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Title: Refining 14C dating of bone >30,000 BP : establishing an accurate chronology for the Middle to Upper Palaeolithic transition in France

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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 CO₂ 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 ¹⁴C 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 CO₂ 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 ¹⁴C 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 ¹⁴C calibration is terrestrial carbonate, such as speleothemes (dropstones/stalagmites in caves). The carbonate of speleothemes is formed from CO₂ in topsoil and from carbonate dissolved from limestone (which is ¹⁴C 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 ¹⁴C 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 $\delta^{18}\text{O}$ 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).

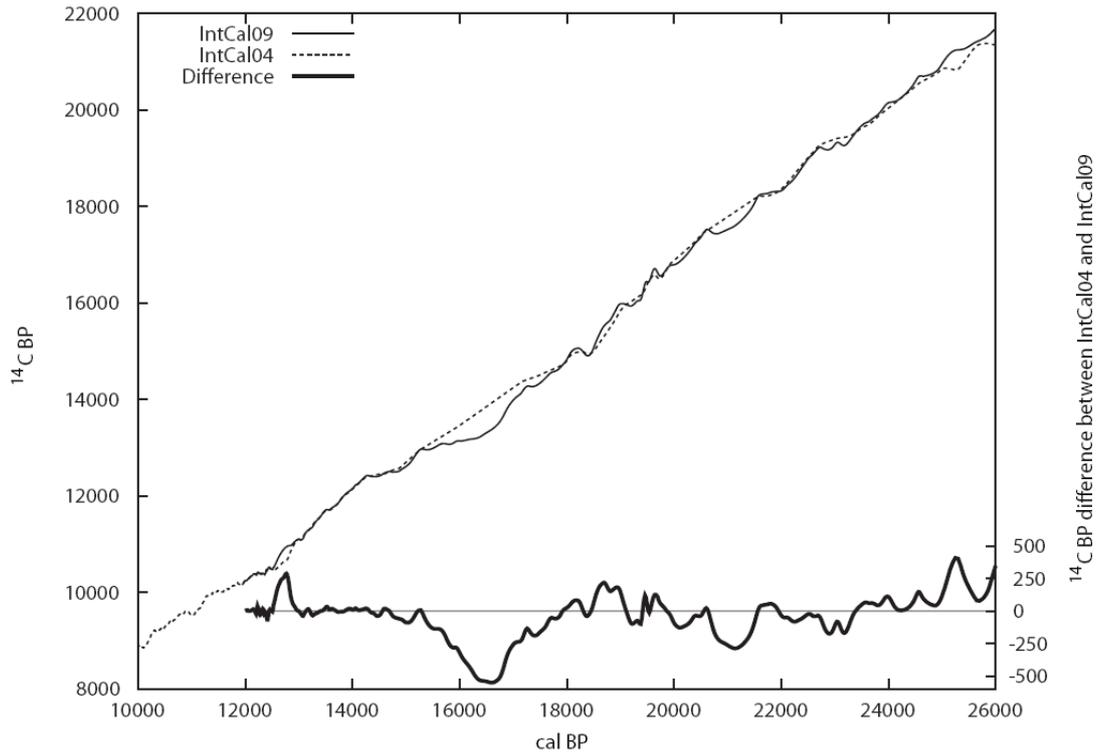
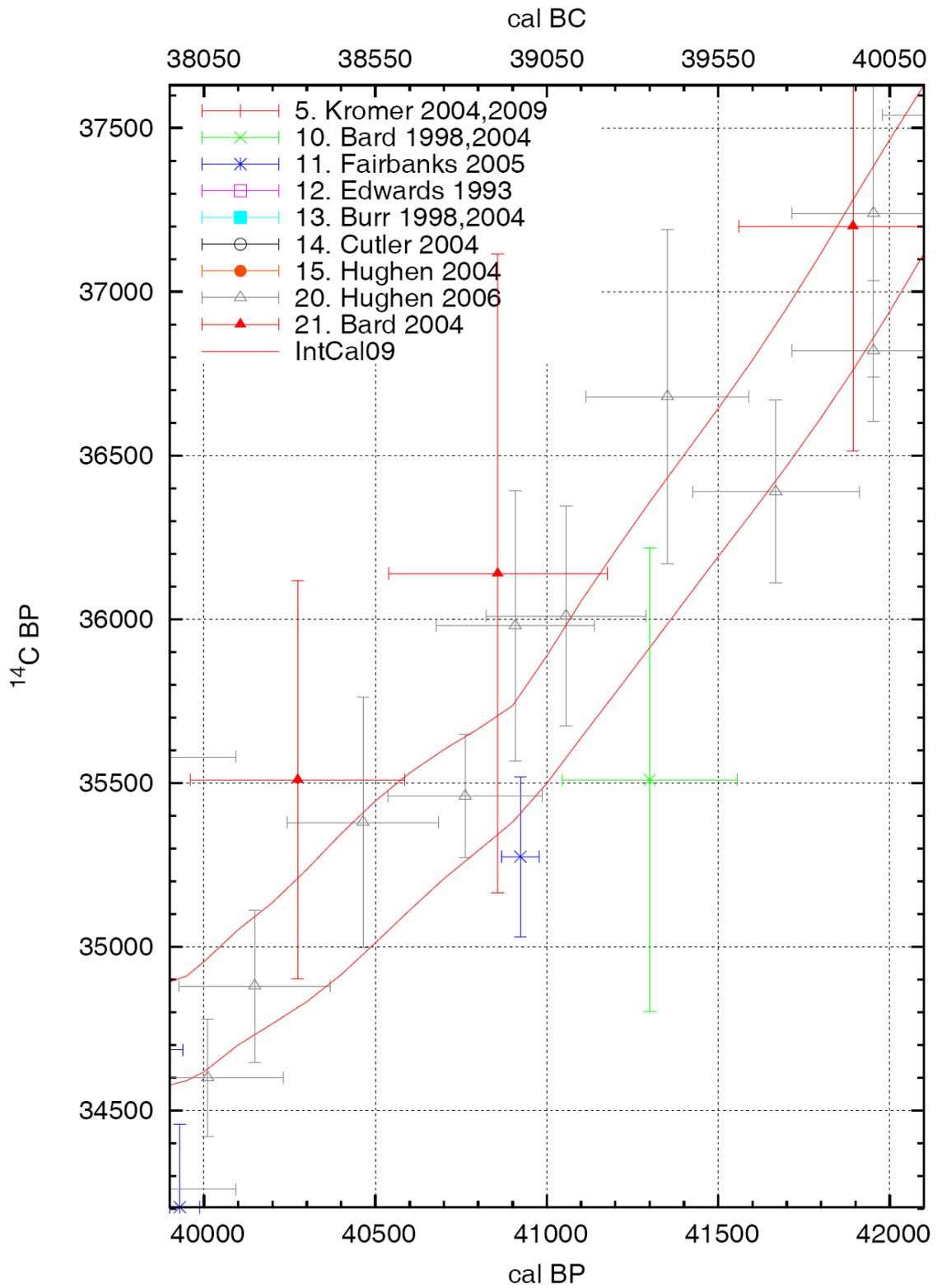
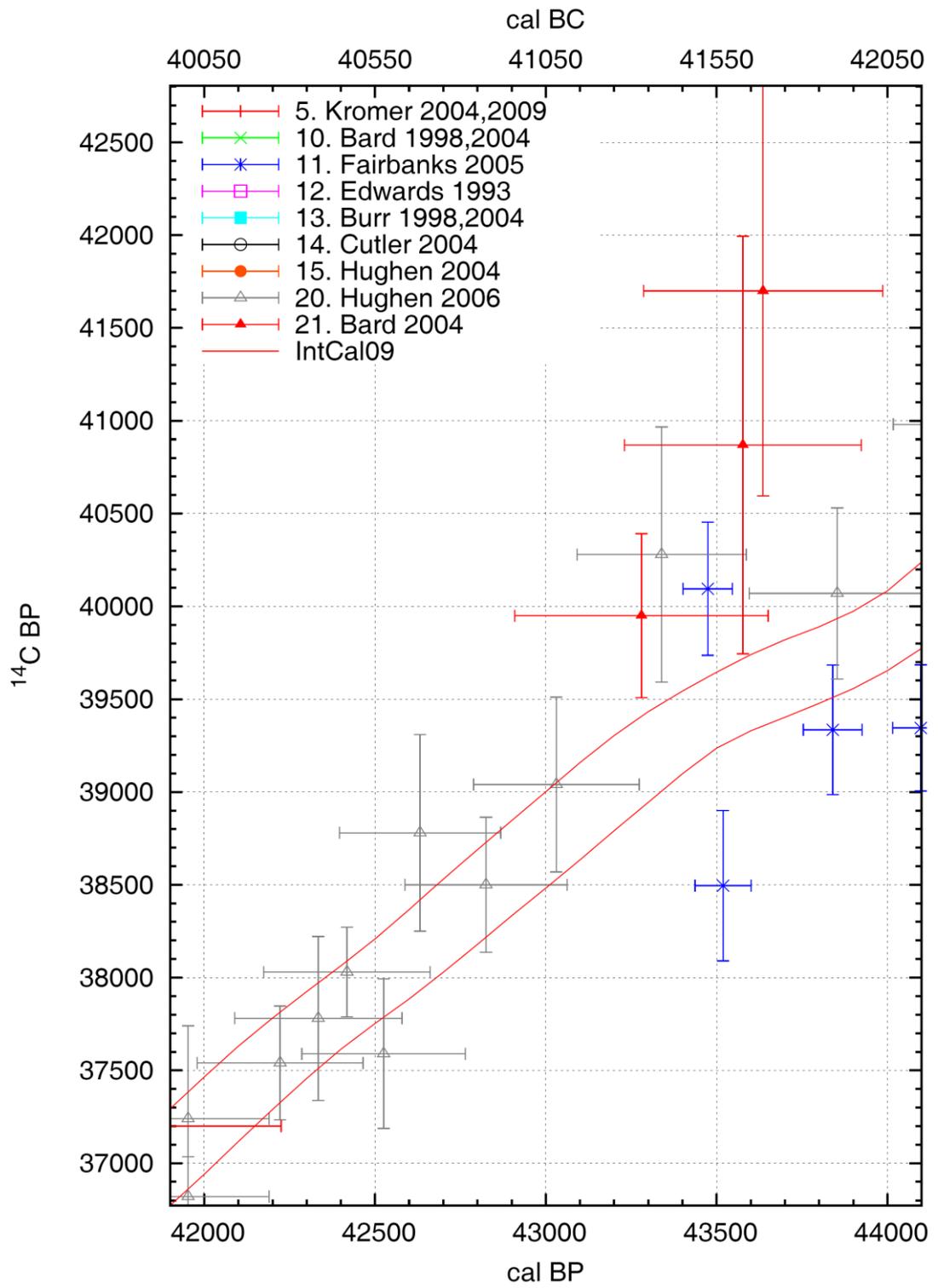


Figure 2.1 Difference between the calibration data curves IntCal04 and IntCal09 in the interval 10,000 to 26,000 cal BP. The shifts are mainly caused by the change of the Cariaco time scale to the Hulu Cave U/Th time scale (Reimer, et al., 2009).

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 ¹⁴C 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).





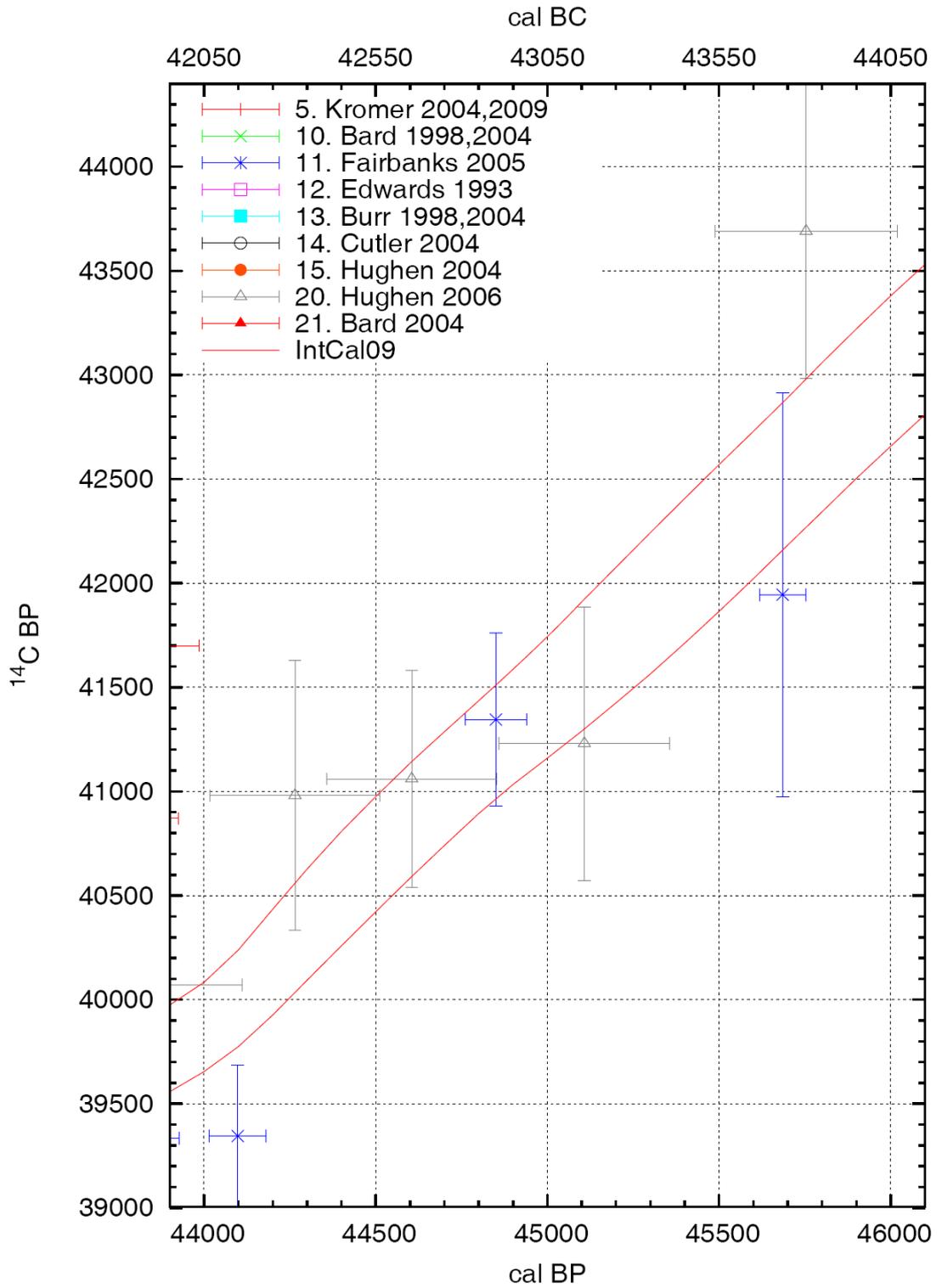
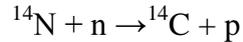


Figure 2.2 Detailed view of the new calibration dataset IntCal09 (Reimer, et al., 2009), including the original datasets from which IntCal09 was calculated.

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}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 $^{14}\text{CO}_2$, which is chemically identical to ordinary $^{12}\text{CO}_2$, 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 $^{14}\text{CO}_2$, 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:

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

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

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.

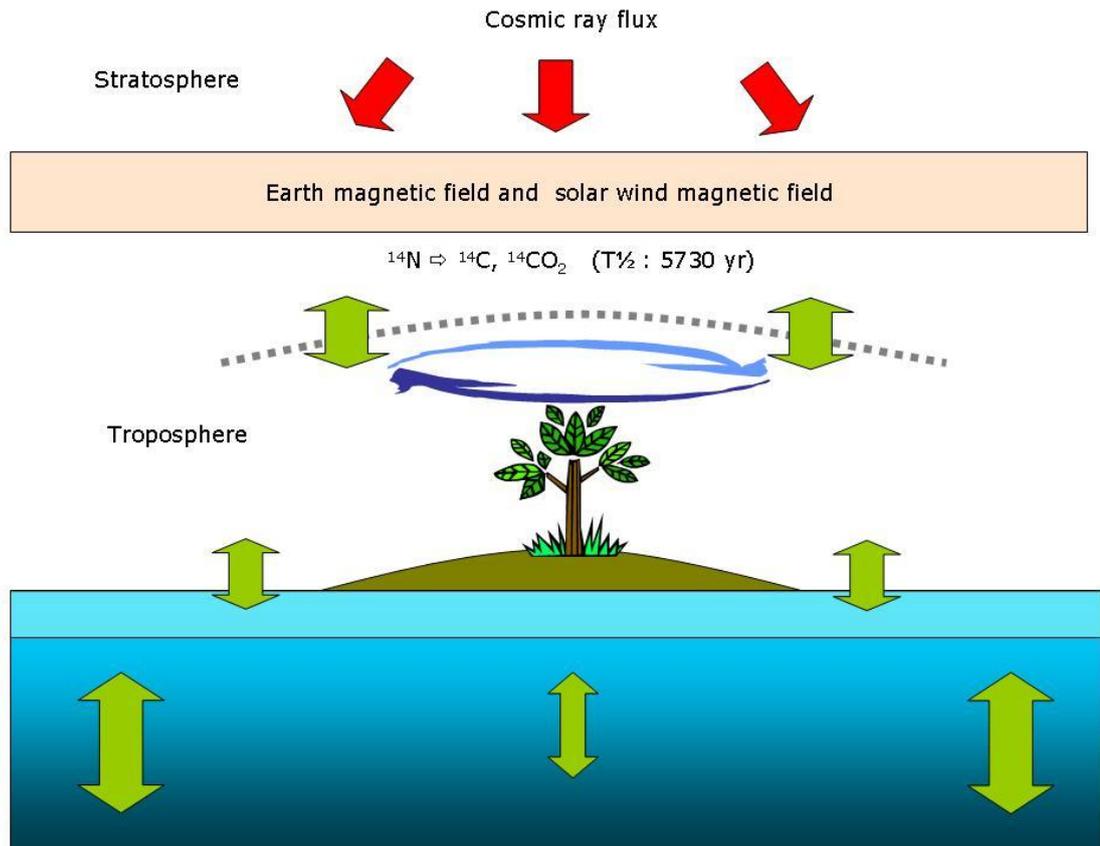


Figure 2.3 Schematic representation of the carbon cycle and the production of ^{14}C , main carbon reservoirs are deep ocean (blue), surface ocean mixed layer (light blue), atmosphere and biosphere.

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

$$(3) \quad A/A_0 = 1/2 = e^{-\lambda T_{1/2}}$$

so that

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

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 $^{13}\text{C}/^{12}\text{C}$ is also measured using an isotope ratio mass spectrometer and is then used to correct for the $^{14}\text{C}/^{12}\text{C}$ fractionation. ^{13}C measurements are reported in the δ notation, which is defined as the relative differences of $^{13}\text{C}/^{12}\text{C}$ 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 $\delta^{13}\text{C}$ at levels around -25‰ and bone samples are slightly enriched with $\delta^{13}\text{C}$ 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 $^{14}\text{C BP}$, 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 $^{14}\text{C atoms}$, 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 $^{14}\text{C}/^{12}\text{C}$ is just 10^{-12} . This small quantity makes radiocarbon difficult to detect, because there are interfering molecules of mass 14, e.g. $^{13}\text{C}^1\text{H}$. 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).

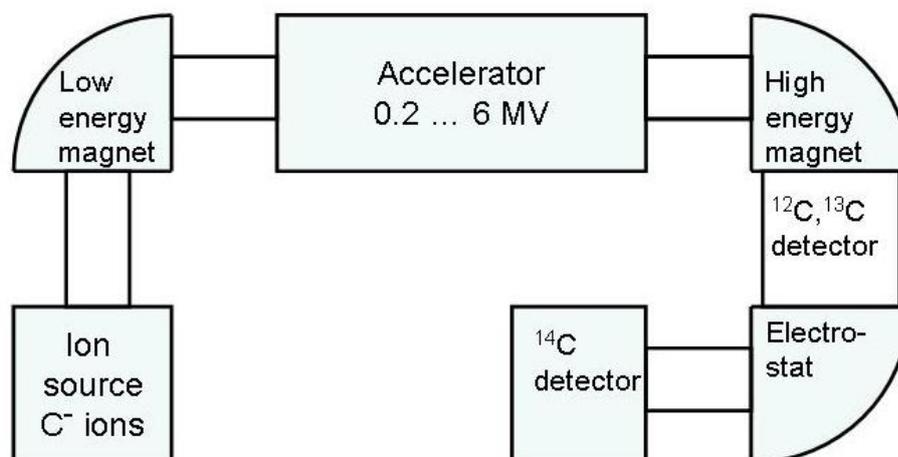


Figure 2.4 Schematic representation of an AMS system.

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 $^{14}\text{C}/^{12}\text{C}$ 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).