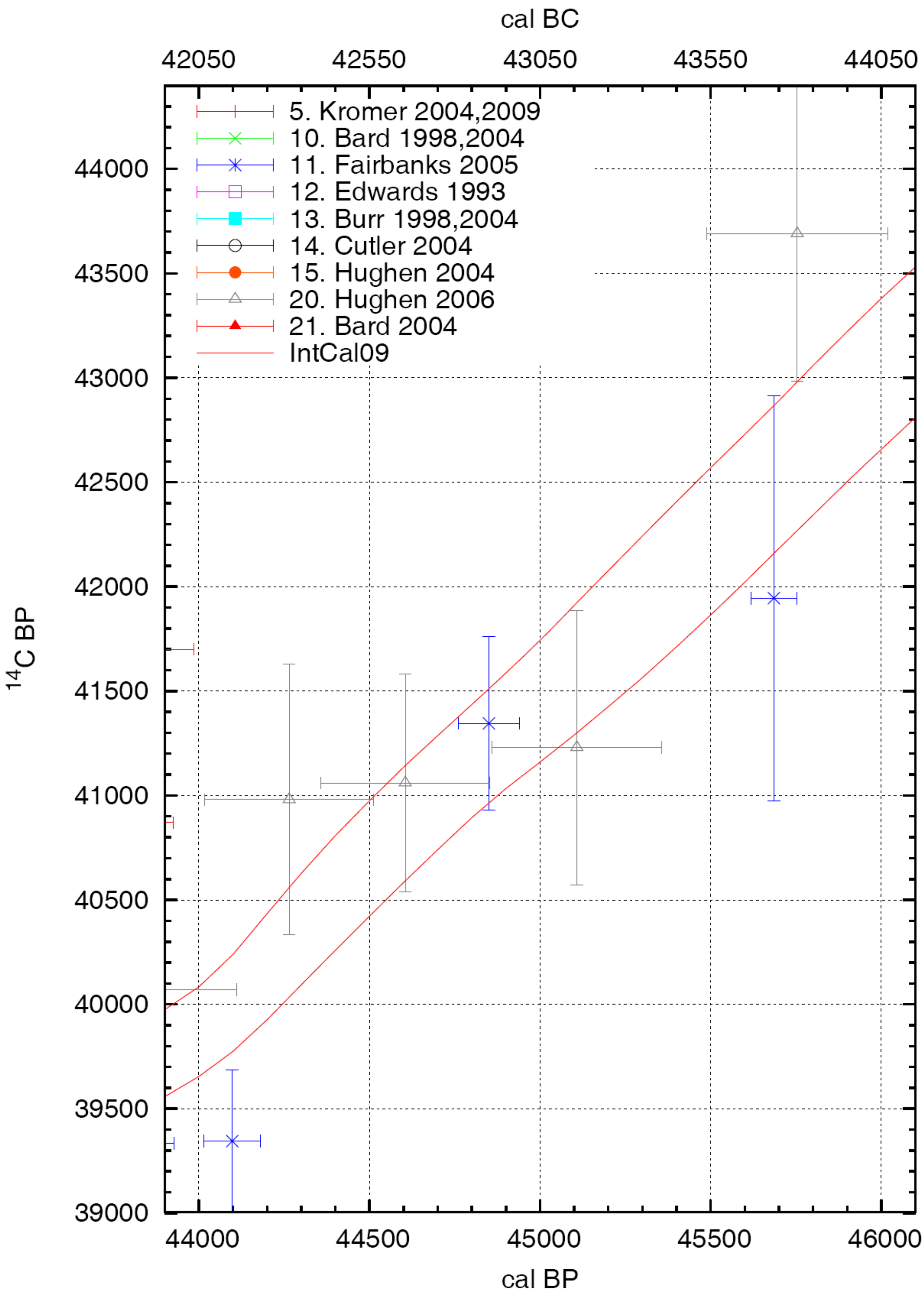


Figure 2.2 Detailed view of the new calibration dataset IntCal09 (Reimer, et al., 2009), including the original datasets from which IntCal09 was calculated.

2.2 ^{14}C Dating

^{14}C is created in the upper atmosphere due to the interaction of cosmic-ray generated neutrons with nitrogen-14 (^{14}N) causing the nuclear reaction:

$$^{14}N + n \rightarrow {}^{14}C + p$$

^{14}C is transported from the atmosphere to the global carbon reservoirs, where the majority finally ends up in marine and continental sediments. After formation, ^{14}C quickly combines with oxygen, and enters the carbon system as $^{14}CO_2$, which is chemically identical to ordinary $^{12}CO_2$, and thus is well mixed within the atmosphere. From this boundary condition the two main fields of radiocarbon dating originate:

a) Photosynthesis fixes CO_2, and hence $^{14}CO_2$, into stable plant matter and into the global food web, which is the basis for the dating of *organic* samples.

b) CO_2 becomes part of the chemical pathways of terrestrial or marine carbonates, which allows the dating of *inorganic* carbonate samples and groundwater (Figure 2.3).

In this thesis we are concerned only with the dating of organic material, therefore I will not discuss carbonate dating further.

Radioactive decay follows the general law:

(1) $$A = A_0 e^{-\lambda t}$$

(2) $$t = 1/\lambda * \ln (A_0/A)$$

where A_0 is the original ^{14}C activity, which is directly linked to the atmospheric ^{14}C activity in the case of plants and indirectly in the case of fauna, A is the measured ^{14}C activity today, and t is the time since the burial of the organism (more specifically since the end of the formation of the carbonaceous material that is dated), and λ is the decay constant.

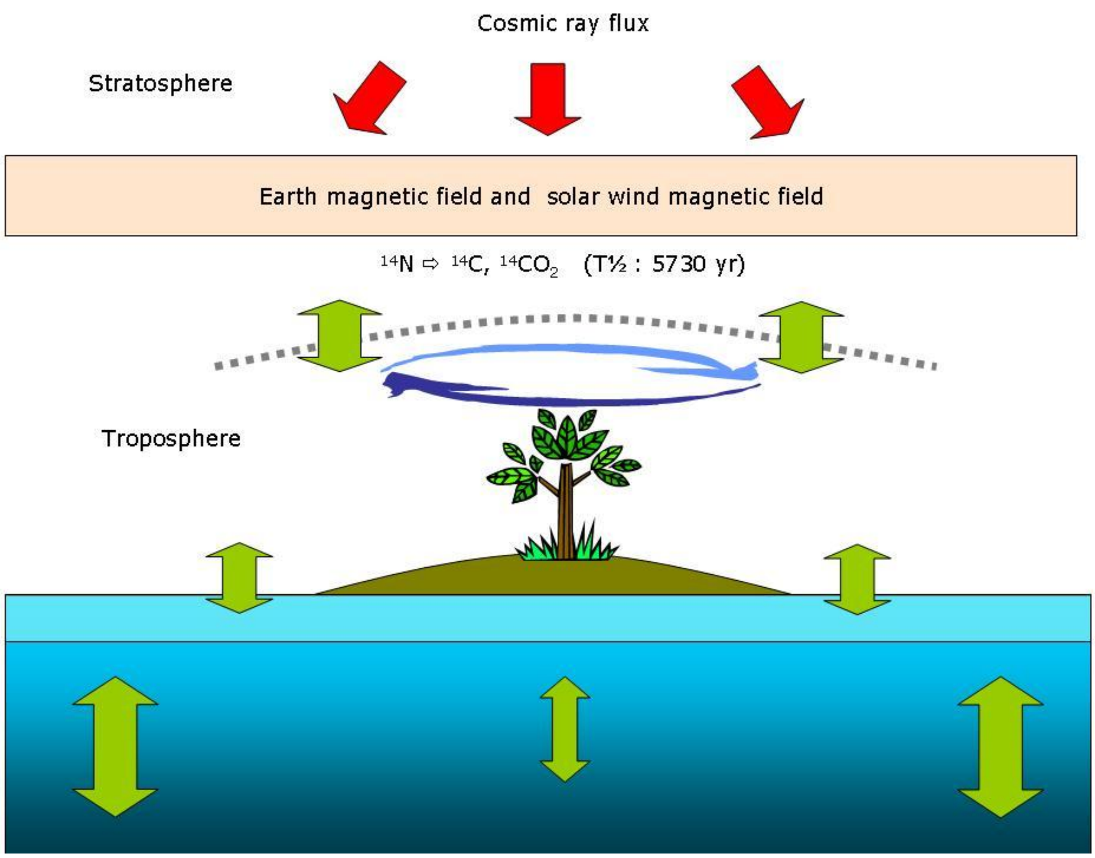


Figure 2.3 Schematic representation of the carbon cycle and the production of ^{14}C, main carbon reservoirs are deep ocean (blue), surface ocean mixed layer (light blue), atmosphere and biosphere.

λ is connected to the radiocarbon half-life, by:

(3) $$A/A_0 = ½ = e^{-\lambda T½}$$

so that

(4) $$\lambda = (\ln 2)/T_{½} = 1/8033\ [1/yr]$$

The value of the half–life established by Libby was 5568 years (Libby, 1955). A more accurate value was determined later to 5730±40 years (Godwin, 1962, Olsson, 1968, Stuiver and Polach, 1977). The Libby value is still used conventionally (Stuiver and Polach, 1977) because so many published radiocarbon dates were based on it and the calibration of radiocarbon ages (see below) eliminates any error in the true value of the half-life.

All organic material can be used for radiocarbon dating. Not only the most common types such as wood, charcoal, bones, charred bones, and peat, but also pottery or ancient iron containing carbon or organic inclusions, the organic fractions of palaeosols or clay sediments, paper, textiles, hair, teeth, antler, ivory, and canvas (Mook and Streurman, 1981).

2.3 Fractionation

The calculation of a radiocarbon age requires a correction to account for the isotope. fractionation that occurs when carbon is exchanged between phases (gas, liquid, solid). The heavy isotopes ^{13}C and ^{14}C are discriminated against in these exchanges in comparison to ^{12}C. For radiocarbon this fractionation effect can be easily corrected because the stable isotope ^{13}C undergoes fractionation at half the magnitude of ^{14}C. Therefore, in all radiocarbon analyses, the ratio $^{13}C/^{12}C$ is also measured using an isotope ratio mass spectrometer and is then used to correct for the $^{14}C/^{12}C$ fractionation
^{13}C measurements are reported in the δ notation, which is defined as the relative differences of ^{13}C /^{12}C ratio in the sample compared to a standard, in units of parts per thousand (per mille, ‰). In this notation organic samples based on the photosynthetic C_3 cycle have $\delta^{13}C$ at levels around -25‰ and bone samples are slightly enriched with $\delta^{13}C$ levels around -19‰ (Lee-Thorp, 2008). In cases where C_3 samples are not the major part of the diet, bone ^{13}C will deviate from this range (Lee-Thorp, 2008).

2.4 Calibration

To calculate the true (calendar) age from a radiocarbon age according to equation (2) we need to know the radiocarbon activity of the atmosphere in the past, A_0. This information can be obtained with the help of an independent dating method that provides radiocarbon samples of known age, such as tree rings dated by dendrochronology or carbonates dated by U/Th. The radiocarbon ages of these samples are calculated using equation (2) but with an A_0 assumed constant and identical to 95% of the radiocarbon activity of the radiocarbon standard Oxalic Acid at 1950 AD. The age obtained in this procedure is no longer a calendar age because A_0 may have varied in the past so it is termed an uncalibrated ^{14}C age. However, by measuring pairs of radiocarbon ages (equation (2)) versus calendar ages we can establish calibration curves, which are used to transform uncalibrated ages to true ages. It is important to note that in this calibration procedure any fluctuation of the radiocarbon activity in the past A_0 is corrected and any error in the determination of the half-life λ is cancelled.

Radiocarbon ages that are calculated according to equation (2) and corrected for isotope fractionation are called uncalibrated ages; in this thesis these are denoted as ^{14}C **BP**, i.e. radiocarbon years before 1950 AD. Calibrated ages are denoted as **cal BP** or **cal BC/AD,** which are calendar years before 1950 AD (Kromer, et al., 1996, Stuiver and Polach, 1977) and Cal BP is also used for calendar ages obtained through other dating methods, such as Ar/Ar or U/Th. Ranges of calibrated ages (i.e. minimum/maximum) can be determined through a simple graphical procedure where the limits of the radiocarbon age interval are transferred via the calibration curve to the calendar axis. More detailed information about the probability distribution is available by means of computer programs_such as CALIB (Stuiver and Reimer, 1993), CalPal (Joris and Weninger, 1998), or OxCal (Bronk Ramsey, 2009, Ramsey, 2001).

2.5 Measurement techniques

In the last 30 years Accelerator Mass Spectrometry (AMS) has become one of the most important tools in prehistory and the geosciences and is used to perform the majority of ^{14}C measurements. In AMS, one counts ^{14}C *atoms,* while the previously used decay-counting methods only registered radioactive *decays* (β particles) (Kromer and Münnich, 1992). This makes the AMS technique 1,000 to 10,000 times more sensitive than the counting of radioactive decay. The main principle of AMS is to detect the different isotopes of carbon (^{12}C, ^{13}C, ^{14}C) by separating them according to their respective mass, like in a conventional isotope ratio mass spectrometer. The challenge with respect to the detection of ^{14}C arises from the extremely low ratio of ^{14}C in respect to ^{12}C because for modern samples $^{14}C/^{12}C$ is just 10^{-12}. This small quantity makes radiocarbon difficult to detect, because there are interfering molecules of mass 14, e.g. $^{13}C^{1}H$. These molecules are eliminated by accelerating the beam of carbon ions and stripping them in a gas, which breaks up the molecules into their individual atoms and subsequently removes them from the beam (see below).

2.5.1 Requirements for AMS

There are many reviews of AMS radiocarbon dating (Fedi, et al., 2007, Fifield, 1999, Jull, 2007, Jull and Burr, 2006, Kieser, et al., 1990, McNichol, et al., 2001, Tuniz, et al., 1998). Here I will focus on the main steps. For AMS, after pretreatment of the sample to remove contamination, the ^{14}C measurement starts with the combustion of the carbon in a sample to CO_2, which is then converted to filamentous carbon using a catalytic reduction process. The resultant material is commonly called “graphite”. Some laboratories use CO_2 gas directly instead of graphite, the advantage being that the combustion and graphitisation is eliminated and that it is possible to use just 5 to 100 µg of sample instead of 1mg (Ruff, et al., 2009).

After graphitization, the carbon is pressed into a target and placed in a sample carousel, which contains a suite of samples, standards, and blanks. The carousel is placed in the accelerator’s ion source. Negative carbon (*C*-) ions are produced by a sputter ion source. The initial separation of the negative ions by mass is performed by low energy magnet. The ions then enter the accelerator which uses a high voltage of several hundred kilovolt to a million volts in order to accelerate the *C*- ions. After the acceleration the beam passes a stripping canal where the C- ions interact with a gas. Molecules such as CH^- are destroyed in this process, and the charge of the ions is reversed. The now positively charged C+ ions are accelerated to the exit of the accelerator and separated by energy and charge, using the high energy magnet and electrostatic deflector (ESA). Finally ^{12}C and ^{13}C currents are measured in Faraday cups and ^{14}C is detected in a special detector, usually a gas counter (see Figure 2.4).

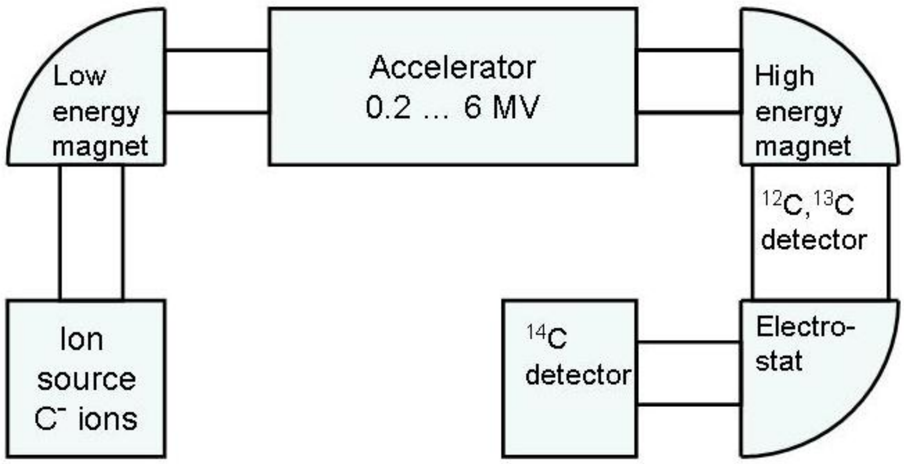


Figure 2.4 Schematic representation of an AMS system.

Recently small and compact radiocarbon dating systems have been introduced (Suter, et al., 2000, Synal, et al., 2007, Synal, et al., 2000), allowing ^{14}C separation to be undertaken at much lower energies (e.g. 0.2MV) than the standard AMS accelerators.

2.5.2 Advantages & disadvantages

The advantages of the AMS method over conventional decay counting are:

- Much smaller sample size is needed, which then allows the almost non-destructive dating of valuable objects (fossil hominids, documents, textiles) and the dating of specific components such seeds or other fractions of plants found in, for example, mortar or pottery.
- fast measurement procedure (30 minutes to 1hr).
- more rigorous sample pretreatment, because of the low amount of carbon required for AMS
- selection of specific fractions of inhomogeneous samples
- capability to sub-sample and repeat the measurements
- High age limit due to low AMS blank

The disadvantages of the AMS technique are:

- complex and expensive spectrometer
- the challenge to obtain stable conditions to measure isotope ratios accurately

- small sample size, which at first glance is the key advantage, but at the same time could be a disadvantage because it makes the method vulnerable to low levels of contamination either within the sample or from the pretreatment process.

2.6 Standard, background and error

Like in any mass spectrometric measurement, in AMS radiocarbon dates are determined relative to a standard, which is Oxalic Acid (Stuiver and Polach, 1977). Pretreatment and measurement procedures may introduce ^{14}C or ions which are identified as ^{14}C. These components are identified by measuring ^{14}C free material (blank samples).

We distinguish two types of uncertainty, which applies to all radiocarbon measurements (Cook and Plicht, 2007, Scott, 2007).

1) *Statistical error*, which is caused by random processes (Gaussian or Poisson error). Radiocarbon age is determined from ratio of ^{14}C to ^{12}C and in the spectrometer only a limited number of ions are detected. Therefore, like in the classical urn experiment of sampling the ratio of rare red and abundant black balls, the determination of the ratio will be associated with an uncertainty, in our case proportional to $1/\sqrt{N}$, where N is the number of ^{14}C ions (or the number of the red balls in the urn experiment) detected.

This means that the statistical error will be lower the longer the sample is measured in the AMS and the higher the ^{14}C activity in the sample is (obviously measurement times are subject to economic considerations). The total statistical error is the combination of sample, standard and blank statistical error. In each AMS run several standard and blank samples are measured and hence the statistical error of the sample usually dominates the total error. This is especially true for older samples like those dealt with in this thesis. Here an important contribution to the total error comes from the blank, because the sample ^{14}C activity is close to the background.

2) *Systematic error*, arising from sample properties and pretreatment. At every stage of sample selection and handling the original $^{14}C/^{12}C$ ratio may be altered by the addition of modern or old carbon. The contribution to the overall error is more difficult to quantify and it requires additional measurement of test samples of known activity. An additional complication comes from the fact that the contributions may depend on the amount of carbon in the sample (Vogel, et al., 1987).

3 Bone dating background

Bone is a body tissue composed of bioapatite (mineral, crystalline carbonate–hydroxylapatite inorganic phase 60-70 wt%), collagen (proteins, the organic fraction 20-30 wt%), and water (ca.10 wt%) (Figure 3.1).

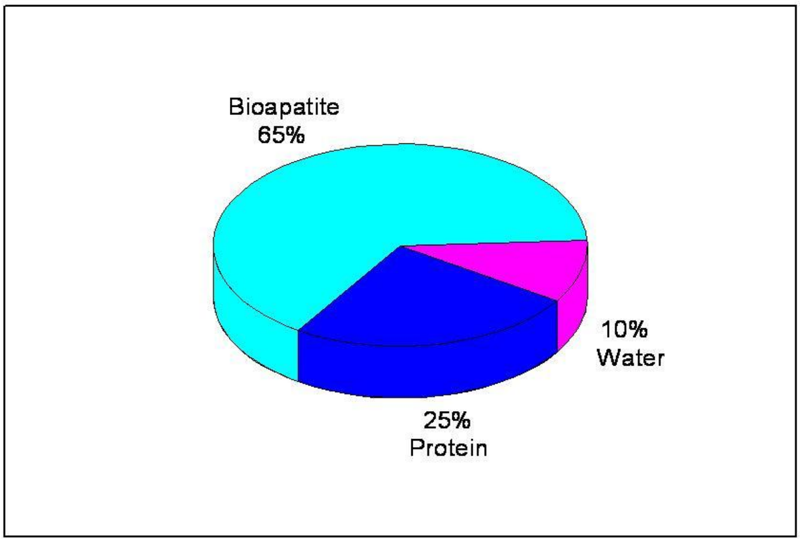


Figure 3.1 Bone composition mineral, crystalline carbonate–hydroxylapatite inorganic phase 60-70 wt%, proteins, the organic fraction 20-30 wt% and circa 10% of water.

Bone collagen is an important substrate for radiocarbon dating (Arnold and Libby, 1951), and stable isotopic analysis (Collins, et al., 2002). In addition, bone is a useful material to date in archaeology as it can be the direct target of the event being dated (i.e. dating a human itself) or closely associated to the event of interest (i.e. animal remains from a site, bone artefacts).

Despite the utility of using bone for radiocarbon dating there are often problems in dating bone from archaeological sites as it is at risk from contamination and it is often degraded. Degradation involves structural alteration and the gradual breakup of the protein chains. Background contamination can then come from the inclusion of exogenous carbonaceous contaminants, either *in situ*, during the excavation, or in the laboratory.

Bones, of course, can be contaminated by old or modern carbon. The shift in radiocarbon age from the true age due to the addition of either of these is illustrated by a series of experiments where I added 10 microgram of either modern or ^{14}C free carbon to 1 mg of the original carbon deriving from different time periods (Table 3.I).

Table 3.I Series of experiments where I have added 10 microgram of either modern or ^{14}C free carbon to 1 mg of the original carbon deriving from different time periods

True age	**Period**	**pmC sample**	**pmC modern added**	**Contam. age**	**Diff. years**	**Weight modern**
42,000	Neanderthal	0.54	1.00	33,545	8455	0.01 mg
25,000	Upper Palaeolithic	4.45	1.00	23,372	1628	0.01 mg
6,000	Neolithic	47.38	1.00	5,832	168	0.01 mg
3,000	Late Bronze age	68.83	1.00	2,884	116	0.01 mg
True age	**Period**	**pmC sample**	**pmC contam.**	**Contam. age**	**Diff. years**	**Weight fossil C added**
35,000	Neanderthal	1.28	1.27	35,080	80	0.01 mg
6,000	Neolithic	47.38	46.91	6,080	80	0.01 mg
3,000	Late Bronze age	68.83	68.15	3,080	80	0.01 mg

As can be seen, a sample dating to 42,000 radiocarbon years, with just 10 micrograms of modern contamination, is shifted to an apparent age of 33,000 years, which is more than 8000 years younger. For an Upper Palaeolithic sample dating to 25,000 years the contamination changes the true age by 1,628 years. For Neolithic and Late Bronze Age samples the shift is smaller, but still much higher than the typical radiocarbon error of 25 to 40 years for these time periods. Adding 1% of fossil material, e.g. from organic solvents of petrochemical origin, shifts all dates to older ages by 80 years. Therefore, fossil contamination is less severe for old samples but for the younger samples it is still larger than the age error. There are a number of real examples of these problems (Conard and Bolus, 2008, Higham, et al., 2006a, Jacobi, et al., 2006).

Initial attempts to date bone apatite largely failed (see review by Surovell, 2000) because carbonates exchange readily with surrounding inorganic carbonate (e.g. dissolved in ground water). In contrast, collagen is much more stable. Longin (1971) proposed a method to isolate bone collagen. This aspect is treated in detail in chapter 6 (introduction of paper (Talamo and Richards, 2011)) As an indicator of contamination and/or degradation of collagen different authors use C:N ratios, $\delta\ ^{13}C$ and $\delta\ ^{15}N$, and amino acid composition (Ambrose, 1990, DeNiro, 1985, Harbeck and Grupe, 2009, Hedges, 2002, Klinken, 1999, Schoeninger, et al., 1989, Strydonck, et al., 2004). Usually it is assumed that contamination is likely when atomic C:N ratio falls outside the range observed for modern animals and humans (2.9-3.6). $\delta^{13}C$ and $\delta^{15}N$ values in bone collagen depends on diet, used to distinguish herbivores from carnivores and furthermore between marine and terrestrial diet. Typical values for animal bone collagen are taken from Strydonck et al.(2004, p.128), and are shown here in table 3.II.

Table 3. II Typical values for animal bone collagen, taken from Strydonck et al. (2004)

Bone collagen from animals having q 100% diet of:	**$\delta^{13}C$‰**	**$\delta^{15}N$‰**
C-3	-21	+5
meat C-3 herbivores	-18	+8
C-4 plants	-7	+5
marine food	-13	+18
river fish	-24	+16
lake fish	-20	+16

An illustrative figure of regional variations in the isotopic values, and of variations among species, is shown in Katzenberg (2008, p.427). The full range of these parameters needs to be considered to determine if collagen extracted from an archaeological bone is of sufficiently good quality (Lee-Thorp, 2008, Richards and Hedges, 1999, Richards and Hedges, 2003, Richards, et al., 2005, Richards, et al., 2000, Richards, et al., 2008). Another simple but important criterion is the quantity of collagen that can be recovered. Usually a limit of 1% weight is considered necessary as a minimum condition (Hedges and Van Klinken, 1992) and samples of lower yield are potentionally problematic (Brock, et al., 2007, Higham, et al., 2006b).

There are advanced techniques to characterize the state of preservation of bone, such as Fourier transform infrared spectroscopy (FT-IR) which gives an index of crystallinity of the bone mineral (Weiner and Bar-Yosef, 1990, Yizhaq, et al., 2005), X-ray diffraction (XRD) and transmission electron microscopy (TEM) (Reiche, et al., 2002).

4 Establishing ^{14}C dating at MPI-EVA

In this thesis I focus on the pretreatment of bone to obtain pure collagen and convert it into graphite for AMS measurements to obtain reliable radiocarbon dates. The individual steps of pretreatment involve extraction of collagen from bone, cleaning all the equipment used in the procedures and the conversion of collagen to graphite (graphitization). I chose to use the extraction method (method C in chapter 6; paper (Talamo and Richards, 2011)) that best avoids lab contamination. In the field I collected good quality bone samples, which were selected due to their potential for high carbon yields.

All the bone samples presented in this thesis were subject to the following pretreatment procedures, usually in batches of up to 12 samples:

- Entry in database
- Pulverisation of bone
- Decalcification
- Removal of humics
- Gelatinization
- Cleaning of the filters and checking for the removal of contamination
- Ultrafiltration
- Freeze drying

These procedures are outlined in detail below.

4. 1 Database entry

A S-EVA number is assigned to the sample and it is inserted in our database. Important fields of the sample record are S-EVA number, submitter name, sample code assigned by the submitter, name of the project or site, weight of the sample as received and a photo. All the subsequent pretreatment steps are entered into the database.

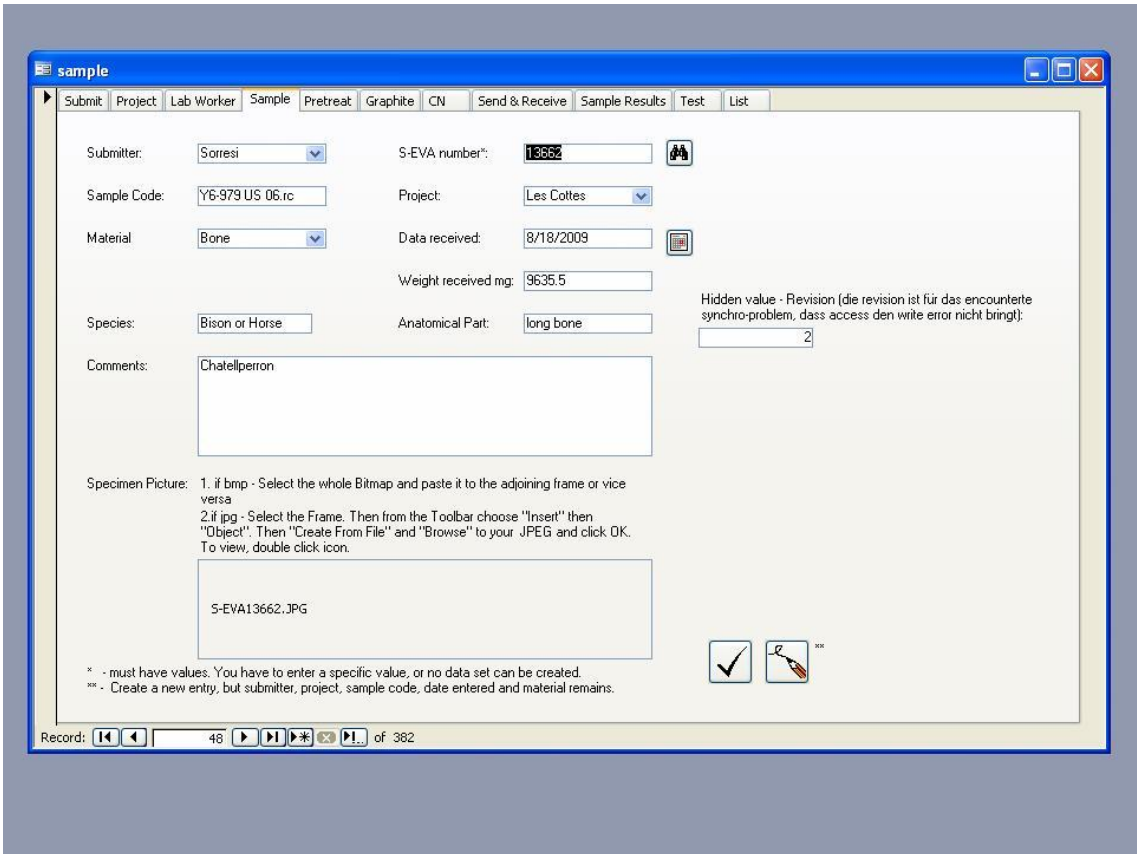


Figure 4.1 Entry page of the database at MPI

4.2 Pulverisation of bone

The bone is first cleaned by sand-blasting and then, using a dental drill, 500 mg of bone powder is taken. In the case of bone fragments a mortar is used to grind the bone. Bone powder is essential for a fast and efficient decalcification.

4.3 Decalcification

The sample is kept in 0.5M HCl at room temperature until no CO_2 effervescence is observed, which usually takes 4 hours. This interval is divided into two 2-hour segments after which the sample is rinsed in ultrapure water and centrifuged. Then it is kept overnight in 0.5 M HCl in a refrigerator.

4.4 Removal of humics

The following day 0.1M NaOH is added for 30 minutes to remove humics, which could have been introduced to the bone sample by ground water during the interval between burial and excavation. The NaOH step must be complemented by a final HCl step (15 minutes), to remove potential contamination from modern CO_2 taken up by the NaOH.

4.5 Gelatinization

The gelatinization step follows the method outlined in Longin (1971), at pH3 in a heater block at 75°C for 20h.

4.6 Cleaning of the filters and checking for the removal of contamination

The cleaning procedures for the ultrafilters are essential for a valid radiocarbon date (Higham, et al., 2006b). The ultrafilters are Sartorius “Vivaspin 15” of 30 KDalton size with 50ml plastic centrifuge tubes. The cleaning is designed to remove carbon-containing humectants. It is very important not to clean the filters more than 24 hours in advance as they may soften or dry out. The ultrafilters are rinsed 5 times in the centrifuge with ultrapure water for 15 to 20 minutes. Then they are bathed in ca 1 liter of ultrapure water in the ultrasonic bath for one hour, and after that rinsed 3 times.
Before the 4th centrifuge step, 1 ml of ultrapure water is added to one of the filters, and removed for analysis of remaining carbon. For this measurement the water sample is freeze-dried, another *ca*. 20 µl ultrapure water is added and inserted with *ca*. 8 mg chromosorb into a large tin capsule. The amount of carbon is determined by combustion in the EA (see step below). The burn yield must be below 5 to 10 µg C for this sample to indicate that the filter is not contaminated by carbon-containing humectants.
The Eeze-Filter™’ (Elkay Laboratory Products (UK) Ltd.) is bathed for 20 minutes in *ca*.1 liter of ultrapure water.

4.7 Ultrafiltration

The gelatine obtained in step 5 is filtered in the Eeze-filter to remove mineral particles. Then the liquid is transferred to the ultrafilter and centrifuged until the liquid in the filter is below 0.5 ml.

4.8 Freeze-drying

The filtered sample is frozen to a solid. The tube is sealed with parafilm and kept in a -28°C freezer. The tubes are kept in an inclined position so that the solution is thinly distributed along the tube, with no more than 10 mm at the thickest part. The samples stay in the freezer for at least 12 hours so that they are solidly frozen. Then the samples are transferred to the freeze-drier and lyophilized for 48 hours.

The specific lab protocol procedures for each sample (Figure 4.2) is entered into the database (Figure 4.3).

Collagen extraction protocol

S-EVA [ ] Notes ______________________

Date ______________________ Total Bone ______________________ mg

Sample taken ______________________ mg Rest ______________________ mg

Date ____________ HCl for 2h ☐ HCl for 2h ☐ Fridge all night ____________

Date ____________
HCl for 2h ☐ Wash 3 times H2O ☐
NaOH 30min ☐ Wash 3 times H2O ☐
HCl 15min ☐ Wash 3 times H2O ☐

Date Heater in with 10ml of Ph3 ______________ Time in ______________

Date Heater out ______________ Time out ______________ 75ºC for 20h

Cleaning Eeze – Filter

Date ______________ 20 minutes in Ultrasonic water

Cleaning Ultrafilter procedures

Date ______________

15 min centrifuge with H2O pure ☐
15 min centrifuge with H2O pure ☐
1 Hour in Ultrasonic water ☐
15 min centrifuge with H2O pure ☐
15 min centrifuge with H2O pure ☐
15 min centrifuge with H2O ☐

Date Centrifuge and Samples in the fridge ______________________

Date Freeze – dryer in ______________ Time in ______________

Date Freeze – dryer out ______________ Time out ______________

Collagen mg ______________

Circa 0.5mg of Collagen for C/N ______________________

Sent Collagen ______________ mg Remaining Collagen at MPI ______________ mg
Sent Collagen to ______________________ Date ______________
Graphite ☐ Sent graphite to ______________________ Date ______________

Radiocarbon Age ______________ Collagen back from the AMS Lab ______________ mg

Figure 4.2 Lab protocol with all the procedures made during the pretreatment

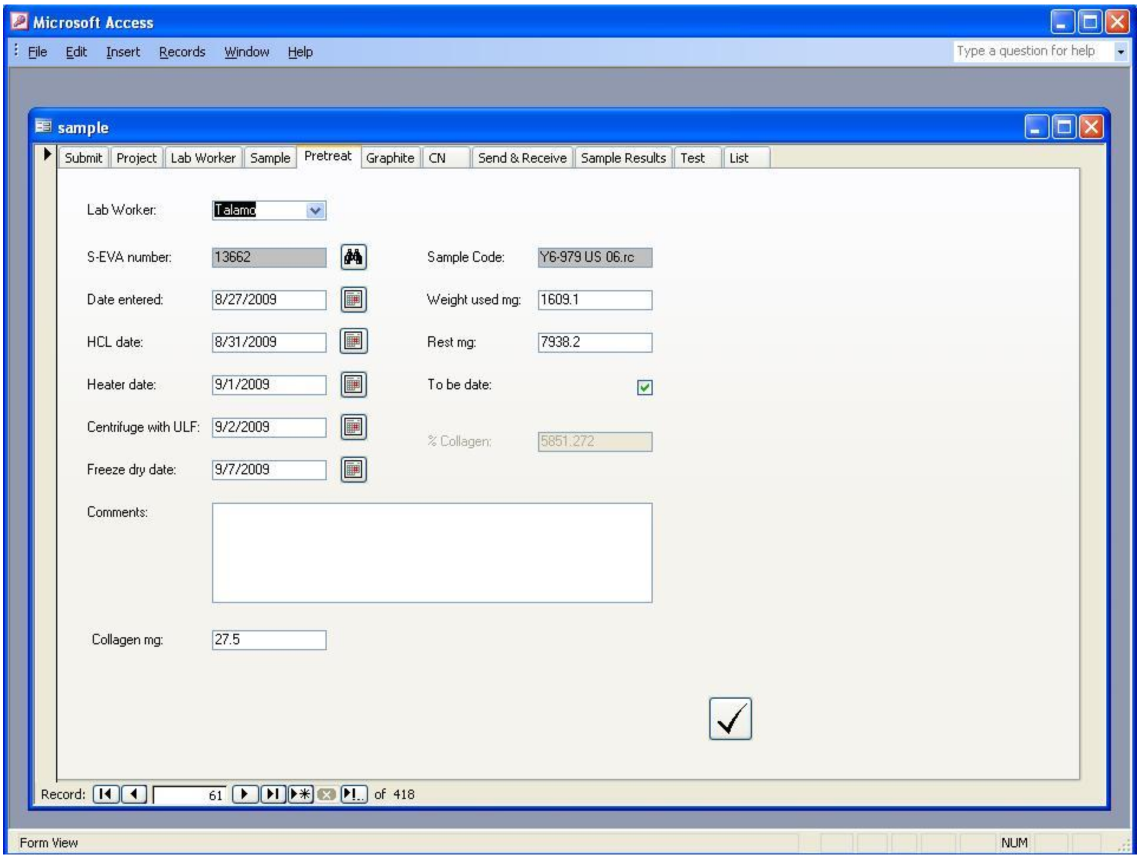


Figure 4.3 Input of the lab protocol of the pretreatment and calculation of the % collagen

Important parameters are the date of the various steps, the weight used and the final weight of the collagen. At this point the collagen yield is available, which should be a minimum of 5 mg for 500 mg initial bone powder (1% yield limit). The minimum amount of collagen for graphitization is 3 mg.

4.1 Graphitization steps

All the collagen obtained after the pretreatment outlined above is graphitized according to the following procedures:

- Loading of collagen into tin caps
- Combustion in an Elemental Analyser (EA)
- Determination of carbon yield and C:N ratio
- Determination of $\delta^{13}C$ and $\delta^{15}N$ in a mass spectrometer
- Cleaning the CO_2 gas containers and conditioning of the iron catalyst
- Collection of CO_2 in the rigs

- Addition of hydrogen
- Conversion of CO_2 into graphite in the graphitizer
- Check of graphitization parameters
- Preparation of blank samples
- Preparation of shipment to an AMS facility and submission to the AMS laboratory for radiocarbon measurement.

4.1.1 Loading collagen into tin caps

The collagen is loaded into tin capsules, which are pre-cleaned in cyclohexane and acetone. An empty tin capsule is combusted to check that the blank contribution is < 2 μg C.

4.1.2 Combustion in Elemental Analyser (EA)

The collagen is combusted in the EA (CHN analyzer) system, in a sequence of up to 10 samples limited by the amount of available gas containers. Each sample combustion is preceded by the combustion of an empty tin capsule to purge the system. The sample is injected into the furnace together with a stream of helium and oxygen. The combustion furnace is at a temperature of 1000°C and with the addition of tin the combustion temperature reaches 1500°C; the subsequent reduction furnace is used to complete the combustion at 600 °C (Figure 4.4).

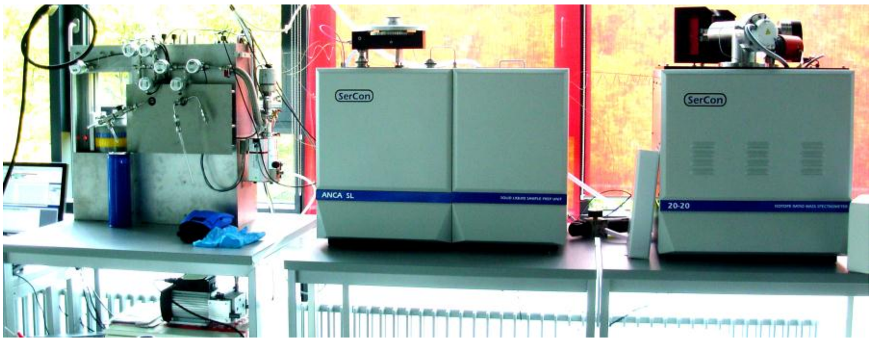


Figure 4.4 Elements of the graphitization: combustion in the EA (middle), $\delta^{13}C$ and $\delta^{15}N$ determination in the mass spectrometer (right) and the graphitizer (left).

The helium acts as carrier gas. The combustion products are sent through several gas chromatographic columns (GC) to purify and to separate the components of interest, nitrogen (N), CO_2 carbon (C), and hydrogen (H). This information is recorded by the EA software (Figure 4.5).

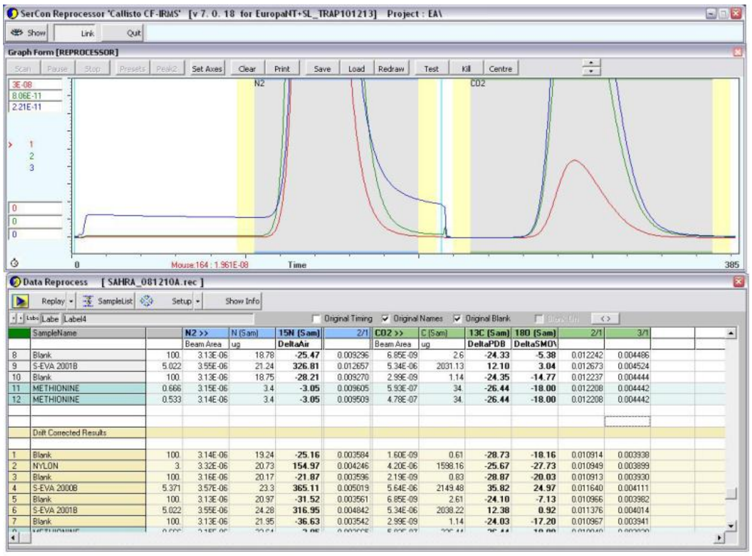


Figure 4.5 Protocol of the elemental analyser. The peaks represent the separation of C (CO_2) and N

4.1.3 Determination of carbon yield and C:N ratio

After the successful combustion of a sample the key parameters for quality control of bone collagen are available. These are the amount of carbon and nitrogen in the sample, which is used to determine the C:N ratio, These data and isotopic data from the next step are then entered into the database (Figure 4.6)

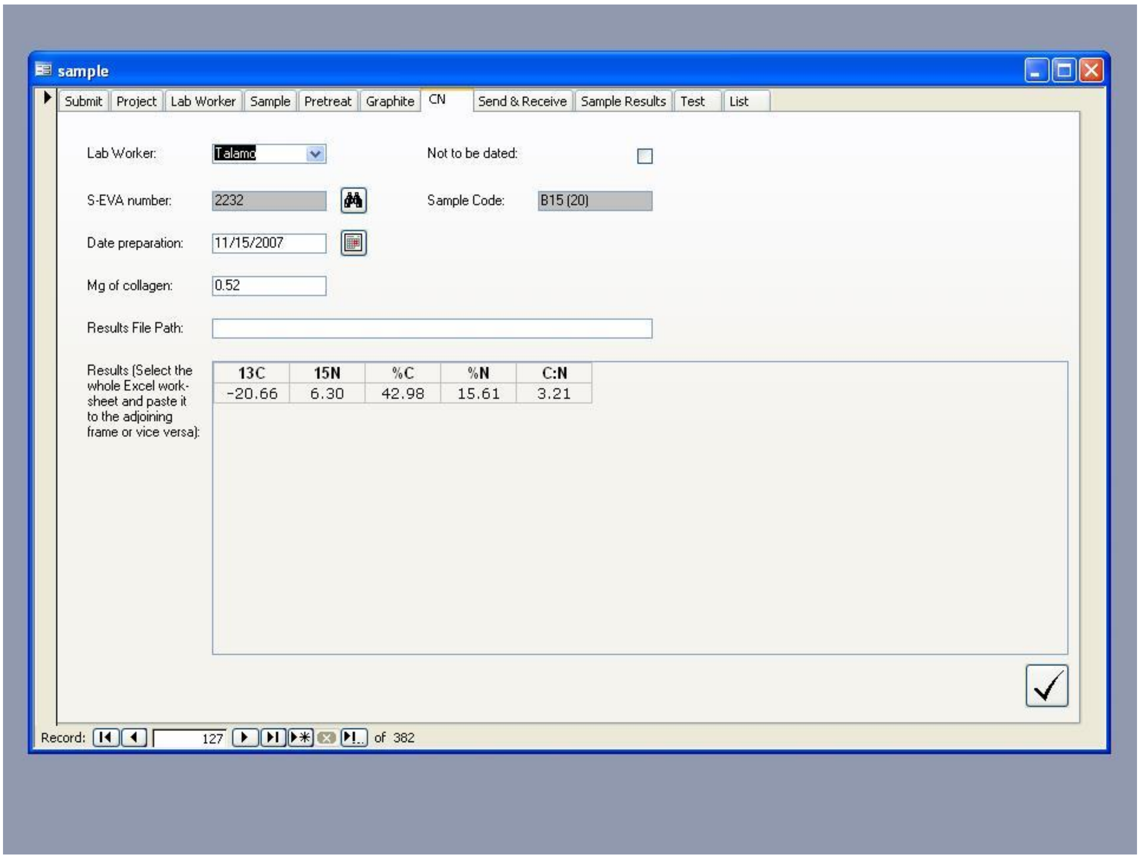


Figure 4.6 Input of isotope data into the database

4.1.4 Determination of $\delta^{13}C$ and $\delta^{15}N$ in a mass spectrometer

A small fraction, approximately 1%, of the purified gases are sent to the mass spectrometer (Figure 4.7), connected to the EA, to measure the stable isotope values ($\delta^{13}C$ and $\delta^{15}N$) (Table 4.I).

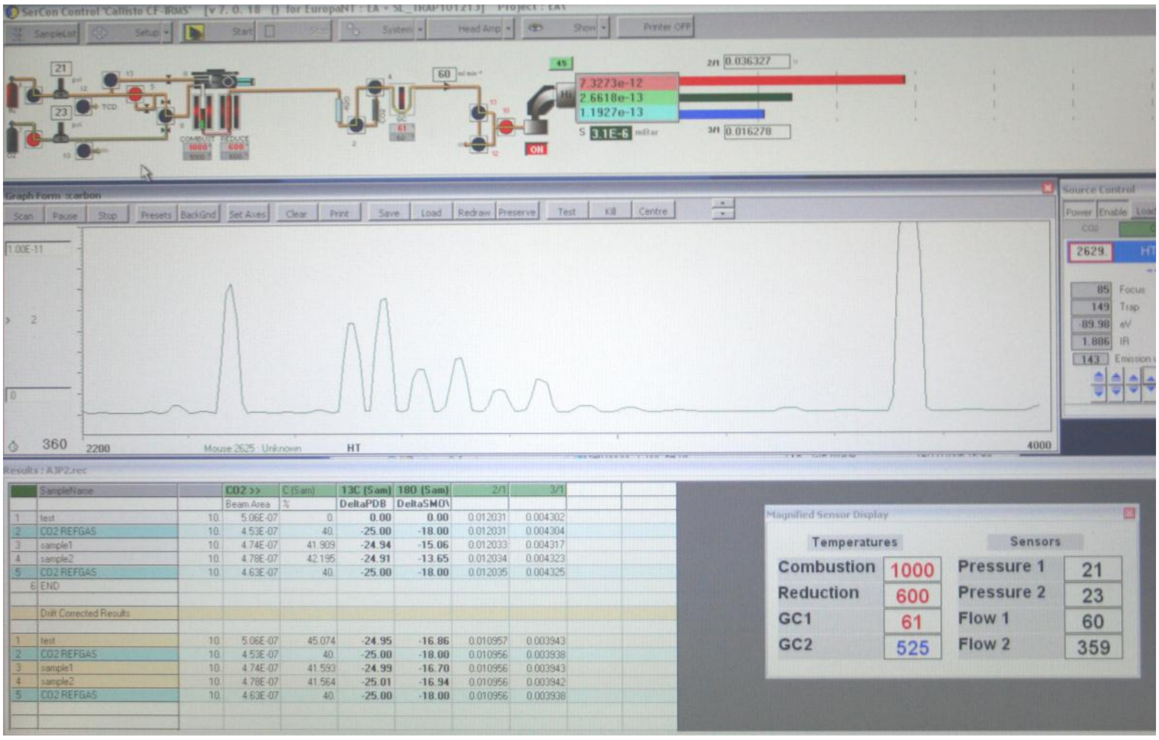


Figure 4.7Output page of the mass spectrometer for $\delta^{13}C$.

Table 4.I Example of a determination of stable isotope ^{13}C and ^{15}N for the reference material of Nylon 66

Name	Weight/Vol	^{13}C (Sam)	^{15}N (Sam)	C	N	C:N
	mg	**DeltaPDB**	**DeltaAir**	%	%	
EVA 0008 Nylon	4.092	-29.5	1.6	60.90	11.80	6.02
EVA 0008 Nylon	4.802	-29.5	1.6	60.90	11.80	6.02
Nylon 66 B2 Sample	4.708	-29.5	1.2	60.81	11.85	5.99
Nylon 66 B3 Sample	4.745	-29.5	1.2	60.83	11.80	6.01
	average	-29.54	1.52	60.86	11.83	
	stdev	0.04	0.24	0.05	0.03	

4.1.5 Cleaning the CO_2 gas containers and conditioning of the iron catalyst

The CO_2 gas containers are glass tubes closed by metal valves, called rigs (Figure 4.8).

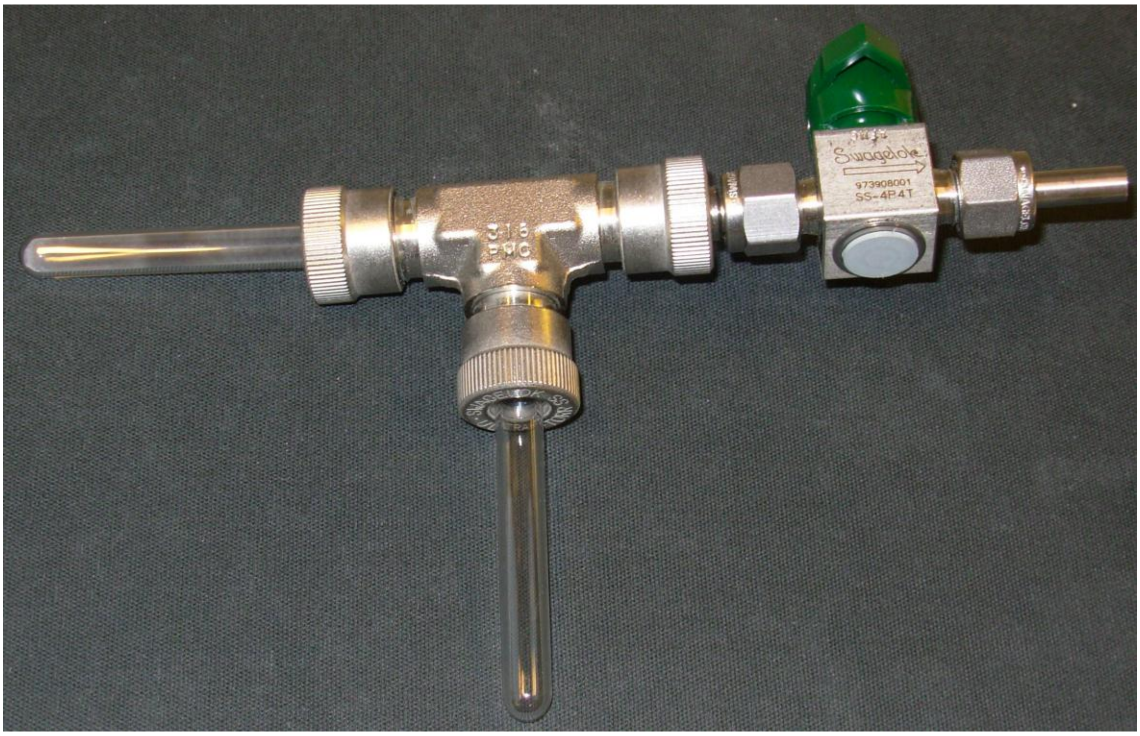


Figure 4.8 CO_2 gas container (rig) filled with iron catalyst.

The rigs are filled with 1.5 to 3 mg iron catalyst (Aldrich Chem. Co. <10micron 99.9%) and the optimal ratio of iron to carbon was determined to be 3 to 1 (Vogel, et al., 1984). To avoid contamination from absorbed CO_2 or particulates the iron and the glass surfaces are cleaned by adding H_2 (99.999%) at 500 mbar into the rigs and placing them in the oven at 450 °C for 1 hour.

4.1.6 Collection of CO_2 in the rigs

Most of the CO_2 is collected in a rig attached to the gas collection system (Figure 4.9) and is trapping using liquid N_2.

Hydrogen is added to the frozen CO_2 in a quantity sufficient to guarantee a complete reduction of CO_2. In our system an excess of H_2 is used with the ratio H_2:CO_2= 2.2 : 1

Figure 4.9 Graphitization system manufacture by the Oxford laboratory

4.1.7 Conversion of CO_2 into graphite in the graphitizer

The rig is placed in the oven at 560 °C for 6 hours, where CO_2 is reduced to carbon and water vapour. The latter is removed by cooling one finger of the rig (Figure 4.10).

Figure 4.10 Reduction of CO_2 to graphite using iron as catalyst in an oven (top section); water vapour is removed by immersing the vertical finger of the rig into a cooling bath (left and right section).

4.1.8 Check of the graphitization parameters

During the reduction of CO_2 to carbon hydrogen is consumed at the ratio 2:1 with respect to carbon. Therefore the pressure in the rigs after reduction will be low reflecting the excess amount of hydrogen. Typically we use 400 mbar of hydrogen which results in a residual pressure of *ca*. 80 mbar. This pressure is checked by reconnecting the rigs to the gas collection system. All these parameters are entered in the database (Figure 4.11).

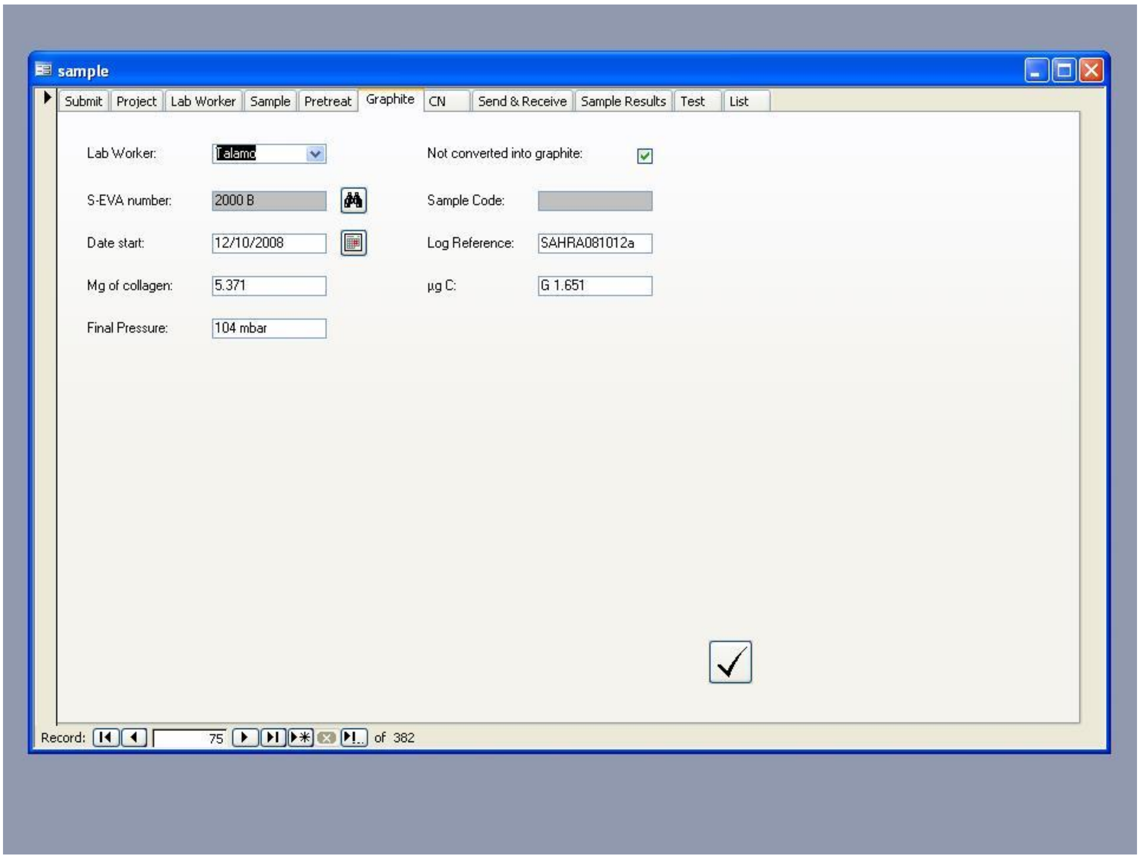


Figure 4.11 Input of graphitization parameters into the database

4.1.9 Preparation of blank samples

All steps of pretreatment and graphitization may contribute exogenous carbon (contamination). Therefore ^{14}C free material (old bone, Nylon 66, Pliocene wood) is pretreated and graphitized in the lab. These samples are called blank samples and they are prepared at the same time as the archaeological samples, and are also sent to the AMS facilities to establish the level of ^{14}C activity in the blanks.

4.1.10 Preparation of shipment to an AMS facility and submission

At this point the samples are ready to be sent to an AMS facility, where the graphite will be pressed into a target and measured in batches in the accelerator. A batch of target usually consists of a number of samples, standards and blanks. For this thesis the samples were submitted to the laboratories of Oxford. Kiel and Mannheim/Zurich. All dates of shipments and the dating results are recorded in the database providing the final list of samples and their ages (Figure 4.12 – 4.13 – 4.14)

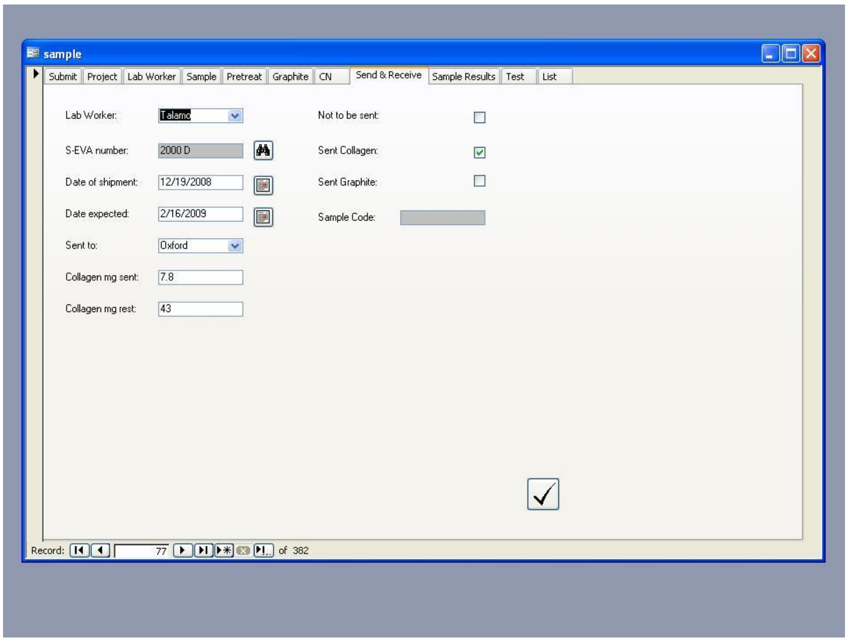


Figure 4.12 Table of shipment and dating results of a sample

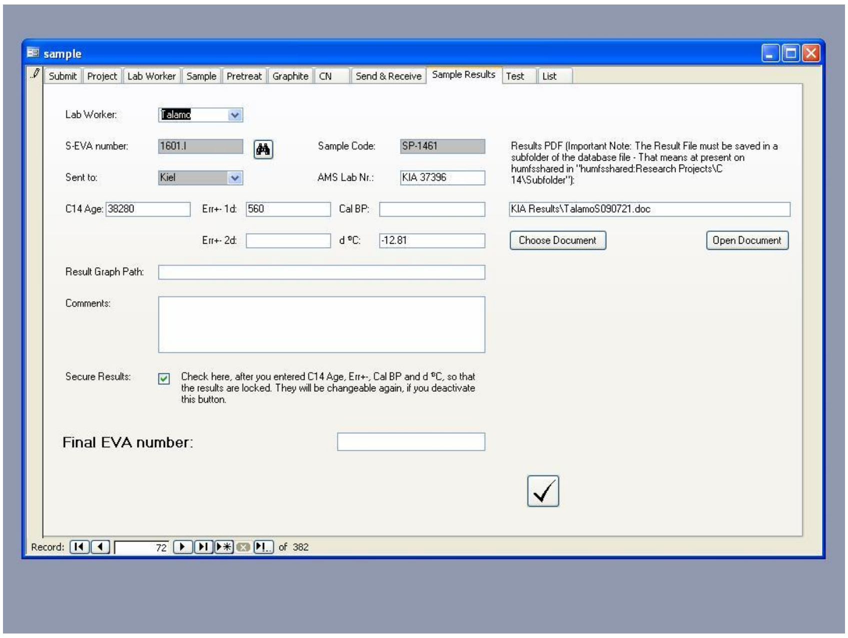
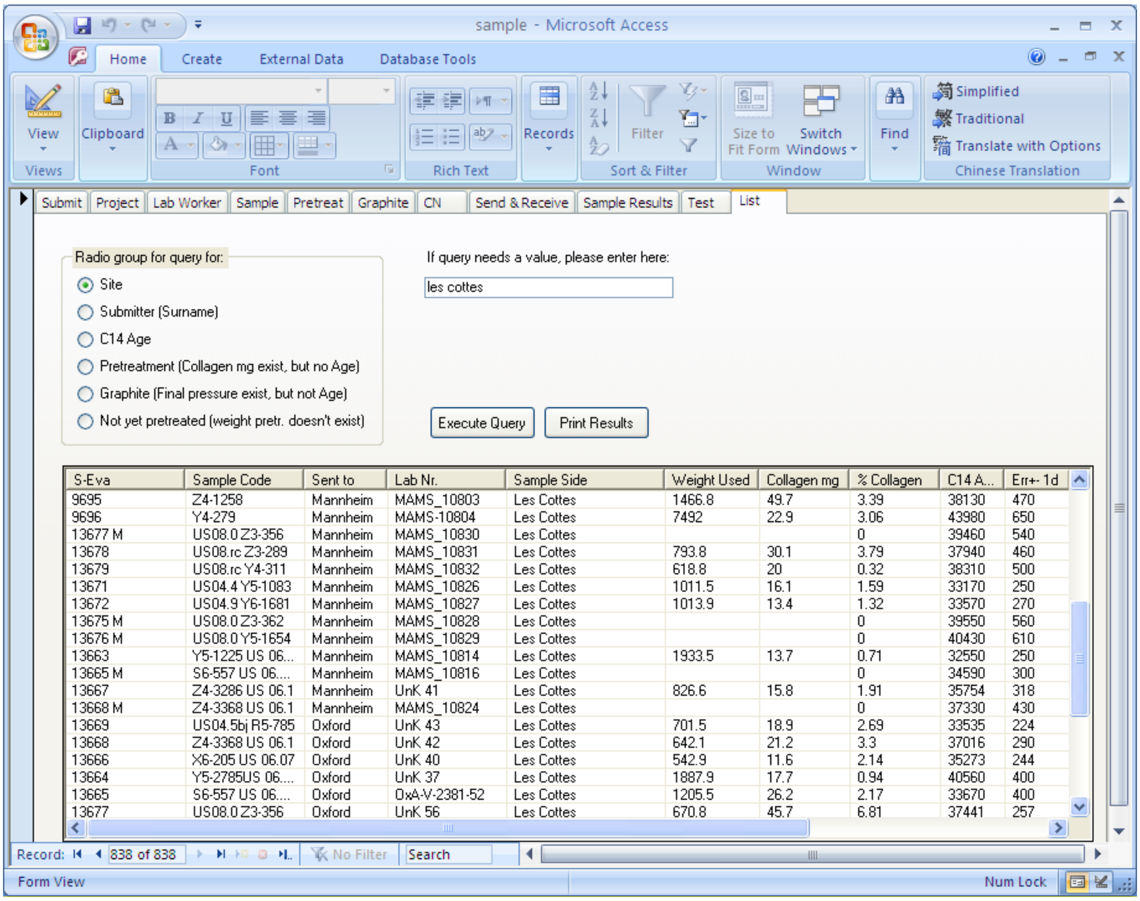


Figure 4.13 Input of data as reported by the AMS facility



S-Eva	Sample Code	Sent to	Lab Nr.	Sample Side	Weight Used	Collagen mg	% Collagen	C14 A...	Err+- 1d
9695	Z4-1258	Mannheim	MAMS_10803	Les Cottes	1466.8	49.7	3.39	38130	470
9696	Y4-279	Mannheim	MAMS-10804	Les Cottes	7492	22.9	3.06	43980	650
13677 M	US08.0 Z3-356	Mannheim	MAMS_10830	Les Cottes			0	39460	540
13678	US08.rc Z3-289	Mannheim	MAMS_10831	Les Cottes	793.8	30.1	3.79	37940	460
13679	US08.rc Y4-311	Mannheim	MAMS_10832	Les Cottes	618.8	20	0.32	38310	500
13671	US04.4 Y5-1083	Mannheim	MAMS_10826	Les Cottes	1011.5	16.1	1.59	33170	250
13672	US04.9 Y6-1681	Mannheim	MAMS_10827	Les Cottes	1013.9	13.4	1.32	33570	270
13675 M	US08.0 Z3-362	Mannheim	MAMS_10828	Les Cottes			0	39550	560
13676 M	US08.0 Y5-1654	Mannheim	MAMS_10829	Les Cottes			0	40430	610
13663	Y5-1225 US 06...	Mannheim	MAMS_10814	Les Cottes	1933.5	13.7	0.71	32550	250
13665 M	S6-557 US 06....	Mannheim	MAMS_10816	Les Cottes			0	34590	300
13667	Z4-3286 US 06.1	Mannheim	UnK 41	Les Cottes	826.6	15.8	1.91	35754	318
13668 M	Z4-3368 US 06.1	Mannheim	MAMS_10824	Les Cottes			0	37330	430
13669	US04.5bj R5-785	Oxford	UnK 43	Les Cottes	701.5	18.9	2.69	33535	224
13668	Z4-3368 US 06.1	Oxford	UnK 42	Les Cottes	642.1	21.2	3.3	37016	290
13666	X6-205 US 06.07	Oxford	UnK 40	Les Cottes	542.9	11.6	2.14	35273	244
13664	Y5-2785US 06....	Oxford	UnK 37	Les Cottes	1887.9	17.7	0.94	40560	400
13665	S6-557 US 06....	Oxford	OxA-V-2381-52	Les Cottes	1205.5	26.2	2.17	33670	400
13677	US08.0 Z3-356	Oxford	UnK 56	Les Cottes	670.8	45.7	6.81	37441	257

Figure 4.14 Example of a summary sheet of an archaeological site (Les Cottés)

5. Debates over Palaeolithic chronology – the reliability of ^{14}C is confirmed

Paper accepted for publication in JAS

Authors: Sahra Talamo, Konrad A. Hughen, Bernd Kromer, Paula J. Reimer

Abstract

The debate about the complex issues of human development during the Middle to Upper Palaeolithic transition period (45-35 ka BP) has been hampered by concerns about the reliability of the radiocarbon dating method. Large ^{14}C anomalies were postulated and radiocarbon dating was considered flawed. We show here that these issues are no longer relevant, because the large anomalies are artefacts beyond plausible physical limits for their magnitude. Previous inconsistencies between ^{14}C radiocarbon datasets have been resolved, and a new radiocarbon calibration curve, IntCal09 (Reimer, et al., 2009), was created. Improved procedures for bone collagen extraction and charcoal pretreatment generally result in older ages, consistent with independently dated time markers.

1. Introduction

The period of the Middle to Upper Palaeolithic presents one of the major intellectual challenges in archaeology, fuelled by the demise of the Neanderthals and the dispersal of the Anatomically Modern Humans (AMH) in central Europe. Did they ever encounter each other? Did they exchange technology, culture or genes? Is the Neanderthal a forger of the AMH techno-complex, or did AMH invent it independently? Does the Aurignacian reflect the dispersal of the first Modern Humans in Europe? Common to all these questions is chronology, and radiocarbon dating is a central tool to provide this.

Until now, the prospect for a precise Middle to Upper Palaeolithic chronology was controversial in the archaeological world and the reasons are many. First are the intricacies of the radiocarbon method including the requirement of calibration, which has left room for ambiguity (Mellars, 2006). Secondly, there have been doubts about the radiocarbon method being capable of dating this time period because of the alleged extreme fluctuations of the atmospheric radiocarbon level (Conard and Bolus, 2003, Conard and Bolus, 2008, Fedele, et al., 2008, Giaccio, et al., 2006, Pettitt and Pike, 2001). Last but not least, there are the methodological difficulties of using radiocarbon dating close to its limits, with higher errors due to the low remaining ^{14}C activity of samples from this time period, and resultant vulnerability to contamination *in situ* and in the laboratory. Here the prime dating materials are bone and charcoal; hence the quality of the dates depends strongly on the ability to extract pure collagen from bone and remove traces of contamination from charcoal. This field has seen strong progress over the past two decades. Bone, which is considered closest to the archaeological context, represents a challenge in the extraction of genuine collagen and here the risk of obtaining anomalously young dates is high. Collagen cleaned by ultrafiltration (Brown, et al., 1988) appears to deliver generally older ages, consistent with established time markers such as the Campanian Ignimbrite (CI), but there are still controversial issues as exemplified by a recent exchange of opinions (Higham, et al., 2006, Hüls, et al., 2007)

We observe that different authors arrive at quite different conclusions regarding the temporal framework of crucial sites and some authors even question the validity of radiocarbon dating. For this reason we consider it useful to revisit some fundamental radiocarbon issues and outline the intense work in the radiocarbon community over the past few years, which has created a solid chain of evidence supporting the use of radiocarbon dating in the time period 30,000 to 45,000 cal BP.[1]

2. Special events in the Middle /Upper Palaeolithic time period

The time period prior to 38,000 cal BP experienced strong climate excursions, Dansgaard-Oeschger cycles (DO) 12 to 9 concluding in Heinrich Event 4 (HE 4) (Wang, et al., 2001). Dansgaard-Oeschger cycles are characterized by warm periods ca.1500 years long, with very fast warming (<100 years) and subsequent gradual cooling. The cause could be shifts of the location of the deep water formation in the North Atlantic, i.e. during warm phases the location is further north, near where it is today, whereas during cold phases it is located south of Iceland (Bard, 2002, Rahmstorf and Alley, 2001). Heinrich events are periods in which a greatly increased number of icebergs enter the North Atlantic. The resulting freshwater input may have considerably slowed the major ocean circulation engine, i.e. Meridional Overturning Circulation (MOC) leading to strong cold phases in mid and high latitudes of the Northern hemisphere.

A major volcanic eruption also occurred in this time range; the Campanian Ignimbrite (CI), dated by $^{40}Ar/^{39}Ar$ to 39,395±51 cal BP (Fedele, et al., 2002, Pyle, 1992, Pyle, et al., 2006, Ton-That, et al., 2001). The CI is an important time marker in the Mediterranean and south-eastern Europe. Finally the Laschamp geomagnetic excursion (an interval of extremely low geomagnetic field intensity) is a global stratigraphic tie-point dated to 40,400 ± 1100 cal BP (Guillou, et al., 2004). The potential effect of these events on atmospheric ^{14}C is presented in detail below.

3. Fundamentals of carbon cycle and ^{14}C calibration

^{14}C dates cannot be used in a straightforward way because the atmospheric radiocarbon level, which determines the initial setting of the ‘clock’, has varied in the past. This is remedied by using ^{14}C dates of known age material (e.g. tree-rings) to correct, or calibrate, the radiocarbon dates to calendar (cal) ages. The variability of atmospheric ^{14}C is due primarily to two factors, the first of which is the change in the shielding of the earth against cosmic rays that produce ^{14}C. The shielding has two components, the Earth's geomagnetic field and the magnetic field in the solar wind. Decreasing magnetic field shielding increases ^{14}C production and vice versa. The second factor is the distribution of ^{14}C between global carbon reservoirs. Carbon is primarily exchanged between three reservoirs, the atmosphere, biosphere and ocean.

[1] In this paper radiocarbon ages are denoted ^{14}C **BP**, i.e. radiocarbon years before 1950 AD. Calibrated radiocarbon ages are denoted **cal BP** which are calendar years before 1950 AD and cal BP is used also for calendar ages obtained by other dating methods, such as Ar/Ar or U-Th.

The fraction of carbon in the atmosphere and biosphere is only a few percent compared to the carbon stored in the deep ocean. Deep ocean ventilation (i.e., MOC) controls the distribution of carbon between the atmosphere and ocean, and hence atmospheric ^{14}C levels. A reduction of MOC would serve to lower the flux of ^{14}C into the ocean and therefore increase atmospheric ^{14}C.

The portion of carbon in the biosphere (e.g. plants, soil, sediments and peat) also contributes to atmospheric ^{14}C variability, but on a much smaller scale than the ocean. To obtain quantitative estimates of the ^{14}C content of these carbon reservoirs and, most importantly, their temporal development, a number of carbon cycle models have been developed. These models use scenarios of changes in the above-mentioned parameters, including ^{14}C production or rate of MOC, to calculate the atmospheric ^{14}C level (Hughen, et al., 2006, Laj, et al., 2002, Siegenthaler, et al., 1980, Stuiver and Braziunas, 1993). In the period of interest, the factors which were the primary contributors to atmospheric ^{14}C variability are the enhanced production of ^{14}C (because of the low geomagnetic dipole during the Laschamp Event) and the reduced MOC (due to fresh water input into the North Atlantic during Heinrich event H4).

4. Evidence and discussion of ^{14}C fluctuations in published datasets

Several ^{14}C datasets have been taken as evidence for extremely large ^{14}C fluctuations around 40,000 cal BP – the Bahamas stalagmites (Beck, et al., 2001) and the Tyrrhenian Sea core CT85-5 (Giaccio, et al., 2006) with ages that are systematically too young (ca. 32,000 ^{14}C BP) found in stratigraphical context underlying the CI (ca. 35,000 ^{14}C BP). This latter point appears fully resolved now due to the revised ^{14}C ages of important Italian sites like "Fumane" in the recent contribution of Higham et al. (2009), where they show that advanced pre-treatment techniques of charcoal lead to ^{14}C ages in full agreement with the CI age. A recent review of pretreatment of bone and charcoal is given by Ascough et al. (2009) and Higham (2011).

Here we focus on the presence or absence of strong fluctuations of the atmospheric ^{14}C level, conventionally reported as $\Delta^{14}C$, the deviation from an international standard (Stuiver and Polach, 1977). The CI event coincides with an interval of weak geomagnetic field (Laschamp Event, LE) during which the production of cosmogenic nuclides (^{14}C, ^{10}Be, ^{36}Cl) was enhanced. For ^{10}Be and ^{36}Cl, this effect is seen clearly in the polar ice cores (Beer, et al., 2002), but the signal in radiocarbon is attenuated by buffering through the large ocean reservoir. At the time of its first publication, a Bahamas stalagmite (Beck, et al., 2001) showed a very strong $\Delta^{14}C$ spike around 40,000 cal BP which was attributed to a scenario of changes in ^{14}C production and in carbon reservoirs. However, the strong $\Delta^{14}C$ spike in this speleothem record was later determined to be an artefact of an erroneous background correction (Beck, et al., 2008, Hoffmann, et al., 2010). Subsequently, another stalagmite record was obtained from the Bahamas that does not display as strong a signal (Hoffmann, et al., 2008, Hoffmann, et al., 2010), in agreement with other ^{14}C records (Hughen, et al., 2006).

5. Limits to amplitude of large atmospheric ^{14}C fluctuations

The strongest evidence of radiocarbon anomalies comes from the ^{14}C age sequences of the Tyrrhenian Sea core CT85-5, covered in more detail in chapter 16 of the book: "When Neanderthal and Modern Human met" (Giaccio, et al., 2006). A total of 44 AMS ^{14}C measurements have been performed on foraminifera which show extremely large ^{14}C age fluctuations. Within about 800 years the ^{14}C ages jump from circa 35,000

^{14}C BP to circa 25,000-20,000 ^{14}C BP and subsequently return to circa 33,000-32,000 ^{14}C BP (Giaccio, et al., 2006). Foraminiferal species and pretreatment have not been specified so it is difficult to evaluate this dataset without further information.

We consider the interpretation of this last dataset as evidence of extremely strong atmospheric ^{14}C fluctuations as erroneous, primarily because carbon cycle models impose limits to the magnitude and rate of change of atmospheric $\Delta^{14}C$. We imposed extreme scenarios over the characteristic time scales of Heinrich events, DO cycles and the Laschamp Event (ocean ventilation MOC shut off partially or completely, vanishing earth magnetic field, low solar activity) using a previously published carbon cycle model as outlined in the suplementary information, and we obtain a maximum increase of 500 to 1550‰ in $\Delta^{14}C$. These values can be compared to the ranges calculated from the ^{14}C age drop of the CT85-5 core. The apparent age of 20,000 ^{14}C BP at a true age of 40,000 cal BP corresponds to an atmospheric $\Delta^{14}C$ value of more than 9000‰, i.e. more than 6 times the maximum value of the model calculations. Such a high value is completely outside of the range covered by plausible manipulations of the ^{14}C and the carbon cycle.

The second argument against drastic $\Delta^{14}C$ fluctuations is based on the Cariaco Basin ^{14}C dataset, which has several data points at 150-200 year sampling resolution in the age range of the CI (Hughen, et al., 2006), but does not show unusually large fluctuations. $\Delta^{14}C$ in Cariaco has a peak of up to 700‰ between 44,000 and 36,000 cal BP (Hughen, et al., 2006) changing smoothly in this interval, mainly caused by the low geomagnetic field during LE. While the marine radiocarbon reservoir will no doubt attenuate a peak in atmospheric ^{14}C to a certain extent, depending on the rate of change of ^{14}C, we know from nuclear weapons testing measurements that such a large attentuation as that required to support a 9000‰ value for the atmosphere could not have occurred, even for decadal scale or shorter anomalies. In fact, the longer centennial-to-millennial time scales of the purported ^{14}C anomaly at 40,000 cal BP would result in the marine signal being in near equilibrium to the atmosphere.

The observed gradual changes in $\Delta^{14}C$ do not invalidate radiocarbon dating at all, because the calibration procedure is designed to account for these anomalies (Fig. 1). We conclude that the ^{14}C age inversion of up to 15,000 ^{14}C years in the Tyrrhenian Sea core could not have been caused by fluctuations of the atmospheric ^{14}C level.

6. Calibration of radiocarbon dates by IntCal09 back to 50,000 cal BP

Due to new data and the application of stringent quality criteria, the previous limitation for calibration of ^{14}C dates (26,000 cal BP, IntCal04 (Reimer, et al., 2004)) no longer exists. After four years of intense discussion and review of new datasets the IntCal Working Group created an extension back to 50,000 cal BP, IntCal09 (Reimer, et al., 2009) which was approved by the radiocarbon community. Using this data set, reliable and statistically robust calibrated ages close to the limit of the method can be obtained. While the IntCal Working Group will continue to make refinements to the radiocarbon calibration curve, particularly with regard to marine reservoir ages, there are unlikely to be substantial changes in this time period.

7. Conclusions

The unusual sequence of events during Middle to Upper Palaeolithic leaves ample room for speculation and competing theories, even more so when a rigid age control is lacking. At least for chronological issues, we can provide a remedy. The putative radiocarbon dating anomaly during Middle to Upper Palaeolithic lasting for millennia does not exist. ^{14}C production fluctuations lead to intervals of both accelerated change of radiocarbon years *versus* calendar years and decreased change (i.e., radiocarbon age plateaux), which are well resolved in the current radiocarbon calibration dataset IntCal09. The radiocarbon community solved the issues of inconsistent ^{14}C datasets and created a valid calibration curve back to 50,000 BP (Reimer, et al., 2009). Improved protocols for bone collagen extraction and charcoal pretreatment result in calibrated ages in agreement with the CI time marker.

^{14}C dating of samples older than 30,000 years is still challenging and requires outstanding efforts in sample selection and in laboratory procedures. Published dates need to be critically assessed for being too young due to incomplete decontamination, before they are incorporated into archaeological concepts. We see a bright future for radiocarbon dating even at ages close to the limit of the method.

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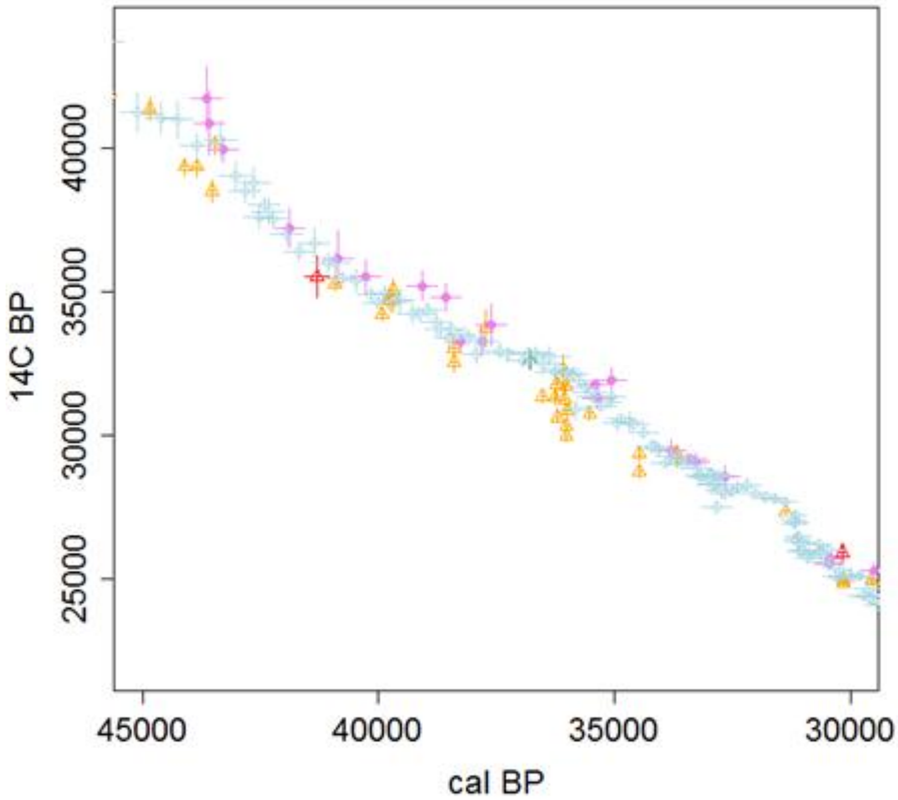

Fig. 1: ^{14}C calibration data in the interval 30,000 to 45,000 cal BP, Cariaco (Hughen, et al., 2006, light blue), Corals (Fairbanks, et al., 2005, orange), Iberian margin marine sediments (Bard, et al., 2004, pink), Corals (Bard, et al., 2004, red) , Corals (Cutler, et al., 2004, dark green).

Supplementary information

If we consider a reduction of the geomagnetic field intensity to zero (maximum case) lasting for 1000 years (Laj, et al., 2002), the atmospheric $\Delta^{14}C$ increases by ~420‰ as calculated by carbon cycle models. For a reduction of the geomagnetic field lasting 2000 years, the $\Delta^{14}C$ increase is only slightly more (~550‰). Another scenario could be the reduction in MOC by 30%; this causes atmospheric $\Delta^{14}C$ to increase by 40‰, in agreement with Delaygue et al.(Delaygue, et al., 2003) and a reduction of MOC by 50% results in an atmospheric $\Delta^{14}C$ increase of 85‰.The simultaneous reduction in geomagnetic field and MOC (lowering geomagnetic field intensity to 0 and MOC by 30% for 1000 years) yields an atmospheric $\Delta^{14}C$ increase of 500‰ (650‰ if the MOC is reduced by 50%). The most extreme scenario would be reducing both geomagnetic field intensity and solar activity to 0 for 1000 years, together with a 50% reduction in MOC, resulting in an atmospheric $\Delta^{14}C$ increase of 1550‰.

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6. A comparison of bone pretreatment methods for AMS dating of samples >30.000 BP

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The focus of this paper was to find the best pretreatment method to minimise or remove modern contamination in bone samples older than 30,000 cal BP.

The study involves two different bone samples. The first one is a Mammoth rib from North Sea (lab code S-EVA 2000, Figure 6.1) and the second is a bison bone, also from North Sea (lab code S-EVA 2001, Figure 6.2)

Figure 6.1 Mammoth rib sample involved in this work

Figure 6.2 Bison sample involved in this work

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A COMPARISON OF BONE PRETREATMENT METHODS FOR AMS DATING OF SAMPLES >30,000 BP

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ABSTRACT. Bone is a commonly used material for radiocarbon dating, yet at ages close to the limit of the method (>30,000 BP), it is a substantial challenge to remove contamination and produce accurate ages. We report here on the preliminary results of a dating study of 2 bones older than 30,000 yr, which were each treated with a suite of pretreatment procedures, including ultrafiltration (Brown et al. 1988). Substantial differences in the ^{14}C ages were observed, which is most likely linked to crucial steps in the removal of contamination both in the bone and in the laboratory. Using a comprehensive sequence of pretreatment procedures, including ultrafiltration, we obtain generally older ages.

INTRODUCTION

Bone is one of the most important archaeological materials used for radiocarbon dating, but at the same time it is also one of the most difficult materials to date as bone can be susceptible to contamination and is also often degraded. Prior to 1970, whole bone was generally used for dating, and often included bone carbonate, which itself could be postdepositionally contaminated. Longin (1971) proposed a method to isolate bone collagen, which was seen to be a much more stable material and less susceptible to contamination than bone mineral. The main challenge in chemically pretreating bones for ^{14}C dating is therefore to extract collagen and then confirm that the extracted collagen is indeed largely intact and free from contamination, usually through the measurement of a suite of indicators, including C:N ratio, collagen yield, and %C and %N in the collagen extract.

Most laboratories use some variation of the Longin (1971) method, but other laboratories have specialized in bone dating and have dramatically improved collagen extraction and purification techniques. For instance, in 1992 the Oxford Radiocarbon Accelerator Unit (ORAU) published the HPLC technique, which is one of the most sophisticated methods to carefully extract and purify amino acids from bone collagen (Van Klinken et al. 1994). Another way to purify the bone samples was proposed earlier by a Canadian research team (Brown et al. 1988), to separate the high-molecular weight (>30 kD) from the low-molecular weight fraction using ultrafiltration, and then produce dates using only the >30-kD fraction. In 2000, the ORAU adopted this ultrafiltration method (Bronk Ramsey et al. 2000, 2004) for their extracted gelatin, and also included a primary filtration step using an Ezee-Filter™ (Elkay Laboratory Products Ltd., UK). After various tests of potential contamination from both the ultrafilters and the Ezee-Filters, the ORAU lab found that both of the filters require careful cleaning in an ultrasonic bath (Brock et al. 2007). The ultrafilter has a humectant coating (glycerol) added to maintain the flexibility of the filter. As glycerol can be manufactured from either plant or animal extracts, or alternatively from petroleum processing byproducts, this glycerol needs to be removed as it could add young or old carbon to the sample. Bronk Ramsey et al. (2004) suggested that the best way to eliminate this glycerol without damaging the filter is repeated washes and sonification, and after 3 washes showed that the humectant was effectively removed as shown by no measurable carbon in the eluent. Despite the apparent beneficial role in removing the low-molecular weight fraction of the collagen (Higham et al. 2006), there is an ongoing discussion in the ^{14}C community about the utility and accuracy of ultrafiltration. Hüls et al.

(2007) tested 2 different ultrafilters, a Vivaspin™ 15R and a Vivaspin 20, using bones of various ages. They showed that in spite of careful cleaning of the ultrafilter, small amounts of contaminant young carbon remained, which probably came from glycerin; hence, they recommended caution in the use of the ultrafilter. In at least one example, dates of mammoth bone samples have been obtained without ultrafiltration, where the ages compare well with contemporary peat and wood (Hajdas et al. 2007).

The ^{14}C activity of the humectant has been shown to be bimodal, i.e. essentially modern or of fossil origin (Brock et al. 2007). For bones older than 30,000 BP, contamination by modern carbon will alter the true age much more dramatically than the addition of ^{14}C-dead carbon of a similar size.

At our institution (MPI, EVA Leipzig, Germany), we developed techniques to extract collagen from Pleistocene-age bone for stable isotope analysis and the resultant collagen was often sent to accelerator mass spectrometry (AMS) facilities for ^{14}C dating. In 2005, well-preserved bison and mammoth bones from the North Sea of unknown age were adopted as the long-term quality control material, especially to test for background contamination in the sample preparation, with the assumption that these 2 bones were at least Pleistocene in age, and ideally older than 50,000 BP. Initial ^{14}C results from 2 AMS laboratories on collagen prepared at MPI showed the bones to be in the age range of 30,000 to 45,000 ^{14}C BP, but we observed large discrepancies in the ^{14}C ages between different ^{14}C labs. These inconsistencies could have been caused by deficits in the pretreatment methods that we had established for collagen extraction, by insufficient removal of contamination in the samples, in the AMS measurements themselves, or all three.

We therefore designed a study to investigate the source of these inconsistent dates, and we also compared the results of our pretreatment methods against results from the methods from two of these AMS labs.

METHODS

We obtained 2 bones, the first a mammoth (S-EVA 2000) and the second a bison (SEVA 2001) from the Pleistocene North Sea plain. Both bones have relatively well-preserved collagen. Bone powder was drilled from the 2 bones and pretreated in 3 different ways (methods A–C) as outlined in Table 1. Method A was the pretreatment method employed when we first ran stable isotope analysis and later on dated the mammoth and bison samples. The bone is decalcified in HCl over several days while refrigerated (~4 °C) until no effervescence is observed. The gelatinization step is at pH 3 at 70 °C for 48 hr. The ultrafilter (Vivaspin 15, 30 kD) is rinsed in NaOH (1×) and H_2O (4×). Method B differs only in the cleaning of the ultrafilter, which was modified by removing the NaOH cleaning, and adding a 1-hr ultrasonic bath after the third H_2O rinse. In initial tests, we also used Millipore ultrafilters but in agreement with ORAU (Brock et al. 2007), we found Vivaspin 15 to be better suited for our purposes.

In Method C, the decalcification is at room temperature for 4 hr, with an additional NaOH step to remove humics and followed by an HCl step to remove potential contamination from modern CO_2 taken up by the NaOH. The gelatinization is done at pH 3 but at 75 °C for 20 hr. The ultrafilter is cleaned by centrifuging in H_2O (5×) without the NaOH rinse, and kept for 1 hr in ultrasonic bath after the third H_2O rinse. The cleaning is checked by monitoring the carbon level in the eluent.

We also submitted unpretreated samples (2 pieces of each bone) directly to the Oxford and Kiel laboratories, which were then pretreated in each laboratory following standard in-house pretreatment methods (**Method D_K, Method D_O**). The specifics of these methods are given below.

Table 1 Pretreatment steps for all 3 methods.

	Decalcification				Cleaning of the ultrafilter			
Method	HCl	NaOH	HCl	Gelatinization	NaOH centrifuge	H_2O centrifuge	Ultrasonic bath	H_2O centrifuge
A	Several days at ~4 °C	No	No	pH 3, 70 °C for 48 hr	1×	4×	No	No
B	Several days at ~4 °C	No	No	pH 3, 70 °C for 48 hr	No	3×	1 hr	2×
C	4 hr at room temperature	Yes	Yes	pH 3, 75 °C for 20 hr	No	3×	1 hr	2×

Method D_K, Kiel-Leibniz Laboratory: Demineralization of bone pieces 0.5 to 2 mm in size with 1% HCl at room temperature, keeping pH < 1, and then subsequent washes with Milli-Q™ water (Millipore Corp.) until pH > 4. Then, an extraction was done for 1 hr at room temp with 1% NaOH, followed by washing with Milli-Q until pH < 9, and then again an extraction with 1% HCl for 1 hr at room temperature followed by a water rinse. The resulting extract is then hydrolyzed overnight at pH = 3 at 85 °C in a water bath. The gelatin solution is then filtered through a precleaned 0.45-μm silver filter. This laboratory normally does not use ultrafiltration because they are still investigating potential contamination by the filters.

Method D_O: Oxford Laboratory: This method is described fully in Brock et al. (2007).

RESULTS

The stable isotope data (C:N, $\delta^{13}C$, $\delta^{15}N$, and %C and %N content) for mammoth and bison collagen is presented in Table 2 for all methods. We do not observe significant differences in these values between the different preparation methods and the parameters indicate well-preserved collagen (DeNiro 1985; Ambrose 1990).

Table 2 Atomic C:N ratio and stable isotope analysis of collagen from the mammoth (S-EVA 2000) and bison (S-EVA 2001) bones. The collagen was prepared according to methods A–C. For $\delta^{13}C$, the standard is VPDB; for $\delta^{15}N$, the standard used is IAEA N1 and N2. Typical analytical precision is 0.1‰ for $\delta^{13}C$ and 0.2‰ for $\delta^{15}N$.

	Method	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	%C	%N	C:N
Mammoth						
2000	A	–21.1	7.0	41.9	15.4	3.2
2000-XXII	B	–21.2	6.8	39.4	13.9	3.3
2000 D	C	–21.4	6.8	44.2	16.2	3.2
Bison						
2001	A	–20.8	3.1	38.8	13.9	3.3
2001-XII	B	–20.5	2.4	40.5	14.5	3.3
2001 C	C	–20.5	2.6	41.4	15.2	3.2

Dating results for the mammoth (S-EVA 2000) are given in Table 3a. The collagen prepared at the Max Planck Institute (MPI) by methods A–C was submitted to both Kiel and Oxford for dating. For methods A and C, separate preparations had to be made to obtain enough material for analysis. For Method B, collagen yields allowed us to split the same collagen sample to be sent to the different labs. The resulting mammoth ages from the different methods and different labs range between

31,660 and 35,280 ^{14}C BP with 1σ errors between 200 and 510 yr. The youngest results are associated with Method A, while methods B and C tend to give older ages (Figure 1). Within each method, the results of methods A, B, and C agree within 1 σ between the AMS labs of Kiel and Oxford, but for Method D the results are statistically different. For these samples submitted as bone to the 2 ^{14}C labs for pretreatment in their laboratories (methods D_K and D_O), the difference between the dates is 2620 yr and the results in the labs do not agree statistically with their respective results of Method C (Figure 1).

Table 3a ^{14}C results of mammoth samples prepared using methods A to D. Missing values were not reported. The $\delta^{13}C$ reported is derived from the AMS sample combustion procedure. OxA-V indicates that the material was combusted and graphitized/dated in Oxford, but the chemical pretreatment of the bone was done at MPI.

S-EVA mammoth	Method	Lab code	% yield of collagen	C content (%)	pMC	^{14}C age	Error ±1 σ	$\delta^{13}C$ (‰)
2000	A	KIA-28337		46	1.94 ± 0.06	31,660	240	–21.2
2000	A	KIA-29434		45.5	1.90 ± 0.12	31,820	510	–22
2000	A	OxA-V-2166-47				31,910	200	–19.7
2000-XXII[a]	B	KIA-35978	3.3	48.8	1.59 ± 0.06	33,280	320	–19.1
2000-XXIIa[a]	B	OxA-V-2281-52	3.3	45.3	1.51 ± 0.05	33,670	200	–21.2
2000 XXIII	C	KIA-44753	4.2		1.53 ± 0.06	33,560	320	–23.7
2000 D[a]	C	OxA-UnK;54	9.4		1.50 ± 0.05	33,733	257	–19.2
2000 D_[a]	C	MAMS-10399	9.4		1.27 ± 0.04	35,075	260	–23.3[b]
2000	D_K[c]	KIA 29435		38.6	1.71 ± 0.07	32,660	350	–20.6
2000	D_O	OxA-15908			1.24 ± 0.05	35,280	340	–20.5

[a]Split collagen.
[b]$\delta^{13}C$ AMS.
[c]No ultrafiltration step.

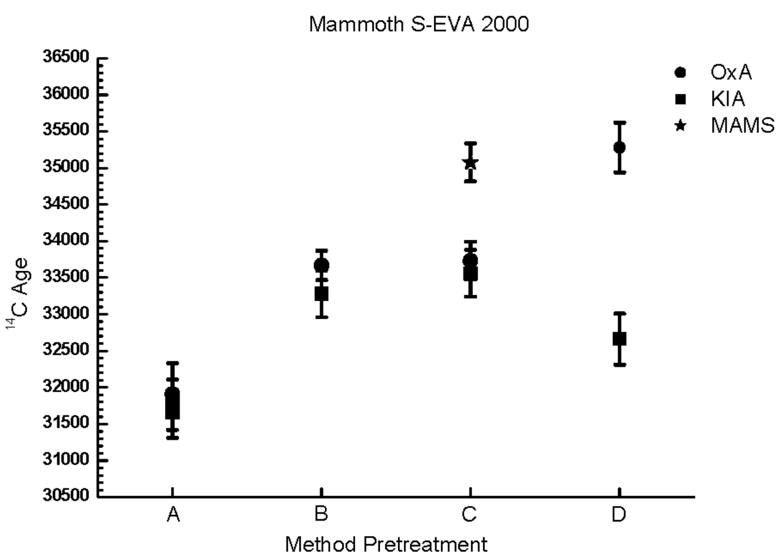

Figure 1 ^{14}C ages of mammoth bone obtained from methods A to D

The bison bone (S-EVA 2001) ^{14}C ages range between 37,090 and >44,800 ^{14}C BP with errors from 360 to 1630 yr (Table 3b). The results of Method B agree between the 2 AMS labs involved, but they are more than 2000 yr younger than the results of the other methods (except for Method D_K, which is the youngest of the results). The results of methods A and C agree statistically at the 2σ level (Figure 2).

Table 3b ^{14}C results of bison samples prepared using methods A to D. Missing values were not reported. The $\delta^{13}C$ reported is derived from the AMS sample combustion procedure. OxA-V indicates that the material was combusted and graphitized/dated in Oxford but the chemical pretreatment of the bone was done at MPI.

S-EVA bison	Method	Lab code	% yield of collagen	C content (%)	pMC	^{14}C age	Error ±1 σ	$\delta^{13}C$ (‰)
2001	A	KIA 28338		45.5	0.49 ± 0.05	42,660	790	–21.7
2001	A	KIA 29436		45.3	0.39 ± 0.09	44,480	1630	–20.4
2001	A	OxA-V-2166-48			0.28 ± 0.03	47,300	900	–19.3
2001-XII[a]	B	KIA 35982	2.5	49.6	0.69 ± 0.05	40,200	640	–22.1
2001-XIIa[a]	B	OxA-V-2281-53	2.5	44.5	0.64 ± 0.03	40,630	360	–20.8
2001 XIII	C	KIA-44754	7.1		0.34 ± 0.05	45,740	1420	–21.3
2001 C[a]	C	OxA-UnK;53	3.7		0.43 ± 0.03	43,674	450	–18
2001 C_[a]	C	MAMS-10398	3.7		0.29 ± 0.04	47,000	1250	–21.6[b]
2001	D_K[c]	KIA 29437		39.5	0.99 ± 0.07	37,090	570	–19.3
2001	D_O	OxA-15909				>44,800	—	–20.1

[a]Split collagen.
[b]$\delta^{13}C$ AMS.
[c]No ultrafiltration step.

Figure 2 ^{14}C ages of bison bone obtained from methods A to D

As an additional test of possible contamination in the *graphitization* stage, we also sent the collagen prepared using what we believe is the most stringent preparation method, Method C, to a third AMS lab, Mannheim (lab code MAMS), to compare the results between the 3 labs. Surprisingly, the Mannheim lab for both the mammoth and bison samples had older ages than both Kiel and Oxford, for the same collagen extract. The combination of Method C preparation in our lab and then subsequent graphite production and AMS measurement in the Mannheim lab resulted in the same, or very similar, older ages as the bone samples prepared and measured entirely in the Oxford lab (Table 3a,b, Figures 1 and 2).

DISCUSSION AND CONCLUSION

To obtain reliable bone dates, good quality collagen is required, which can be confirmed through the measurement of the C:N ratio, yield, %C, and %N. As shown in Table 2, collagen from both of our samples is well preserved for all of the pretreatment methods. There was very little difference in the collagen isotope values and preservation criteria indicators between the 3 methods.

With the pretreatment methods we used, almost all of these criteria remained the same, with the exception of collagen yield. We observed a significant increase in yield when the decalcification in HCl was performed relatively quickly at room temperature (Method C) compared to Method A that required decalcification for several days at a constant temperature (5 °C). For example, we obtained 50% more for the bison and up to 3 times more collagen for the mammoth.

The true ages of the 2 bone samples is unknown, but the influence of contamination at ages older than 30,000 yr BP is very asymmetric, with young contamination dominant relative to the original ^{14}C content of an old sample, even at low percent levels of exogenous carbon, contrary to relatively small effect that the addition of ^{14}C-free (dead) carbon has (Mook and Streurman 1981). We know that in the recent shipments of the filters the humectant is modern (Brock et al. 2007), so there is good reason to consider the oldest ages the real ones, and younger ages resulting from modern contamination. In a case when modern contamination is substantial in the collagen to be dated, one might even obtain the paradoxical result that the measured ages appear more homogeneous compared to the case when samples of very low ^{14}C activity, without added contamination, are analyzed.

The age results indicate that the 2 bone samples need to be discussed separately. For the mammoth bone (Table 3a, Figure 1), the picture would be consistent if only the results of methods A to C for Oxford and Kiel are considered. They indicate incomplete removal of modern contamination in the collagen of Method A, and the lack of any measurable effect of the NaOH step, which is the main difference between methods B and C. But the results for Method D, where each of the labs are in full control of all procedures, are clearly incompatible, both among the 2 labs but also compared to the results of these labs with collagen of methods C and B. This was one of the reasons we then sent an aliquot of the collagen prepared in our lab using Method C to a third AMS lab (Mannheim), which resulted in an age identical to the older ages of Oxford with Method D.

We must conclude that either the ages of Oxford (D_O) and Mannheim (C) are true or the 4 results younger by about 1500 yr are the correct ones. As explained above, a shift to older ages compared to the true age is much less probable than the opposite effect of modern contamination. We therefore conclude that the true age of the mammoth is most likely around 35,000 ^{14}C BP, and the younger ages as being caused by modern contamination in the AMS labs, e.g. during graphitization.

The bison sample is older than the mammoth; therefore, we expect the effects of contamination to be more severe for this bone (Table 3b, Figure 2). Again, methods C and D_O show the oldest ages, but Method A has 2 similarly old results as well. An explanation could be that the filters may contain a variable amount of humectant, which might have been removed by the basic cleaning used in Method A. If this is the case, then this means that regular checks on the cleaning efficiency of the ultrafilters are necessary and this is part of methods C and B. The latter method does not include the NaOH step to remove humics; therefore, for bones of this antiquity, contamination by humics could alter the ^{14}C age, and thus, the NaOH step becomes important.

When samples are close to the lower age limit of ^{14}C dating, the low ^{14}C activity level and difficulty of obtaining sufficient and well-preserved collagen means that bone is an especially problematic material to accurately date. In this study, as in earlier exercises (Higham et al. 2006; Hajdas et al. 2007; Hüls et al. 2007), we observed that by using elaborate pretreatment procedures that eliminate both modern laboratory contamination and contamination from degenerated proteins and humic acids we were able to obtain older ages. We still observe discrepancies between the results of different AMS labs, highlighting the many challenges of ^{14}C dating at very low ^{14}C activity.

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7. A Radiocarbon chronology for the complete Middle to Upper Paleolithic transitional sequence of Les Cottés (France)

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A radiocarbon chronology for the complete Middle to Upper Palaeolithic transitional sequence of Les Cottés (France)

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A B S T R A C T

The Middle to Upper Palaeolithic transition is the key period for our understanding of Neanderthal and modern human interactions in Europe. The site of Les Cottés in south-west France is one of the rare sites with a complete and well defined sequence covering this transition period. We undertook an extensive radiocarbon dating program on mammal bone which allows us to propose a chronological framework of five distinct phases dating from the Mousterian to the Early Aurignacian at this site. We found that the Mousterian and Châtelperronian industries are separated from the overlying Protoaurignacian by a gap of approximately 1000 calendar years. Based on a comparison with Upper Paleolithic sites in Europe we see an overlap in the ages of Châtelperronian industries and Aurignacian lithic assemblages, which are usually associated with Anatomical Modern Humans, which is consistent with an acculturation at distance model for these late Neanderthals. The Proto and Early Aurignacian appear contemporaneous indicating that this transition was rapid in this region. Anatomically Modern Humans are present at the site of Les Cottés at least at 39,500 cal BP roughly coincident with the onset of the cold phase Heinrich 4.

1. Introduction

The nature of the Middle to Upper Palaeolithic transition (MUP) in Western Europe is one of the key ongoing debates in Palaeoanthropology, and it is an area where accurate chronology is essential. Central to this debate is the biological nature of the makers of the different lithic assemblages (Neanderthals and modern humans), and contradictory models have been proposed to explain the cultural evolution of these hominins (Hublin et al., 1996). Although two sites have yielded Neanderthal remains in association with Châtelperronian lithics (Bailey and Hublin, 2006; Lévêque and Vandermeersch, 1980), this association has been recently challenged (Bar-Yosef and Bordes, 2010; Higham et al., 2010). Similarly, although the assignment of later Aurignacian assemblages to modern humans is generally widely accepted (Bailey et al., 2009; Klein, 1999), doubts have been raised about the biological identity of the makers of the earliest phases of this industry (Conard et al., 2004). It is, however, generally accepted that the "Protoaurignacian" is the initial stage of the Aurignacian in Europe (Bon, 2006; Laplace, 1966; Mellars, 2006). Bon (2006) recently changed the perception of the Middle to Upper Paleolithic transition in Europe by identifying, based on detailed technological analysis, two techno-complexes within the first phase of the Aurignacian, the Protoaurignacian, and Early Aurignacian.

Sites which have a complete sequence covering this period and have been excavated using modern excavation techniques are few. The site of Les Cottés is one of these rare sites where each of the cultural phases occur in the stratigraphy: Mousterian, Châtelperronian, Protoaurignacian and Early Aurignacian, hence the complete sequence of industries have been identified and recently analyzed. Due to several sterile layers between these phases we cannot consider the site of Les Cottés a continuous site across time but a well preserved site with a clear and complete sequence during the period of the Middle to Upper Palaeolithic transition (Soressi et al., 2010).

Refinement of AMS ^{14}C bone dating methods, including ultrafiltration, a new calibration curve (IntCal09, (Reimer et al., 2009)) and advanced calibration programs (OxCal 4.1, (Bronk Ramsey, 2009)) allow us to apply radiocarbon dating to bones from late Middle and Upper Palaeolithic sites in Europe to provide more accurate chronologies for these industries. We, therefore, obtained

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a series of radiocarbon dates on bone from the main stratigraphic units at Les Cottés.

2. Overview of Les Cottés

Les Cottés is a cave located at the southwestern margins of the Parisian basin, close to the Aquitaine basin (Fig. 1). The site is on the northern limit of the known distribution of the Châtelperronian industry (Pelegrin and Soressi, 2007). Les Cottés was discovered at the end of the nineteenth century, and during the first excavation led by Rochebrune (1881a,b), anatomically modern human remains were found in an Aurignacian layer at the entrance of the cave. Pradel (1961) later defined a sequence of Mousterian, Châtelperronian, Early Aurignacian and Gravettian layers at the site. Les Cottés is best known for its well preserved Aurignacian industry with split-based points and as the type site for "Les Cottés point" lithics from the so-called "evolved" variant of the Châtelperronian (Pradel, 1963). During Pradel's research, conventional radiocarbon dates were obtained on teeth and bone from the site (Evin et al., 1985; Pradel, 1967; Vogel and Waterbolk, 1967). However, the teeth and bone used for dating had been coated in a turpentine solution saturated with beeswax which likely influenced the obtained ages (Evin et al., 1985; Vogel and Waterbolk, 1967) which are listed in Table 1.

In 2006, a new excavation program was started at this site using a multidisciplinary approach including micromorphological, taphonomic, faunal and lithic studies, and dating by OSL, which is in progress, and radiocarbon dating (Soressi et al., 2010).

2.1. Stratigraphy and cultural sequence

The 2006–2009 excavation focused on the 13 m long contiguous section (north, east and south sections) left by Pradel in the 1950s from his original approximately 20 m^2 excavation area (Fig. 2).

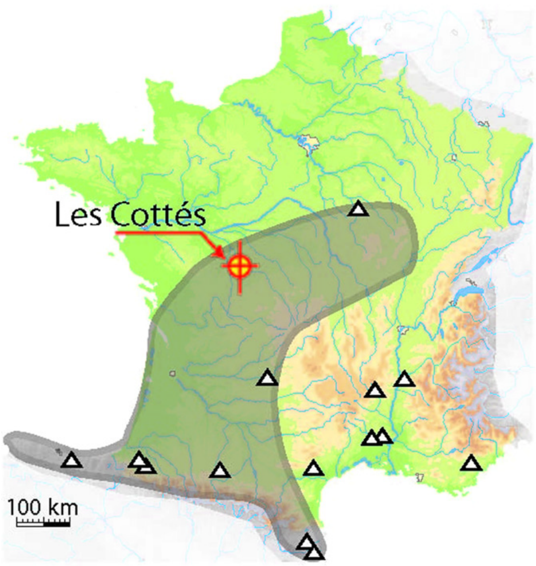

Fig. 1. Map of Les Cottés and of Châtelperronian as well as Protoaurignacian sites in France and north of Spain (map drawn by Soressi and Roussel).

Table 1
Radiometric ^{14}C ages of Les Cottés obtained between 1965 and 1985 (Evin et al., 1985; Pradel, 1967; Vogel and Waterbolk, 1967).

Culture facies	Lab code	^{14}C Age	Err
Gravettian	Ly-2752	23,420	710
Early Aurignacian	Grn-4258	30,800	500
Early Aurignacian	Grn-4296	31,000	320
Early Aurignacian	Grn-4509 teeth	31,200	410
Châtelperronian	Grn-4510	31,900	430
Châtelperronian	Grn-4333 teeth	33,300	500
Mousterian Quina	Grn-4334	32,300	400
Mousterian Quina	Grn-4421	37,600	700

The excavation extended down to the Mousterian levels (Unit 08). The sequence had been preserved by small blocks and gravels fallen from the limestone walls in a clayish sand matrix transported by run-off during the formation of the more recent unit (Unit 02) (Texier, in Soressi et al., 2010), and by run-off but also probably debris-flow for unit 04 and 06 (Liard, unpublished data). The Châtelperronian (Unit 06) is separated from the preceding Mousterian by a 12–15 cm sterile unit. The Protoaurignacian (Unit 04 lower) is separated from the Châtelperronian by a sterile deposit of up to 12 cm in thickness. A small sterile level separates the Protoaurignacian from the overlying Early Aurignacian (Unit 04 upper) in squares 4 and 5 on the north section, although the two stratigraphic units come into contact in the south section. Unit 02 is separated from Unit 04 upper by Unit 03 which is a low density layer.

The formation processes of the sterile layers are, for now, not understood, and will be the focus of future investigations. Flint artefacts show no patination and there are no lithics with natural edge damage except for a few pieces from the Châtelperronian (Soressi et al., 2010). Site formation processes certainly modified the spatial organization of artifacts, but each unit can be considered to be homogenous because of the combination of three types of observations: sterile layers occur between these units, the flint artifacts at the site are well preserved, and the composition of each unit is different.

2.2. Cultural sequence

The large sample size of 3-D plotted artifacts ($n = 13{,}296$) allowed us to determine a precise chrono-cultural attribution for each layer. The specific type of Mousterian present in Unit 08 cannot yet be precisely determined as the number of artifacts is small ($n = 350$: among which only one third are larger than 3 cm, Table 2). In Pradel's publications this Mousterian assemblage has been characterized as a "Moustérien sans biface" even if though one biface was recovered during the excavation in the 1950's (Pradel, 1961). This layer has also been characterized as a Quina Mousterian, even if the reasons for making this attribution was not clearly explained but is likely due to the high proportion of scrapers (Lévêque, 1993). Further work at the site will allow us to increase our sample of Mousterian artifacts and to then determine the specific type of Mousterian.

Châtelperronian retouched tools are mostly backed pieces ("Châtelperron" points as well as "Les Cottés" points). Backed pieces represent 36% of the 83 retouched tools from Unit 06. Blades with a continuous marginally retouch are also well represented (17% of the 83 retouched tools). The production (2273 numbered lithics, Table 2) is orientated towards the production of rectilinear blades. Among the 23 Châtelperronian cores, none of them show an organized flake production and instead they all show blade production characteristic of the Châtelperronian (Connet, 2002;

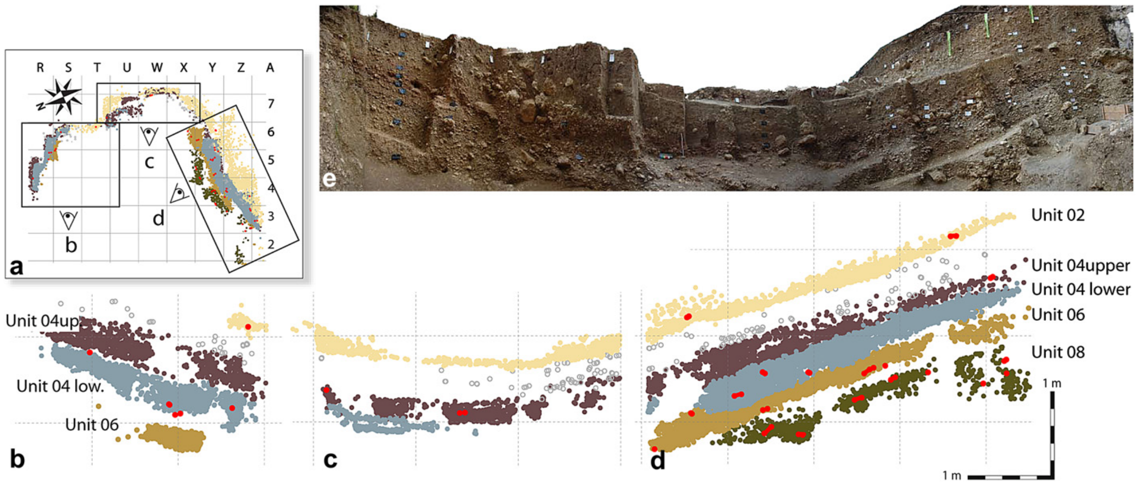

Fig. 2. Top pane: distribution of all archaeological finds on a plan view of numbered lithics and bones. Cultural phases are indicated by color (see legend). Bottom pane: section view of excavation, samples selected are marked in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Pelegrin, 1995). Blades are unipolarly removed by sequential series, on both narrow and wide surfaces (Roussel, 2011).

The Châtelperronian blade cores show a triangular or a rectangular section which is different from the hemi-conical section of Aurignacian cores (Roussel, 2011). The definition of "evolved" Châtelperronian proposed by Pradel (Pradel, 1961, 1963) for this layer cannot for now be accepted or rejected. Comparison with other Châtelperronian layers preserved in a same stratigraphical sequence, such as Quinçay (46 km West of Les Cottés) (Roussel, 2011; Roussel and Soressi, 2010) would help to better evaluate this chrono-cultural attribution.

The Protoaurignacian (Unit 04 lower) lithic production (6466 numbered lithics, Table 2) was aimed towards the production of slightly curved and large bladelets. Bladelet cores (62% of 47 cores) are more numerous than blade cores (32% of 47 cores), which were used to produce a few blades only. Bladelet cores are made out of flakes or out of blocks; bladelet cores are of prismatic or pyramidal morphology. The size of the bladelet cores as well as the absence of blade scars on them may indicate that these bladelet cores are not reduced blade cores (Bon, 2002). Independent bladelet production has been described in the Protoaurignacian of the Grotte du Renne, level VII (Bon and Bodu, 2002), of Isturitz, level C4dIII (Normand, 2006) of l'Observatoire (Porraz et al., 2010,) and of Mandrin (Slimak et al., 2006). Retouched tools are mainly retouched bladelets which are almost always Dufour sub-type Dufour (44% of the 195 retouched tools). These characteristics are typical of the Protoaurignacian from France, Spain and Italy (Arrizabalaga and Altuna, 2000; Bartolomei et al., 1994; Bazile, 2006; Bon and Bodu, 2002; Bordes, 2006; Kuhn and Stiner, 1998; Laplace, 1966; Onoratini, 1986; Slimak et al., 2006).

Table 2
Cultural attribution of the different stratigraphical units (major units are in bold font).

Units	Cultural attribution	Numbered lithics 2006–2009
01	non applicable (n.a.)	45
02	**Final Early Aurignacian**	**1183**
03 top	na	2
03 bottom	Early Aurignacian	116
04upper	**Early Aurignacian**	**2840**
04lower	**Protoaurignacian**	**6466**
05	na	15
06	**Châtelperronian**	**2273**
07	na	6
08	Mousterian	350

Bladelets from the Early Aurignacian (Unit 04 upper) are not morphologically different from the Protoaurignacian, although they are retouched much less often. Bladelets are mostly produced from large carinated endscrapers or from "rabots". Blades from Unit 04 upper are wider, thicker and also more robust (in the width to thickness ratio) than in Unit 04 lower. Retouched tools ($n = 112$) are mostly retouched blades, among which one in five is a blade with Aurignacian retouch. Blades with Aurignacian retouch do not exist in the Unit 04 lower. Simple endscrapers account for 25% of the retouched tools, while they are less numerous in the Protoaurignacian, Unit 04lower (8%). Also, retouched bladelets are much less numerous (13%) than in the Protoaurignacian where they composed 47% of the 195 retouched tools. These features are characteristic of the classic Early Aurignacian (Bon, 2002; Sonneville-Bordes, 1960).

The final assemblage (Unit 02) preserved at the top of the sequence is currently attributed to a final Early Aurignacian. Unit 02 bladelets are smaller than in older levels, most of the time they are curved, and they are never retouched including bladelets found in the systematically sorted 2 mm screen. These small bladelets could have been produced from carinated endscrapers, which are rare, but present, in this layer. Blades are wider than in the oldest levels, and some of them are intentionally fractured. Simple endscrapers are the more numerous retouched tools in this final level (49% of 35 retouched tools), and blades with Aurignacian retouch are present (6% of 35 retouched tools).

2.3. Faunal remains

Faunal remains (3337 bigger than 2.5 cm) are relatively well preserved and rounding and weathering is infrequent (Rendu, in Soressi et al., 2010). Reindeer is the most abundant species (it counts for up to 96% of the 716 identified bones in Unit 02) except

Table 3
Isotopic data, %Collagen, %C and %N and C:N for the samples taken during the 2007 and 2008 field campaigns. Radiocarbon results of Les Cottés: CPh = Culture phases, EA = Early Aurignacian, PA = Protoaurignacian, C = Châtelperronian and M = Mousterian.

S-EVA	US	Square Nr	CPh	%Coll.	$\delta^{13}C$	$\delta^{15}N$	%C	%N	C:N	EVA Code	^{14}C Age Graphite MPI dated at ORAU	1σ Err	MAMS Code	^{14}C Age Collagen MAMS	1σ Err	OxA Code	^{14}C Age Collagen OxA	1σ Err
9717	02.1	T6-61	EA	0.8	−19.6	7.4	35.2	12.7	3.2							OxA-V-2381-46	31,750	280
9718	02.1	Z3-3	EA	2.5	−19.3	8.6	40.6	13.6	3.5	EVA-2	32,150	160	MAMS-10810	31,470	180	OxA-V-2381-47	31,640	260
[a]9719	02.1	Y6-321	EA	2.3	−19.2	8.2	43.2	14.5	3.5	EVA-3	32,530	170	MAMS-10811	32,940	220	OxA-V-2381-48	32,590	280
[a]9706	04	A3-218	EA	1.4	−20.2	7.2	42.2	14.3	3.4	EVA-9	34,330	210				OxA-V-2381-44	34,050	350
9711	04.0r	T7-109	EA	1.6	−19.2	7.4	40.3	14.6	3.2	EVA-8	33,050	250	MAMS-10807	33,240	230	OxA-V-2384-10	33,340	390
9709	04.1r	W7-206	EA	3.1	−20.5	7.5	42.2	14.4	3.4	EVA-10	34,350	190	MAMS-10805	35,160	280	OxA-V-2381-45	34,650	340
[a]9720	04.2r	R4-271	EA	1.5	−19.0	6.8	44.0	14.6	3.5	EVA-22	33,750	250	MAMS-10812	33,960	280	OxA-V-2381-49	33,920	320
9713	04.4b	S6-363	PA	2.9	−19.7	5.2	33.6	11.4	3.4				MAMS-10808	35,150	280			
[a]13671	04.4	Y5-1083	PA	1.6	−19.1	4.5	39.2	14.2	3.2				MAMS-10826	33,710	230			
[a]13672	04.9	Y6-1681	PA	1.3	−19.6	7.7	38.8	14.1	3.2				MAMS-10827	34,080	250			
[a]13663	04,6	Y5-1225	PA	0.7	−19.6	7.1	36.9	13.4	3.2				MAMS-10814	33,080	230			
[a]13665	04.5 BJ	S6-557	PA	2.2	−19.2	8.5	38.9	14.1	3.2	EVA-7	34,380	210	MAMS-10816	35,250	280	OxA-V-2381-52	34,220	400
[a]13669	04.5 BJ	R5-785	PA	2.7	−19.3	6.4	38.7	14.1	3.2	EVA-14	34,250	220				OxA-V-2382-47	34,870	340
9695	06 rc	Z4-1258	C	3.4	−20.4	5.3	45.9	15.6	3.4				MAMS-10803	38,540	270			
[a]13662	06	Y6-979	C	1.7	−20.4	5.3	37.5	13.7	3.2	EVA-21	41,280	340				OxA-V-2381-50	40,280	650
[a]13664	06	Y5-2785	C	1	−18.9	6.8	37.4	13.6	3.2	EVA-5	42,410	400				OxA-V-2381-51	42,090	900
[a]13666	06	X6-205	C	2.1	−19.1	4.2	41.9	15.2	3.2	EVA-11	36,180	240				OxA-V-2381-53	36,410	450
[d]13667	06	Z4-3286	C	1.9	−21.6	6.3	38.3	14.0	3.2	EVA-12	36,720	320	MAMS-10823	38,430	420	OxA-V-2382-45	37,400	500
13668	06	Z4-3368	C	3.3	−19.9	5.2	42.7	15.6	3.2	EVA-13	38,150	290	MAMS-10824	38,210	420	OxA-V-2382-46	37,850	450
[a]13673	08	Y4-625	M	1	−20.2	7.9	20.7	7.5	3.2	EVA-15						OxA-V-2384-11	39,760	1600
[a]13674	08	Y5-1575	M	1	−20.1	4.8	24.7	9.0	3.2	EVA-16	34,390	250				OxA-V-2384-12	35,330	900
[c]13675	08	Z3-362	M	3.4	−19.8	7.6	39.6	14.4	3.2	EVA-17	41,730	330	MAMS-10828	40,800	530	OxA-V-2382-48	42,870	750
[b]13676	08	Y5-1654	M	3.6	−20.1	4.9	41.6	15.2	3.2	EVA-18	42,200	350	MAMS-10829	41,780	600	OxA-V-2382-49	42,690	750
[c]13677	08	Z3-356	M	6.8	−20.4	7.7	43.1	15.7	3.2	EVA-19	38,650	260	MAMS-10830	40,710	510	OxA-V-2382-50	40,280	550
[c]13678	08.rc	Z3-289	M	3.8	−20.3	6.8	40.7	14.8	3.2				MAMS-10831	38,970	440			
[a]13679	08.rc	Y4-311	M	3.2	−19.5	7.7	39.0	14.1	3.2				MAMS-10832	39,390	470			
[a]13680	08.rc	Z3-308	M	1	−18.4	6.8	34.9	12.6	3.2	EVA-20	37,640	270				OxA-V-2384-13	38,970	900

[a] bone with cut marks.
[b] retouchoir.
[c] digested bone.
[d] carnivore bite marks.

for in the Mousterian levels, where bovids are more abundant than reindeer (Soressi et al., 2010). In the Mousterian layer (Unit 08), 15.5% of the 220 numbered bones were modified by carnivores, and about an other 17% show evidence of human activity, suggesting the contribution of two different accumulators. Although the human impact on the material increase significantly with the Châtelperronian (24% of Unit 06 bones show human impact), the carnivore ratio stays the same as with the Mousterian. Carnivore action almost disappear with the Protoaurignacian and the Early Aurignacian. Less than 2% of the total number of bone show evidence of carnivore action in Unit 04 lower, Unit 04 upper and Unit 02. Within these top layers, up to 31% of bones show human modifications (Rendu, unpublished data).

3. Radiocarbon dating

3.1. Samples selection and pretreatment

At Les Cottés we selected bone samples for dating from all of the layers excavated during the 2007 and 2008 seasons (Fig. 2 and Table 3). To date the human presence in a site it is important to select bones which document human activity (Higham et al., 2011) and at the same time it is important to find out if processes like intrusion, mixing, taphonomic reworking, cryoturbation, bioturbation occurred. In the case of Les Cottés we selected 27 mammal bones, 15 with cut marks, one retouchoir, 6 without any marks and 5 which document the presence of carnivores.

Bone samples were pretreated at the Department of Human Evolution, Max Planck Institute for Evolutionary Anthropology (MPI-EVA), Leipzig, Germany, using the following method (Talamo and Richards, 2011): the outer surface of the bone samples are first cleaned by a shot blaster and then 500 mg of bone powder is taken. The samples are then decalcified in 0.5 M HCl at room temperature until no CO_2 effervescence is observed, usually for about 4 h 0.1 M NaOH is added for 30 min to remove humics. The NaOH step is followed by a final 0.5 M HCl step for 15 min. The resulting solid is gelatinized following Longin (1971) at pH3 in a heater block at 75 °C for 20 h. The gelatin is then filtered in an Eeze-Filter™ (Elkay Laboratory Products (UK) Ltd.) to remove small (<8 μm) particles. The gelatin is then ultrafiltered with Sartorius "Vivaspin 15" 30 kDa ultrafilters (Brown et al., 1988). Prior to use the filter is cleaned to remove carbon containing humectants (Higham et al., 2006). The samples are lyophilized for 48 h.

In the past we sometimes observed discordant results for test samples in the Middle and Upper Palaeolithic time ranges between different AMS labs (Talamo and Richards, 2011). We therefore designed an extended dating procedure. Samples which gave sufficient collagen were separated into three aliquots; one was then sent to the Klaus-Tschira-AMS facility of the Curt-Engelhorn Centre, Mannheim, Germany, one was sent to the Oxford Radiocarbon Accelerator Unit (ORAU) and the last one was graphitized at the MPI-EVA and the graphite was dated at the ORAU. Samples with low amounts of collagen were sent to one of these two AMS labs. The crucial step is the collagen preparation, hence the replication of dates provided by the choice of two AMS facilities does not provide checks on the bone pretreatment itself, but instead provides a check on the dates produces by the different laboratories, and also improves the precision of the radiocarbon ages.

Table 4
Combined radiocarbon results of Les Cottés.

S-EVA	SquareNr	CPh	EVA Code	MAMS Code	OxA Code	Weighted Mean	1σ Err
9717	T6-61	EA			OxA-V-2381-46	31,750	280
9718	Z3-3	EA	EVA-2	MAMS-10810	OxA-V-2381-47	31,810	[a]250
9719	Y6-321	EA	EVA-3	MAMS-10811	OxA-V-2381-48	32,670	120
9706	A3-218	EA	EVA-9		OxA-V-2381-44	34,260	180
9711	T7-109	EA	EVA-8	MAMS-10807	OxA-V-2384-10	33,180	160
9709	W7-206	EA	EVA-10	MAMS-10805	OxA-V-2381-45	34,610	140
9720	R4-271	EA	EVA-22	MAMS-10812	OxA-V-2381-49	33,860	160
9713	S6-363	EA		MAMS-10808		35,150	280
13671	Y5-1083	PA		MAMS-10826		33,710	230
13672	Y6-1681	PA		MAMS-10827		34,080	250
13663	Y5-1225	PA		MAMS-10814		33,080	230
13665	S6-557	PA	EVA-7	MAMS-10816	OxA-V-2381-52	34,620	[a]390
13669	R5-785	PA	EVA-14		OxA-V-2382-47	34,430	180
9695	Z4-1258	C		MAMS-10803		38,540	270
13662	Y6-979	C	EVA-21		OxA-V-2381-50	41,070	300
13664	Y5-2785	C	EVA-5		OxA-V-2381-51	42,360	370
13666	X6-205	C	EVA-11		OxA-V-2381-53	36,230	210
13667	Z4-3286	C	EVA-12	MAMS-10823	OxA-V-2382-45	37,360	[a]610
13668	Z4-3368	C	EVA-13	MAMS-10824	OxA-V-2382-46	38,100	210
13673	Y4-625	M	EVA-15		OxA-V-2384-11	39,760	1600
13674	Y5-1575	M	EVA-16		OxA-V-2384-12	34,460	240
13675	Z3-362	M	EVA-17	MAMS-10828	OxA-V-2382-48	41,640	260
13676	Y5-1654	M	EVA-18	MAMS-10829	OxA-V-2382-49	42,180	280
13677	Z3-356	M	EVA-19	MAMS-10830	OxA-V-2382-50	39,260	[a]770
13678	Z3-289	M		MAMS-10831		38,970	440
13679	Y4-311	M		MAMS-10832		39,390	470
13680	Z3-308	M	EVA-20		OxA-V-2384-13	37,750	260

CPh = Culture phases EA = Early Aurignacian; PA = Protoaurignacian; CP = Châtelperronian; M = Mousterian.
[a] standard deviation of the aliquot.

3.2. *Collagen quality control*

As an indicator of contamination and/or degradation of collagen, C:N ratios, %C, %N, collagen yield and $\delta^{13}C$ and $\delta^{15}N$ values are measured (Ambrose, 1990; DeNiro, 1985; Harbeck and Grupe, 2009; Hedges, 2002; Schoeninger et al., 1989; Strydonck et al., 2004, van Klinken, 1999), and it is assumed that contamination has occurred when the atomic C:N ratio falls outside the range observed for modern animals and humans (2.9–3.6). $\delta^{13}C$ and $\delta^{15}N$ values in bone collagen depend on diet and can be used to distinguish herbivores from carnivores and marine and terrestrial diets. The full range of these parameters needs to be considered to decide if collagen extracted from bone is of sufficient quality (Lee-Thorp, 2008; Richards and Hedges, 1999, 2003; Richards et al., 2005, 2000, 2008). Another simple but important criterion is the quantity of collagen that can be recovered. Usually a limit of 1% weight is considered as a necessary minimum condition (Hedges and Van Klinken, 1992), and samples of lower yield are potentially problematic, although the use of an ultrafilter to extract high quality collagen means that this lower limit is not necessarily valid for ultrafiltered samples (Brock et al., 2007; Higham et al., 2006). For Les Cottés the isotopic results, C:N ratios and collagen yields are given in Table 3. The C:N ratios of all samples are well within acceptable ranges, and the collagen yield is mostly above 1%.

4. Results

4.1. *^{14}C results*

The radiocarbon results from the Mannheim AMS laboratory (Lab code: MAMS), the Oxford laboratory (Lab code: OxA-V) and the MPI-EVA laboratory (Lab code: EVA) are listed in Table 3. All dates were corrected for a residual preparation background estimated from pretreated ^{14}C free bone samples, kindly provided by the ORAU. Radiocarbon dates are available for all layers, from the Aurignacian to the Mousterian.

For the majority of the samples we have results on aliquots from two AMS facilities (Oxford and Mannheim) and for two stages of the preparation (collagen and graphite). Hence we can perform consistency checks on these three types of results, using the R_Combine function of OxCal (Bronk Ramsey, 2009). Of 18 pairs or triplets, 14 pass the agreement test, and the four results flagged as outliers do not show a systematic pattern according to lab or sample type. Therefore we combine the radiocarbon results of each sample using the weighted mean of AMS labs and type and the error of the mean, except for the four flagged samples where the error is the scaled standard deviation of the ^{14}C results (Table 4, Fig. 3).

The uncalibrated radiocarbon dates of all Aurignacian layers range from 31,750 to 35,150 radiocarbon years BP. The Early Aurignacian (US 04 upper) and Protoaurignacian (US04 lower) units cannot be separated in age by radiocarbon dating. Six dates come from the Châtelperronian layer and these range from 36,230 to 42,360 radiocarbon years BP. The Mousterian samples are surprisingly well preserved, with collagen yields of up to 7%. The ^{14}C dates range from 34,460 to 42,180 radiocarbon years BP.

Generally the radiocarbon results of each stratigraphic unit agree with their stratigraphic position, but some samples are observed with ages apparently inconsistent with their stratigraphic location. The obvious case is between Mousterian and Châtelperronian, with one extremely young Mousterian date (S-EVA13674, ^{14}C Age 34,460 ± 240 BP) and two Châtelperronian dates (S-EVA13662, ^{14}C Age 41,070 ± 300 BP; S-EVA13664, ^{14}C Age 42,360 ± 370 BP) which would be considered of Mousterian age. At the present stage of the excavation potential causes of this overlap cannot be determined; vertical mixing appears improbable because of the presence of a sterile layer (US07) between these two phases. These dates cannot be explained at present time and are considered outliers. They are reported here for completeness, but are excluded

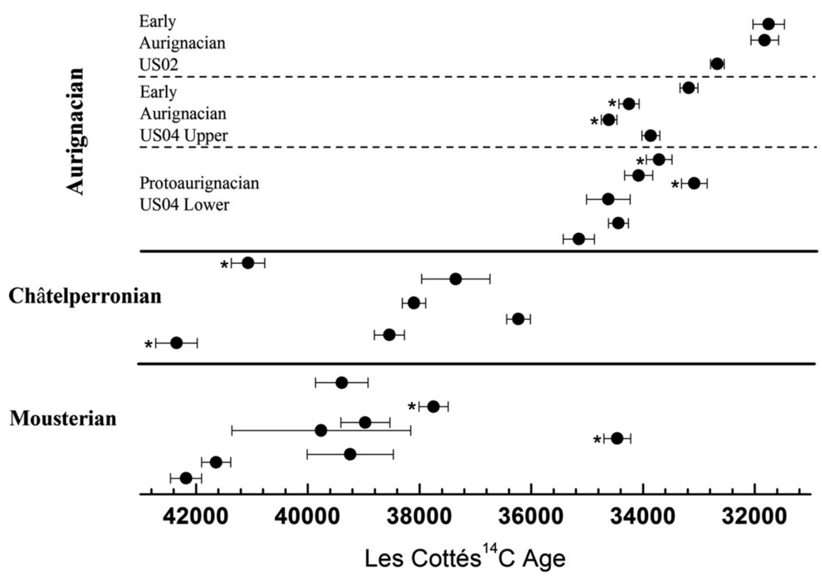

Fig. 3. Radiocarbon ages of the weighted means of Les Cottés. The dates are arranged according to the archaeological layer; within each layer they are sorted by depth. The bars indicate 1σ error. The asterisks indicate the outliers for the Bayesian analysis.

from the subsequent discussion. More samples are expected from future excavation in the northern part of this area.

Compared to the earlier radiometric ^{14}C dates (Table 1), our results, older by 500–5000 radiocarbon years (Table 4, Fig. 3), demonstrate the importance of the advanced pretreatment techniques of bone, made possible by the low amount of carbon required for AMS and ultrafiltration. Moreover, the design of the study with age determination of sample aliquots by two independent AMS facilities allows additional checks of the credibility of the dating.

4.2. Calibrated results

Radiocarbon calibration for dates older than 25,000 years BP was controversial until recently. In 2009 radiocarbon calibration saw substantial progress through the publication of the calibration curve IntCal09 (Reimer et al., 2009). Earlier discrepancies between various ^{14}C datasets were largely resolved; especially the apparent ^{14}C excursions between 30,000 and 40,000 ^{14}C BP were shown not to be real. Consequently, the IntCal working group constructed a new calibration curve back to 50,000 cal BP (Reimer et al., 2009).

The weighted means of the radiocarbon dates we produced (Fig. 3) were calibrated using OxCal 4.1 (Bronk Ramsey, 2009) and IntCal09 (Reimer et al., 2009). Within each layer the dates are arranged according to the stratigraphic level. Bayesian analysis, which is a powerful tool to detect outliers in stratified datasets, was used to build a model which includes a sequence of 5 sequential (non-overlapping) phases. Mainly due to the temporal overlap between the dates of the distinct layers (Fig. 3), OxCal finds no agreement between the full set of dates and stratigraphy. However, we obtained an agreement of 82% (A_overall = 60% indicates good agreement) if 8 dates, marked by asterisks in Fig. 3 (S-EVA13674 ^{14}C age 34,460 ± 240 BP and S-EVA13680 ^{14}C age 37,750 ± 260 BP from Mousterian levels, S-EVA13662 ^{14}C age 41,070 ± 300 BP and S-EVA13664 ^{14}C age 42,360 ± 370 BP from Châtelperronian levels, S-EVA13671 ^{14}C age 33,710 ± 230 BP and S-EVA13663 ^{14}C age 33,080 ± 230 BP from the Protoaurignacian US 04 lower level, and S-EVA9706 ^{14}C age 34,260 ± 180 BP and S-EVA9709 ^{14}C age 34,610 ± 140 BP from the Early Aurignacian US 04 upper level), were removed from the dataset (Fig. 4). There is no clear indication as to the reason of the removal of a sample, e.g. cut marks, % of collagen, isotope ratios or faunal distinction. It is difficult to accept mixing as explanation because as discussed above all sequences are clearly separated in the excavation, and there are even sterile layers between them.

5. Discussion

The Châtelperronian and the Protoaurignacian (US 04 lower) are separated by a gap of about 1000 calendar years, calculated from the difference in the respective boundaries in the OxCal model.

The interpretation of the Châtelperronian as resulting from an acculturation at a distance of late Neanderthals who observed modern human Aurignacian technology (Hublin et al., 1996) clearly depends on the temporal relation between the Châtelperronian and Aurignacian. At Les Cottés the two phases are well separated but a comparison shows that the Châtelperronian of Les Cottés is contemporaneous to the Aurignacian (Proto and Early) of other sites in Europe (Haesaerts et al., 1996; Higham et al., 2009; Hoffecker et al., 2008; Nigst et al., 2008; Sirakov et al., 2007; Szmidt et al., 2010). Potentially the most important site in the region is the Grotte du Renne at Arcy-sur-Cure, which has a complete but shorter sequence and which is almost (there is no Early Aurignacian at Arcy-sur-Cure) analogous to Les Cottés, but a recent re-assessment showed doubts about the validity of the stratigraphy (Higham et al., 2010).

Reconsidering the full dataset of ^{14}C ages between Protoaurignacian US 04 lower and Early Aurignacian US 04 upper (Fig. 3), in which 6 out of 10 dates overlap, indicating that one tradition very quickly replaced the other in this region.

At the top of the sequence at Les Cottés the final Early Aurignacian US 02 is distinctly different from the underlying phases,

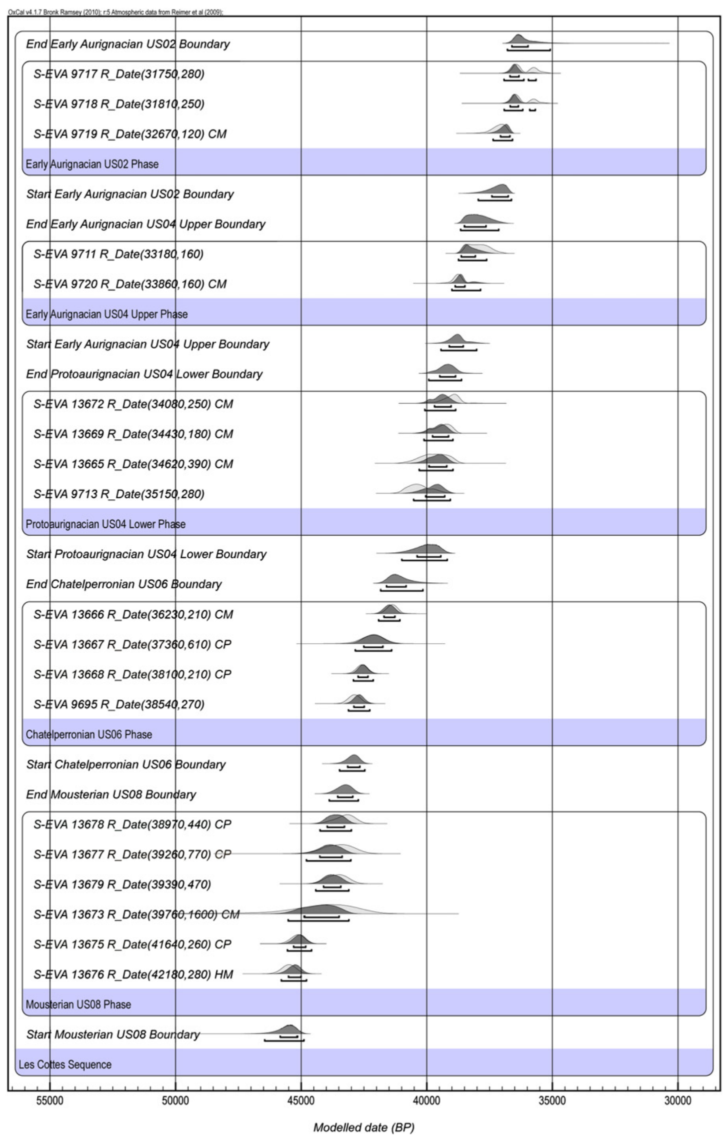

Fig. 4. Bayesian model build using OxCal 4.1 (Bronk Ramsey, 2009) and IntCal09 (Reimer et al., 2009) from the radiocarbon weighted means of Les Cottés. CP = Carnivore Presence, CM = Cut Marks and HM = Human Modification (Retouchoir).

and has the youngest dates for this type of assemblage in Europe (Haesaerts et al., 1996; Higham et al., 2009; Hoffecker et al., 2008; Nigst et al., 2008; Sirakov et al., 2007; Szmidt et al., 2010).

5.1. Comparison to climatic data

It is useful to place cultural changes as indicated by lithic industries in the context of well documented events of rapid climate change in the glacial era (Müller et al., 2011; Tzedakis et al., 2007). Several warm Dansgaard-Oeschger (DO events 12 to 8) and one cold Heinrich Event (HE4) occurred in the Les Cottés time interval as shown in Fig. 5 (Chronology of the climate sequence taken from (Fleitmann et al., 2009).

The shading of the DO bars indicates the rapid initial warming (less than 50 years) of 11 °C–16 °C in Greenland (Wolff et al., 2010), whereas the cooling is gradual. A discussion of links to the decadal scale warming phase of DO events is limited by the unresolved question of synchroneity between Greenland climate markers and mid-latitude ecological response to climate change (Blaauw et al., 2010; Wohlfarth et al., 2008) and because of the error range of the radiocarbon dates in the chronology. HE4, on the other hand, lasted for more than 1500 years, therefore the age distribution

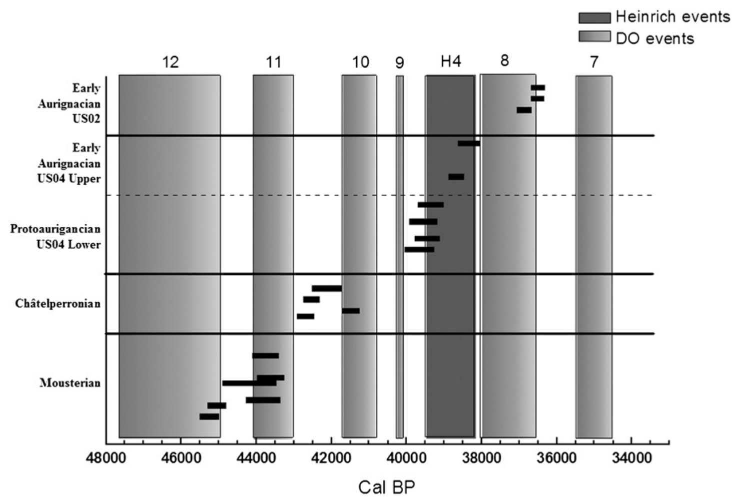

Fig. 5. Temporal relation of the archaeological phases of Les Cottés compared to the rapid climate changes as defined by several climate archives in the northern hemisphere (Fleitmann et al., 2009); for France see also Genty et al. (2003).

in our chronology should document if the area of Les Cottés was less populated during this cold phase.

The ages obtained on Les Cottés Protoaurignacian confirm that the Anatomically Modern Humans associated with this industry entered this part of Europe with the onset of HE4 and that they populated this area even during this phase, as observed also for Eastern Europe (Hoffecker, 2011, 2009).

6. Conclusion

Les Cottés is one of the few sites with a complete and well defined sequence covering the Middle to Early Upper Palaeolithic periods in Europe. We obtained radiocarbon dates on 27 bone samples from each archaeological level at this site. We created a chronological framework of five phases from the Mousterian to Early Aurignacian periods. The Mousterian and Châtelperronian are separated from the overlying Protoaurignacian level by a gap of approximately 1000 calendar years. The internal temporal relation between the Mousterian and Châtelperronian is not fully resolved by our dates, this aspect will be addressed by future work at the site. The fact that a substantial part of the Proto and Early Aurignacian appear contemporaneous, within the resolution of ^{14}C dating, indicates that this transition was rapid in this region. Anatomically Modern Humans are presents at the site of Les Cottés at least at 39,500 cal BP roughly coincident with the onset of the strong cold phase Heinrich 4.

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8. Conclusion and Future work

The main focus of this thesis was developing methods for radiocarbon dating bone from archaeological sites dating to the Middle to Upper Palaeolithic transition in Europe, and then applying those methods to obtain dates from a key site from this time period.

The key findings of this thesis are as follows:

Internationally agreed radiocarbon calibration back to 50,000 cal BP

To overcome the ambiguities created by the co-existence of several conflicting ^{14}C datasets beyond 25,000 cal BP the IntCal working group has constructed the calibration curve 'IntCal09' (Reimer, et al., 2009). Earlier problems calibrating samples older than 30,000 cal BP were resolved in 2004 through collaboration between a number of labs and international scientists (including the author of this thesis), which involved discussion about the absolute time scales of the various datasets as well as improvements in the ^{14}C technique itself.

The Radiocarbon dating method is not flawed between 35,000 and 42,000 cal BP

It has been stated by some authors that ^{14}C dating is not possible around 39,000 cal BP because of two key reasons. First, until recently there was a choice of conflicting ^{14}C datasets to calibrate radiocarbon dates in the Palaeolithic age range, which has left room for ambiguity (Mellars, 2006). Second, there have been doubts about the radiocarbon method being capable of producing dates in this time period because of alleged fluctuations of the atmospheric radiocarbon level at this time (Conard and Bolus, 2003, Conard and Bolus, 2008, Fedele, et al., 2008, Giaccio, et al., 2006, Pettitt and Pike, 2001). However, this putative radiocarbon dating anomaly during MUP lasting for millennia simply does not exist. ^{14}C production fluctuations lead to intervals of both accelerated change of radiocarbon years *versus* calendar years and decreased change (i.e., radiocarbon age plateaux), which are well resolved in the current radiocarbon calibration dataset IntCal09. The radiocarbon community has now solved the issues of inconsistent ^{14}C calibration and created a valid calibration curve back to 50,000 cal BP (Reimer, et al., 2009). It is well documented that a geomagnetic minimum (Laschamp Event) and reduction in the circulation in the North Atlantic (Heinrich event 4) resulted in gradual changes in ^{14}C, but these anomalies are not strong enough to prevent accurate radiocarbon calibration.

Optimising techniques to obtain pure and uncontaminated bone collagen

At the lower age limit of radiocarbon dating, the low ^{14}C activity level and the difficulty of obtaining sufficient and well-preserved collagen, means that bone is an especially challenging material to accurately date. In this thesis I investigated several collagen extraction techniques. I identified a combination of steps which lead to consistent and reliable ages. These procedures combined with the recently installed CO_2 gas collection and graphitization system, enable the department at human evolution at Max Planck-EVA Leipzig, to perform all the required steps in bone dating, from sampling to graphite production for AMS ^{14}C dating.

Well preserved bison and mammoth bones from the North Sea of unknown age were adopted as the long term quality control material, especially to test for background contamination in the sample preparation, with the assumption that these two bones were at least Pleistocene, and ideally older than 50,000 BP. Initial radiocarbon results from two AMS laboratories on collagen prepared at MPI showed the bones to be in the age range of 30,000 to 45,000 ^{14}C BP, but we observed large discrepancies in the radiocarbon ages between different radiocarbon labs. These inconsistencies could have been caused by deficits in the pretreatment methods which we had established for collagen extraction, by insufficient removal of contamination in the samples, in the AMS measurements themselves, or all three.

Therefore we designed a study to investigate the source of these inconsistent dates, and we also compared the results of our pretreatment methods against results from the methods from two of these AMS labs. In this study, as in earlier exercises (Hajdas, et al., 2007, Higham, et al., 2006b, Hüls, et al., 2007), we observed that by using elaborate pretreatment procedures that eliminate both modern laboratory contamination and contamination from degenerated proteins and humic acids we were able to obtain older ages. We still observe discrepancies between the results of different AMS labs, highlighting the many challenges of radiocarbon dating at very low ^{14}C activity.

Accurate chronology of sites covering the transition of Middle to Upper Palaeolithic in France, with a link to climatic events

The radiocarbon dating application in this thesis targeted the site of Les Cottés in France (paper 3 in this thesis).

The nature and duration of the Middle to Upper Palaeolithic transition (MUP) in Western Europe is one of the key ongoing debates in Palaeoanthropology, and it is an area where accurate chronology is essential. Central to this debate is the biological nature of the makers of the different lithic assemblages (Neanderthals and modern humans), and contradictory models have been proposed to explain the cultural evolution of these hominids

Les Cottés is one of the few sites with a complete and well defined sequence covering the Middle to Early Upper Palaeolithic periods in Europe. Refinement of AMS ^{14}C bone dating methods, including ultrafiltration, a new calibration curve (IntCal09, (Reimer, et al., 2009)) and advanced calibration programs (OxCal 4.1, (Bronk Ramsey, 2009)) allow the application of radiocarbon dating to bones from late Middle and Upper Palaeolithic sites in Europe to provide more accurate chronologies for these industries. Radiocarbon dates of 27 bone samples from each archaeological level at this site were obtained. A chronological framework consisting of five phases from the Mousterian to Early Aurignacian periods was created. The results show that the Mousterian and Châtelperronian are contiguous and separated from the overlying Protoaurignacian level by a gap of 1000 years. The fact that a substantial part of the Proto and Early Aurignacian appear contemporaneous, within the resolution of ^{14}C dating, indicates that this transition was rapid in this region. Anatomically Modern Humans are present at the site of Les Cottés at least at 39,500 cal BP, which is roughly coincident with the onset of the strong cold phase Heinrich 4.

Future work

It has been observed in several instances that radiocarbon dates obtained previously from transition period sites could be considered too young, and using more elaborate pretreatment techniques resulted in older ages (e.g. (Higham, 2011, Higham, et al., 2009). Therefore, it would be useful to revisit these key sites and apply the suite of radiocarbon procedures outlined here. Additionally, we aim to continue dating new sites from this time period with the protocol established here.

9. References

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Samenvatting

Zoals Colin Refrew opmerkte heeft koolstof ouderdomsbepaling een revolutionaire rol gespeeld in de archeologie sinds de vijftiger jaren van de vorige eeuw. De eerste bijdrage die koolstof ouderdomsbepaling maakte was nauwkeurige directe dateringen te leveren voor archeologische materialen. De tweede grote bijdrage was het verschaffen van kalender tijdschalen voor de Europese prehistorie, vooral vanaf de zeventiger jaren voor het neolithicum en latere perioden. Tegenwoordig beleven wij een derde belangrijke bijdrage van koolstof ouderdomsbepaling, omdat het wordt gebruikt om nauwkeurige chronologieën te krijgen voor prehistorische perioden die dichtbij de limieten van deze methode liggen, zoals de overgang van het midden- naar het jong-paleolithicum.

Beginselen van koolstof ouderdomsbepaling

^{14}C wordt gevormd in de hogere atmosfeer en wordt opgenomen in de mondiale koolstof reservoirs hoofdzakelijk als $^{14}CO_2$ in de atmosfeer. Door fotosynthese wordt ^{14}C opgenomen in planten en uiteindelijk in alle levende organismen. Na het afsterven van een organisme vindt er geen uitwisseling meer plaats met het koolstof reservoir en vervalt ^{14}C tot ^{14}N met een bekende snelheid (halveringstijd). Het meten van de hoeveelheid overgebleven ^{14}C in de overblijfselen van afgestorven organismen is de basis voor de koolstof methode.

Aangezien er in het verleden schommelingen zijn geweest in de aanmaak van ^{14}C, is het nodig om koolstof ouderdom te ijken aan ouderdom in kalenderjaren. Koolstof ouderdom wordt omgezet in kalenderjaren met behulp van calibratie curves, die gebaseerd zijn op onafhankelijk gedateerde organische overblijfselen, zoals jaarringen, zeekoralen of meer- en zee-afzettingen. In 2009 heeft de IntCal werkgroep een nieuwe calibratie curve opgesteld, die teruggaat tot 50.000 jaar cal BP, een ontwikkeling die zeer belangrijk is geweest voor dit proefschrift. De koolstof dateringen die in dit proefschrift gegeven worden werden gemeten met de Accelerator Mass Spectrometry (AMS) techniek. AMS wordt gebruikt om de verschillende isotopen van koolstof (^{12}C, ^{13}C, ^{14}C) aan het licht te brengen door ze te scheiden op basis van hun respectieve massa's.

Koolstof calibratie rond 40.000 jaar cal BP

De overgang van het midden- naar het jong-paleolithicum is de periode waarin de Neanderthalers verdwenen en moderne mensen voor het eerst verschijnen in Europa. Koolstof dateringen van organische overblijfselen van laat-midden en vroeg-jong-paleolithische vindplaatsen en hun calibratie zijn vooral omstreden gebleken. Verscheidene ^{14}C databestanden zijn opgenomen als bewijs voor extreem grote ^{14}C schommelingen rond 40.000 cal BP, zoals het bestand met dateringen van de Tyrrheense Zee kern CT85-5, die op het eerste gezicht duiden op grote koolstof afwijkingen voor dat tijdstip. De reeks dateringen van de bovengenoemde Tyrrheense Zee kern lijkt te suggeren, dat in een periode van 800 jaar de ^{14}C leeftijden variëren van circa 35.000 ^{14}C jaar BP tot circa 25.000-20.000 ^{14}C jaar BP en dan terug naar circa 33.000-32.000 ^{14}C jaar BP. Ik beschouw de interpretatie van dit databestand als onjuist, omdat een ^{14}C ouderdoms inversie van 15.000 ^{14}C jaren niet veroorzaakt kan zijn door schommelingen in het ^{14}C niveau in de atmosfeer. De toegenomen ^{14}C productie tijdens het magnetische dieptepunt van het Laschamp Event is goed gedocumenteerd in hoge resolutie ^{14}C rapporten, zoals Cariaco, die een solide basis vormen voor koolstof calibratie voor dit tijdsbestek.

Voorbehandling van bot

Ondanks de aanzienlijke mogelijkheden die bot collageen biedt voor koolstof ouderdomsbepaling, kan het dateren van botten problematisch zijn, omdat deze organische materialen vaak van slechte kwaliteit zijn en in archeologisch verband onderhavig kan zijn aan vervuiling. Het effect van koolstof vervuiling op de koolstof ouderdom wordt ernstiger naarmate het te dateren bot ouder is. Als een aanwijzing van vervuiling en/of verslechtering van het collageen gebruiken verschillende auteurs C : N verhoudingen, $\delta^{13}C$ en $\delta^{15}N$ waarden, en de samenstelling van aminozuur. Algemeen wordt aangenomen dat vervuiling waarschijnlijk plaats gevonden heeft als de atoom verhoudingen C : N buiten het bereik vallen, dat voor moderne dieren en mensen is waargenomen.

Ik heb een reeks verschillende voorbehandelings technieken onderzocht en methoden voor het reinigen van de moleculaire gewicht (MW) extractiefilters en voorfilter elementen. Voor deze experimenten heb ik botten gebruikt van een mammoet en een bison, die in prehistorische afzettingen van de Noord Zee zijn aangetroffen, en ik heb identieke collageen extracten van deze exemplaren naar drie AMS laboratoria gestuurd. De resultaten verschilden aanzienlijk, van 31.660 tot 35.280 ^{14}C BP in het geval van de mammoet, en van 40.200 tot 47.300 ^{14}C BP voor de bison. De meeste van deze verschillen kunnen verklaard worden door de verschillende voorbehandelings methoden die gebruikt werden en door de verschillen in metingen tussen de drie AMS laboratoria. Als gevolg van deze experimenten heb ik een optimaal voorbehandelings protocol opgesteld, dat consistente ouderdoms schattingen oplevert en dat resulteert in een laag intra-monster leeftijdsverschil. Deze voorbehandelings methode is het protocol dat thans gebruikt wordt bij de MPI-EVA.

Volgorde van behandeling van bot voor koolstof ouderdomsbepaling bij MPI

Alle bot monsters die in dit proefschrift genoemd worden, werden onderworpen aan de volgende voorbehandelings procedures, gewoonlijk in groepen van maximaal 12 monsters:

- invoeren in een databestand
- vergruizing van het bot
- ontkalking
- verwijdering van humisch materiaal
- gelatinisatie
- filters reinigen en controleren op de afwezigheid van vervuiling
- ultra-filtratie
- vriesdrogen

Alle collageen, die verkregen is na de bovenstaande voorbehandeling, wordt gegrafietiseerd volgens de volgende procedures:

- tinnen kroesjes worden gevuld met collageen
- verbranding in een Elemental Analyser (EA)
- bepaling van de koolstof opbrengst en C : N verhouding
- bepaling van $\delta^{13}C$ en $\delta^{15}N$ in een massa spectrometer
- reinigen van de CO_2 vaten en prepareren van de ijzer katalysator
- verzamelen van CO_2 in de opstelling

- toevoegen van waterstof
- omzetting van CO_2 naar grafiet in de grafietisator
- controle van grafietisatie parameters
- klaarmaken van blanke monsters
- klaarmaken voor verzending en verzenden naar een AMS laboratorium voor koolstof meting.

Koolstof chronologie van de midden- tot jong-paleolithische vindplaats Les Cottés

De voorbehandelingsmethoden, die in dit proefschrift ontwikkeld zijn, werden toegepast op bot monsters van de paleolithische vindplaats Les Cottés (Frankrijk). De onderzocht culturele lagen lopen van het Mousterien tot het Aurignacien, inclusief het Châtelperronien. Deze culturele perioden zijn in verband gebracht met episoden van snelle klimaatsverandering, die van rond 47.000 tot 35.000 cal BP plaatsvonden. Tijdens deze periode waren er 6 warmere fasen die Dansgaard-Oeschger (DO) cycli genoemd worden, en een duidelijke afkoelingsperiode, die bekend staat als Heinrich event 4 (H4). De resultaten van het AMS koolstof ouderdomsbepaling programma op bot collageen monsters van Les Cottés heeft het mogelijk gemaakt een chronologisch schema te ontwikkelen dat overeenkomt met de archeologische stratigrafie van de vindplaats.

Les Cottés is een van de weinige vindplaatsen met een compleet en goed gedefinieerde profiel, dat de midden- tot vroeg-jong-paleolithische perioden in Europa beslaat. Koolstof dateringen werden verkregen voor 27 bot monsters van elk archeologisch niveau en werden gegroepeerd op basis van de vijf culturele fasen die op de vindplaats aanwezig waren, van het Mousterien tot het Vroeg-Aurignacien. Het Mousterien en het Châtelperronien zijn gescheiden van het er boven liggende Proto-Aurignacien niveau door een hiaat van ongeveer 1000 kalender jaren. De interne tijdsrelatie tussen het Mousterien en het Châtelperronien wordt niet volledig opgehelderd door onze dateringen, dit aspect zal in toekomstig onderzoek op de vindplaats aan de orde komen.

Het feit dat een aanzienlijk deel van het Proto- en Vroeg-Aurignacien in tijd lijken samen te vallen, binnen de resolutie van ^{14}C ouderdomsbepaling, geeft aan dat deze overgang snel was in het gebied in kwestie. Anatomisch moderne mensen waren al aanwezig op de vindplaats Les Cottés in 39.500 cal BP, ruwweg gelijktijdig met het begin van de duidelijk koude fase van Heinrich event 4.

Summary

As observed by Colin Renfrew radiocarbon dating has had a revolutionary role in archaeology since the 1950s. The first contribution made by radiocarbon was to produce accurate direct dates for archaeological materials. The second main contribution was to provide calendar time scales for European prehistory, especially starting from the 1970s for the Neolithic and later periods. Today we are experiencing a third key contribution of radiocarbon dating, as it is being used to attain accurate chronologies for prehistoric periods close to the limit of the method, such as the transition from the Middle to Upper Palaeolithic.

Radiocarbon basics

^{14}C is created in the upper atmosphere and enters the global carbon reservoirs mainly as $^{14}CO_2$ in the atmosphere. Through photosynthesis ^{14}C enters plants and ultimately all living organisms. After the death of an organism, exchanges with the carbon reservoir no longer take place and ^{14}C decreases by decay to ^{14}N at a known rate (half-life). Measuring the amount of remaining ^{14}C in the remains of dead organisms is the basis of the radiocarbon method.

As there have been fluctuations in the production of ^{14}C in the past, it is necessary to calibrate radiocarbon ages to calendar ages. Radiocarbon ages are converted to calendar years by means of calibration curves based on independently dated organic remains, such as tree-rings, marine corals or lake and marine sediments. In 2009 the IntCal working group constructed a new calibration curve spanning back to 50,000 cal BP, a development of key importance for this thesis. The radiocarbon dates presented in this thesis have been measured using the Accelerator Mass Spectrometry (AMS) technique. AMS is used to detect the different isotopes of carbon (^{12}C, ^{13}C,^{14}C) by separating them according to their respective mass.

Radiocarbon calibration around 40,000 years cal BP

The Middle to Upper Palaeolithic transition is the period during which Neanderthals disappeared and modern humans made their first appearance in Europe. Radiocarbon dates on organic remains from late Middle and early Upper Palaeolithic sites and their calibration have proven especially controversial. Several ^{14}C datasets have been taken as evidence for extremely large ^{14}C fluctuations around 40,000 cal BP, such as the set of dates from the Tyrrhenian Sea core

CT85-5, which if taken at face value indicate strong radiocarbon anomalies at that point in time. The sequence of dates from the above-mentioned Tyrrhenian Sea core appears to suggest that within an 800 year period the ^{14}C ages fluctuated from circa 35,000 ^{14}C yr BP to circa 25,000-20,000 ^{14}C yr BP and then back to circa 33,000-32,000 ^{14}C yr BP. I consider the interpretation of this dataset as erroneous, because a ^{14}C age inversion of up to 15,000 ^{14}C years could not have been caused by fluctuations in the level of atmospheric ^{14}C. The enhanced ^{14}C production during the magnetic low of the Laschamp Event is well documented in high resolution ^{14}C records, such as Cariaco, which provide a solid basis for radiocarbon calibration for this time period.

Bone pretreatment

Despite the considerable potential offered by bone collagen for radiocarbon dating, dating bones can be problematic as these organic materials are often degraded and can be subject to contamination in archaeological contexts. The effect of contaminating carbon on the radiocarbon ages is more severe the older the bone used for dating. As an indicator of contamination and/or degradation of collagen different authors use C:N ratios, $\delta^{13}C$ and $\delta^{15}N$ values, and amino acid composition. It is generally assumed that contamination is likely to have occurred when atomic C:N ratios fall outside the range observed for modern animals and humans.

I investigated a range of different pretreatment techniques and methods of cleaning the molecular weight (MW) separation filters and pre-filter elements. For these experiments I used bones of a mammoth and a bison recovered in prehistoric deposits from the North Sea and I sent the same collagen extracts from these specimens to three AMS facilities. The results varied considerably, between 31,660 and 35,280 ^{14}C BP in the case of the mammoth and between 40,200 and 47,300 ^{14}C BP in the case of the bison. Most of this variability could be explained by the different pretreatment methods employed and by differences in measurements between the three AMS facilities. As a result of these experiments, I devised an optimal pretreatment protocol, which produces consistent age estimates and results in low intra-sample age variability. This pretreatment method is the protocol now in use at the MPI-EVA.

Sequence of bone preparation for radiocarbon dating at MPI

All the bone samples presented in this thesis were subject to the following pretreatment procedures, usually in batches of up to 12 samples:

- Entry in database
- Pulverisation of bone
- Decalcification
- Removal of humics
- Gelatinization
- Cleaning of the filters and checking for the removal of contamination
- Ultrafiltration
- Freeze drying

All the collagen obtained after the pretreatment outlined above is graphitized according to the following procedures:

- Loading of collagen into tin caps
- Combustion in an Elemental Analyser (EA)
- Determination of carbon yield and C:N ratio
- Determination of $\delta^{13}C$ and $\delta^{15}N$ in a mass spectrometer
- Cleaning the CO_2 gas containers and conditioning of the iron catalyst
- Collection of CO_2 in the rigs
- Addition of hydrogen
- Conversion of CO_2 into graphite in the graphitizer
- Check of graphitization parameters
- Preparation of blank samples
- Preparation of shipment to an AMS facility and submission to the AMS laboratory for radiocarbon measurement.

Radiocarbon chronology of the Middle to Upper Palaeolithic site of Les Cottés

The pretreatment methods developed in the present thesis were applied to bone samples from the Palaeolithic site of Les Cottés (France). The cultural levels investigated span from the Mousterian to the Aurignacian, and include the Châtelperronian. These cultural phases were correlated to episodes of rapid climatic change which occurred from around 47,000 to 35,000 cal BP. During this period there were 6 warmer stages called Dansgaard-Oeschger (DO) events, and the marked cooling episode known as Heinrich event 4 (H4). The results of the AMS radiocarbon dating program on bone collagen samples from Les Cottés have allowed the development of a chronological framework that is coherent with the archaeological stratigraphy of the site.

Les Cottés is one of the few sites with a complete and well defined sequence covering the Middle to early Upper Palaeolithic periods in Europe. Radiocarbon dates have been obtained for 27 bone samples from each archaeological level and grouped on the basis of the five cultural phases present at the site, from the Mousterian to the Early Aurignacian. The Mousterian and Châtelperronian are separated from the overlying Protoaurignacian level by a gap of approximately 1000 calendar years. The internal temporal relation between the Mousterian and Châtelperronian is not fully resolved by our dates, this aspect will be addressed by future work at the site. The fact that a substantial part of the Proto and Early Aurignacian appear contemporaneous, within the resolution of ^{14}C dating, indicates that this transition was rapid in the region in question. Anatomically Modern Humans were present at the site of Les Cottés at least by 39,500 cal BP, roughly coincident with the onset of the markedly cold phase of Heinrich event 4.

Curriculum Vitae

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Sahra Talamo **born 1974, In Taranto, Italy**

Studies & Professional experience

2000-2001

Borsa di Studio

Acquaintance with ^{14}C procedures at the University of Heidelberg

2001

Laurea in scienze Naturali

At the University of Milan; entitled

'Le datazioni ^{14}C: Datazioni tradizionali e tecniche di *wiggle-matching* applicate a insediamenti preistorici dell'area Padana'

Adviser : Leone Fasani

Co-adviser: Bernd Kromer

2002-2005

Heidelberg Radiocarbon laboratory;

projects:

Roman Gap (P.Kuniholm, Cornell University)

EMRCP (S.Manning, Reading - UK)

Fieldwork to find subfossil, lateglacial wood

Development of combustion of large wood samples using an oxygen bomb

Since 2007

PhD-thesis at the Max-Planck Institute for Evolutionary Anthropology, Leipzig

Congress participation (Podium-Poster presentation)

EGS/EGU 2003 Nizza

Radiocarbon Conference 2003 Wellington Poster: *"No evidence of systematic regional ^{14}C differences"*

SCIEM 2000 Poster: Bronze age time scale in the Eastern Mediterranean

Archeometria 2004 Bressanone Poster: *"Absolute time frame for the Early and middle Bronze age lake settlements in Northern Italy - combining the strength of Dendrochronolgy and Radiocarbon"*

AGU Fall-session December 2004 San Francisco Poster: *"Atmospheric Radiocarbon fluctuations in the Late Glacial obtained from tree-ring chronologies - aspects of rapid climate change"*

Carlsberg Conference Copenhagen 2005. Icecore and Radiocarbon Chronologies

INQUA-SEQS 2006 Milano 2006

Radiocarbon & Archaeology 5th International symposium, Zurich 2008

- **3rd International Symposium on Biomolecular Archaeology (ISBA3)**, University of York, York, U.K.
  Poster: **Talamo S** and Richards MP (2008) Testing pretreatment methods for the radiocarbon dating of bone collagen.
  Poster : Mannino M, **Talamo S**, Di Salvo R, Schimmenti V, Piperno M, Tusa S, Tagliacozzo A, and Richards MP (2008) Preliminary results of C and N isotope analyses and ^{14}C dating of prehistoric humans and animals from the Mesolithic-Neolithic site of Grotta dell'Uzzo, Sicily, Italy.

20th International Radiocarbon Conferences; Hawaii (2009) Oral presentation: **Talamo S** and Richards MP "AMS sample comparison close to the limit of the method. A limit or challenge?".

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