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## THE END OF OUR FIFTH DECADE

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# Radiocarbon and fossil bones: what's in a date

Hans van der Plicht

*The Radiocarbon dating method has developed into a reliable dating method for organic sample materials, including fossil bone. More than any other material, this category is the subject of discussions concerning the validity of dates, in particular for the older part of the $^{14}C$ time scale.*

## 1 Introduction

The Radiocarbon dating method happens to be just a few years older than the Faculty of Archaeology of Leiden University. The method has contributed significantly to archaeology, since it provides a physical yardstick of time independent of cultural assessments (Libby 1952). Organic samples such as charcoal, bone, wood, peat, shells, plant remains etc. can be directly dated back to about 50,000 years ago. Since the conception of the method in the 1950s, it has continuously been improved; the most significant ones being the introduction of AMS enabling small sample analysis (Tuniz *et al*. 1998), and the establishment of a calibration curve for the complete dating range which makes the dating method more or less absolute (Reimer *et al*. 2009).

Chronological questions have been solved by Radiocarbon dating over the years, spawning 'revolutions' in archaeology. However there always have been debates concerning the acceptance of $^{14}C$ dates (Renfrew 1999). These continue to the present day – witness, to mention a few prime examples, the dating of the Santorini volcanic explosion (Balter 2006a), "low or high" Bronze/Iron Age chronology debates in the Levant (Holden 2003) as well as the larger Mediterranean region (van der Plicht *et al*. 2009 and references therein), and the dating of the cave drawings from the Chauvet cave (Balter 2008). Radiocarbon clashes here with traditional pottery chronologies and the science of parietal art.

In this contribution, the focus will be mainly on a specific category of $^{14}C$ dating: fossil bones. Also here are sometimes vehement discussions concerning validity of dates, sample quality, and methodology. This is also caused by recent developments of the $^{14}C$ method, in particular AMS and sample treatment improvements like the so-called ultrafilter method. The latter was also counted a revolution, in particular for the Neandertal/modern human transition chronology during the Palaeolithic (Mellars 2006).

Bone is the most difficult (or sensitive) material to date, compared with for example charcoal or wood. The literature is polluted by many invalid bone dates; the older the samples, the worse this becomes (e.g., Graf 2009).

The danger of circular reasoning is present. When an improvement in the method produces dates that fit expectations of the archaeologist (usually in the older direction), that does not necessarily mean that the dates are correct. Also, when bone dates are different from expectations (usually in the younger direction), that does not automatically mean they are wrong.

When two independent age assessments are not consistent with each other and there is no obvious objective reason or solution, then all we can say is: at least one of them must be wrong.

All of this concerns collagen, the organic fraction of bones. In this contribution, the present state of the above mentioned affairs will be discussed.

But also the mineral inorganic fraction of fossil bone (apatite) is of interest to the archaeologist. It has been neglected largely because this material too often produces wrong dates. But it works quite well for a special category of archaeological samples: cremated bone.

## 2 The history of bone dating

### *2.1 Collagen vs. apatite*

Bone dating proved to be difficult in the early days of Radiocarbon. Dating of 'bulk' carbon was practised, often giving young ages. Bone samples were originally not even listed among sample materials to be used (Olsson 2009). Sometimes, the dating of bone apatite was successful. But secondary calcite from the burial environment can infiltrate the bone. This obviously hampers bone $^{14}C$ dating based on the inorganic fraction, which must be based on primary (biogenic) and not secondary (diagenetic) carbonate. Longin (1971) therefore developed a collagen extraction technique, enabling $^{14}C$ dating of the organic bone component. Collagen does not exchange carbon with the environment. This therefore has become the main dating tool for bone ever since.

Illustrative examples of bone collagen vs. apatite dating are shown in the table below (table 1). This methodological test was done to gain insight into possible reservoir effects,

| lab number | sample | location | extracted | $^{14}$C (BP) |
|---|---|---|---|---|
| GrA-11815 | human bone | Hardinxveld | collagen | 6530±50 |
| GrA-11442 | "Elvis" | Netherlands | apatite | 6600±80 |
| GrA-11816 | human | Hardinxveld | collagen | 6710±50 |
| GrA-11444 | "Henk" | Netherlands | apatite | 6440±70 |
| GrA-12184 | human | Tomba Alica | collagen | 325±50 |
| GrA-12062 | | Italy | apatite | 320±60 |
| GrA-14109 | human | Jardinga | collagen | 6235±40 |
| GrA-14076 | | Netherlands | apatite | 6560±40 |
| GrA-13526 | human | Norrismount | collagen | 4460±50 |
| GrA-13336 | | Ireland | apatite | 3300±40 |
| GrA-14881 | human | Topped Mountain | collagen | 3340±45 |
| GrA-13333 | | Ireland | apatite | 3520±40 |
| GrA-14635 | duplo | | apatite | 3480±50 |
| GrA-11812 | mammoth | Shestakovo | collagen | 17720±120 |
| GrA-11679 | | Russia | apatite | 9930±50 |
| GrN-24483 | mammoth | Molodova | collagen | 20840±310 |
| GrA-14009 | | Ukraine | apatite | 13420±60 |

Table 1 Dating results for collagen and apatite for the same bone.

and because of the renewed interest in apatite as datable fraction for cremated bone (discussed below).

From the Late Mesolithic Early Swifterbant excavation Hardinxveld-Giessendam (Louwe Kooijmans 2001), human remains were excavated from two male individuals known as Henk and Elvis.

Bone consists of long chains of proteins (collagen) in which particles of poorly crystallized inorganic material are embedded. This inorganic material is known as bio-apatite which incorporates carbonate.

The carbonate originates from the blood of the individual; it is directly related to food intake of the organism. Collagen has its origin solely in proteins in the diets.

Thus, in case of reservoir effects, collagen should date older than apatite (assuming the latter is reliable). Indeed such is the case for Henk. For Elvis, both materials show the same date, within error. There is no measurable reservoir effect here. Could Elvis have eaten (lots of) fish, whereas Henk did not? (see 2.3) Theoretically, that is possible. It assumes that the apatite dates are correct. Both apatite dates differ, but not very significantly considering the relatively large measurement errors.

Apparently there is quite often a slow exchange of carbonate between bone and environment. For samples younger than about 4000 years there is no measurable offset. The difference between carbonate- and collagen dates becomes larger for older samples.

In particular, for the two Pleistocene samples (Siberia and Molodova) are the apatite results bizarre.

Biological apatites can be used for dating under special circumstances. Most notably, post-depositional changes are not a factor in desert environments. This has recently been thoroughly reviewed by Zazzo and Saliège (2011).

### *2.2 Cremated bone*

Cremated bone does no longer contain organic remains such as collagen. The fact that cremated bone could not be dated (until recently) was regarded as a serious drawback for prehistoric chronological assessments. Cremation burials are often associated with pottery and artefacts of diagnostic types.

Previous attempts to date cremated bone failed because it was treated as charred bone. Such material has been heated to relatively low temperatures (200-300 °C). Cremated bones have been heated at much higher temperatures (above 600 °C).

Some collagen may survive in charred bone, but none survives cremation.

It appears that at temperatures >600 °C, the bioapatite recrystallizes forming a stable compound. Most of this structural carbonate disappears, but enough material survives prehistoric pyres and can be used for dating by AMS (Lanting *et al*. 2001).

Before adding cremated bone to the list of datable materials, the method has been tested extensively for known age samples from the Netherlands and Ireland. By "known age" is meant mainly $^{14}C$ dated by charcoal; but also collagen (from unburnt bone) and bones with a historic age have been used. The datelists can be found in Lanting and Brindley 1998 and Lanting 2001.

The success is best illustrated as a plot of charcoal vs. cremated bone dates from the same context (fig. 1).

The dating of cremated bones appears to be generally without a problem for Holocene (post-Mesolithic) sites. Paired dates (cremated bones vs. associated unburnt bone or charcoal) for Holocene/Mesolithic/Palaeolithic sites reveal problems which are not yet understood.

There is one Mesolithic paired set available from the Groningen database. From Oirschot, a charcoal sample was dated to 7790±130 BP (GrN-14506). This was a small conventional sample, and could only be partly chemically pretreated (A only). Later, cremated bone remains were dated by AMS: 8320±40 BP (GrA-13390). In this case, the deviation can theoretically be explained by the incomplete pretreatment.

A few paired dates are available from Federmesser cultural sites from Germany and the Netherlands: Doetinchem, Bad Breisig, Kettig, and Reichswalde. In general, these dates yield satisfactory results. This is in sharp contrast with Late Palaeolithic sites (Hamburger culture) from Poland (Olbrachcice, Hamburger culture) and Germany (Andernach, Federmesser culture). There is here a linear trend between cremated bone dates and the 'real' dates (obtained for other sample materials), but the cremated bone dates are far too young (fig. 2). The deviation becomes smaller for older dates. This effect remains to be explained.

### *2.3 Reservoir effects*

Bone collagen has its origin solely in proteins in the diet, and is therefore liable to reservoir effects when these proteins are derived largely from fish and/or shellfish. These food sources show apparent ages on the $^{14}C$ time scale, which is by definition terrestrial. For marine organisms, this effect is caused by upwelling of deep and old ocean water (and the dissolved $CO_2$ it contains). This causes an offset of 400 $^{14}C$ years for marine organisms; therefore, modern fish and shellfish date 400 BP.

For freshwater reservoirs (rivers and lakes) a reservoir effect also applies, but this is caused by dissolved carbonate of geological age (i.e. does not contain measurable amounts of $^{14}C$). Such reservoir effects can be much greater; for example, fresh fish from the river Rhine date c. 1300 BP.

Reservoir effects also apply to terrestrial organisms consuming marine food, including humans. In such cases, bone collagen shows apparent ages. For archaeological bone in the Netherlands, this has been studied in detail by Lanting and Van der Plicht (1995/1996). For medieval samples from

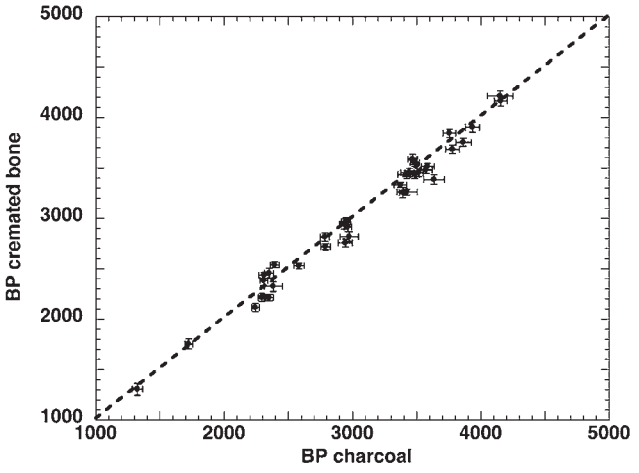


Figure 1 Paired Radiocarbon dates of cremated bone vs. charcoal for the age range 1000-5000 BP.

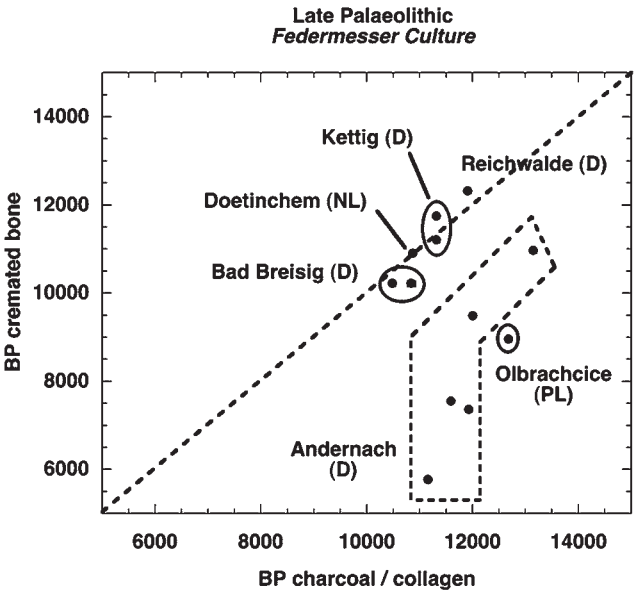


Figure 2 Paired Radiocarbon dates of cremated bone vs. other datable materials (charcoal or unburnt bone) for the Late Palaeolithic.

people with a known date of death (nobles and saints) a systematic study of $^{14}C$ dates shows reservoir effects up to a few centuries. Stable isotope ratios ($^{13}C$ and $^{15}N$) for bone collagen can be used to investigate reservoir effects for $^{14}C$. For a Neolithic case study in the Netherlands, see Smits and Van der Plicht (2009).

### *2.4 Collagen quality and reliability*

The $^{14}C$ laboratories investigate reliability and reproducibility by means of mutual intercomparisons. The most recent one is known as VIRI (Fifth International Radiocarbon Intercomparison). The results of this intercomparison (as well as earlier ones) can be found in the literature (e.g., Scott 2003) and on www.radiocarbon.org.

We show here the results for the fossil bone samples (named E-I) from both Groningen laboratories (conventional and AMS) (table 2). The table shows $^{14}C$ ages in BP, with 1-sigma measurement errors. The consensus value is the average $^{14}C$ date calculated from all participating laboratories.

The results of most laboratories (including Groningen) are good to satisfactory; there are only few exceptions. The intercomparison is 'blind' which means the laboratories only know their own results, which they can publish (like is done here for Groningen), but not each other's results.

The conclusion is that in general, bone dating works for good-quality sample material.

For fossil bones, the main quality parameters are the $\delta^{13}C$ value and the organic carbon content of the collagen (C%). These are generally in the range -18 to -22 ‰ and 40 to 45%, respectively (Mook and Streurman 1983). Impurities generally result in lower $\delta^{13}C$ values, since the insoluble compounds have $\delta^{13}C$ values of -22 to -29‰.

More recently, Nitrogen analysis results have become additional quality parameters: $\delta^{15}N$, N% and the C/N value.

| sample | species | conventional (GrN) | AMS (GrA) | consensus value |
|---|---|---|---|---|
| E | mammoth | 37850 (+1100,-950) | 39950 (+410,-360) | 39305 |
| F | horse | 2540±20 | 2570±30 | 2513 |
| G | human | n/a | 970±30 | 969 |
| H | whale | 9545±35 | 9485±45 | 9528 |
| I | whale | 8295±35 | 8355±40 | 8331 |

Table 2 Intercomparison results for bone dating: Groningen and international consensus values.

The N% value should be in the range 12.5-16%. Such values are based on those valid for fresh animal bone.

The acceptable range for the C/N ratio (which is C%/N% corrected for the atomic mass ratio 14/12) is 2.9-3.6 (DeNiro 1985). Note that the stable isotope ratios $\delta^{13}C$ and $\delta^{15}N$ for bone collagen also depend on the food source of the organism (Kohn 1999).

Further, the same general rules apply to bone as to other samples submitted by archaeologists for dating. These comprise questions such as

- what is the $^{14}C$ event for the sample material;
- how is the $^{14}C$ event associated with the human event;
- does the material for which the $^{14}C$ event has been identified meet the requirements for a conventional $^{14}C$ age?

For a thorough discussion the reader is referred to van Strydonck *et al*. (1999), and to an earlier publication by Mook and Waterbolk (1985).

## 3 Calibration

Originally (during the early 1950's), $^{14}C$ dates were reported in years BP (Before Present), as is common practice in other dating techniques, most notably in the earth sciences. Early dates were significant, often revolutionary, but crude with 1-sigma errors often a few hundred years BP (Libby 1952).

The radioactivity was measured relative to a standard corresponding to values of the "present day", 1950 at the time, which is a chemical substance called oxalic acid. The half-life value of 5568 years, as determined by Libby, was used.

It was soon discovered that there was a problem with both. Modern values appeared to have been changed because of fossil fuels (which do not contain $^{14}C$), so that the 1950 oxalic acid has 5% less $^{14}C$ than the natural value before the anthropogenic effects, affecting atmospheric $CO_2$ (and its isotopic values). Also, de Vries (1958) discovered that significant natural variations occur in the atmospheric $^{14}C$ content. These are caused by a changing cosmic ray flux which produces the cosmogenic isotopes such as $^{14}C$.

Further, the half-life was later accurately determined as 5730 years.

And finally, mass dependent effects (isotope fractionation) were discovered which influence the $^{14}C$ content of a sample (and thus their age).

In order to solve these problems the $^{14}C$ laboratories have agreed to the following convention:

1. The $^{14}C$ activity (i.e. the $^{14}C/^{12}C$ ratio) is measured relative to that of an international standard (the oxalic acid)
2. It is corrected for fractionation using the $^{13}C/^{12}C$ ratio of the sample to a standard value
3. The $^{14}C$ age is calculated using the original half-life (5568)
4. The $^{14}C$ age is reported in the unit "BP".

Thus, the $^{14}C$ time scale is *defined*. Note that the time scale is 'elastic' because of natural variations in the $^{14}C$ content of nature. The defined $^{14}C$ time scale needs to be connected to the calendar time scale by calibration. This calibration automatically takes into account natural $^{14}C$ variations and the half-life uncertainty. The convention cleverly takes into account these ambiguities. The only uneasy element in this definition is BP which does *not* mean Before Present in the literal sense. But the use of this term had been so widespread that all attempts to change it failed.

Calibration of the $^{14}C$ time scale is possible by measuring $^{14}C$ in tree rings, which are dated absolutely by dendrochronology. This is presently possible back to about 12,500 years ago (Friedrich *et al*. 2004).

Only recently, calibration curves became available covering the complete Radiocarbon dating range of 50,000 years (Reimer *et al*. 2009). This calibration curve intcal09 is shown in figure 3. The older part of the curve is derived from marine samples: U-series dated corals and foraminifera. The $^{14}C$ ages are reported in BP, and the calendar time scale is shown in calBP. This is defined as absolute years relative to AD 1950, i.e. calBP = 1950-AD = 1950+BC (Mook and van der Plicht 1999).

Note that therefore it has to be established that the U-series dates are absolute. In addition, the samples are marine, which means the $^{14}C$ dates have to be corrected for the reservoir effect. Some uncertainties in both time scales remain.

In theory, there are prospects for an extension of the dendrochronological record for the complete dating range. Large amounts of Kauri wood from New Zealand are available (Balter 2006b). But it will take many years before this will be established. In the meantime, a varved lake sediment from Japan (Lake Suigetsu) which covers the complete $^{14}C$ dating range is yielding calibration information (Staff *et al*. 2012). The importance of both Kauri wood and Lake Suigetsu varves is that the $^{14}C$ measurements are done on terrestrial material. Thus, they are independent of marine reservoir effect uncertainties.

It is also noteworthy that the possibility of large fluctuations in the $^{14}C$ content around 40,000 years has been refuted recently (Talamo et al. in press).

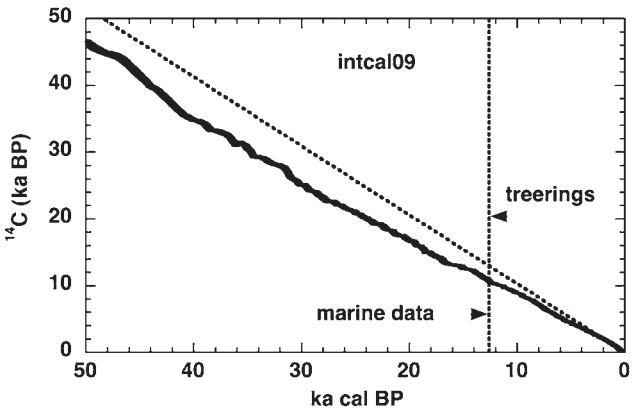


Figure 3 The Radiocarbon calibration curve Intcal09 for the complete 50.000 years.

## 4 The oldest part of the $^{14}C$ time scale

### *4.1 General*

The natural concentration of cosmogenic isotopes like $^{14}C$ is extremely small. The relative $^{14}C/^{12}C$ content in modern material is $10^{-12}$; for 50,000 (50 ka) year old samples, this is decreased to c. $10^{-15}$. To illustrate this extreme sensitivity of the method: the latter number corresponds to one hair of the present human world population, based on $10^{10}$ inhabitants on our planet and an average number of $10^5$ hairs per person. Such low concentrations make the method very sensitive to contamination. Problems with $^{14}C$ dates (in particular bone) are 'amplified' towards the oldest part of the dating range, 30-50,000 BP.

Contaminants become more important when the sample is older. These are usually modern materials, making the samples date too young when not adequately removed. A 45,000 year old sample will be measured as 35,000 BP, when there is 1% modern contamination. For the conventional method, quantitative examples are discussed by Mook and Waterbolk (1985).

For AMS, this effect is more problematic than for the conventional method because of the intrinsically small samples (by a factor of 1000) used. Examples are given by Lanting and van der Plicht (1993/1994), and below (the baby mammoth Lyuba).

In fact, contamination is the most likely cause for the 50 ka dating limit for AMS. The 50 ka limit for the conventional method, which is based on radiometry, is understood as caused by remaining background radiation still able to penetrate the shielding. AMS, however, is not sensitive to allochthonous radioactivity. In fact the background of the machinery proper corresponds to $^{14}C$ ages older than 100,000 years. Nevertheless, samples with infinite age on the $^{14}C$ scale (background material) show ages in the range of 45-50 ka BP. This can be explained by the chemical treatment of the materials, which apparently are not free of C containing contaminants at this level. Various laboratory contributions during sample preparation are investigated by Aerts *et al*. (2001).

This is the $^{14}C$ methodology perspective. But also from an archaeological point of view, 'old bone' samples can easily be problematic. Because of their age, they are rarer, and more easily degraded. The latter makes them then also more

sensitive to contamination. For example, dating Neandertal bones is difficult because (1) only a minimal amount of material is available for dating, which is destructive; (2) some degradation means not an optimal collagen content so that the bones are more susceptible to contamination; and (3) contamination is more problematic for ages close to (or beyond) the 50 ka BP barrier than for samples from more recent periods.

There are various parameters determining the outcome of $^{14}$C dating (correct or wrong) of fossil bone, easily causing confusion. There are good bones and bad bones (in terms of sample quality), and there are good measurements and bad measurements (in terms of $^{14}$C laboratories). But there is not a simple one-to-one correlation between these.

To mention one example: the Muirkirk mammoth, found in 1895 in southern Ontario is the most complete woolly mammoth known from Canada. Two conventional $^{14}$C dates were available: 8390 and 6510 BP. They are very different which is already suspicious. But more importantly, they are unrealistically young, which requires further investigations. Recently, two new samples of the mammoth were taken and re-dated by AMS in Groningen, both yielding 12,190 BP (Harington *et al*. 2012) which is considered much more realistic.

### *4.2 Backgrounds*

One important issue to consider is the background of the $^{14}$C measurement. The usual background material for $^{14}$C dating is anthracite. This material has geological age, which is infinite for the $^{14}$C time scale. Dating this material yields finite ages, because both the chemical treatment and physical measuring processes cannot be done completely $^{14}$C free. The remaining $^{14}$C counts are a measure of the 'noise' or 'background' which in practice corresponds to ages of around 50,000 BP. This works fine for the vast majority of samples. However, for bone of high $^{14}$C age one has to be careful with interpretation of the measurements. Infinitely old charcoal is not necessarily the same as infinitely old bone collagen. It could happen that one takes 50,000 as the laboratory background (based on anthracite) but that the background for collagen with the same quality as the sample is 40,000 BP.

It does not help to use infinitely old bones as backgrounds, such as mid-Pleistocene megafauna bones from Siberia. These can be excellent quality materials while the sample can be degraded. Such backgrounds are then not a proper blank. One might just as well use anthracite; as indeed the laboratories do in practice.

For this reason, the background for bone dates is often stated as 45,000, i.e. no bone dates older than 45,000 BP are reported as finite. Unless it is justified to do so – such as for the Arilakh mammoth, discussed below.

### *4.3 The permafrost*

Most reliable are well-preserved bones from the permafrost. A prime example is the Arilakh mammoth, which yielded extremely well-preserved samples (considering its age) for $^{14}$C dating and other research like ancient DNA. A large piece of bone could be dated in Groningen to 55 ka BP, employing both conventional and AMS methods. For details, we refer to Mol *et al*. (2006).

Another illustrative example is the celebrated baby woolly mammoth "Lyuba". A piece of bone was dated by AMS in Groningen to 42 ka BP (Kosintsev *et al*. 2010). The mammoth was also subjected to further methodological testing, illustrating the difficulties of $^{14}$C dating practice. Skin samples yielded dates in the range 31-37 ka BP; plant remains found in the intestines of the animal yielded dates in the range 26-42 ka BP (Fisher *et al*. 2012). Only the oldest plant date is consistent with the bone collagen date. It was obtained after very rigorous pretreatment. It is not unlikely that the younger plant dates (which were less thoroughly pretreated) were rejuvenated because bacterial activity within the intestine, based on survival of live, but dormant microbes from Lyuba's life. Such effects have been observed before in American Mastodonts (Rhodes *et al*. 1998).

### *4.4 The Palaeolithic*

Bones which are not as well preserved as in the permafrost are often questionable in terms of their $^{14}$C date. Usually they are too young, which must be caused by modern contamination apparently not removed by the collagen preparation procedure. For this reason, the Oxford $^{14}$C laboratory has developed the so-called ultrafilter method. Ultrafiltration is used to purify the collagen, separating out the smaller and lower molecular weight fractions which seem to have been the major source of more modern organic contaminants (Bronk Ramsey *et al*. 2004). Indeed application of this refinement made impossibly young dates older and consistent with their "desired age" (e.g., Jacobi *et al*. 2006). That may be so, but matters are more complicated. There is the danger of circular reasoning. How do we *know* which age is correct – only if it meets our expectations? What is subjective, what objective?

Also from the physical measurement point of view, matters turned out not to be as easy as presented. In the first place, ultrafiltration is dangerous since the filters themselves can easily (and are known to have done so) introduce contaminants. Furthermore, extensive testing by the Kiel $^{14}$C laboratory showed that filtration does not necessarily produce a better date (Hüls *et al*. 2009).

Thus far, ultrafiltration has not been applied in Groningen. Instead some projects are designed to have it both ways: in a collaborative effort, selected samples are dated with ultrafiltration in Oxford, and without in Groningen. This way,

Neandertal bones from various locations are dated; both methods show consistent results, ranging between 32 and 36 ka BP (Semal *et al*. 2009; Crevecoeur *et al*. 2010; Maroto *et al*. 2012). It is important to note that these were all well-preserved bones, yielding good quality collagen, and there were apparently no contaminants removed by ultrafiltration.

### *4.5 The North Sea*

The North Sea is well known for its unique finds of Late Pleistocene mammal fossils – among which most notably mammoth (*Mammuthus primigenius*) and woolly rhinoceros (*Coelodonta antiquitatis*). Most fossils are collected during fishing expeditions (e.g., Mol *et al*. 2008; Mol and Post 2010). A difficult issue has always been the proper geological setting of the finds. Only recently, finds from the Eurogeul region of the North Sea can be studied in a well-developed stratigraphic framework (Hijma *et al*. 2012).

This framework raises questions on $^{14}$C dates available for selected fossils. It would mean that all Late Pleistocene terrestrial mammals dating older than around 30,000 years must have been redeposited from their original location. In addition, Late Pleistocene marine mammals must be 60-85,000 years old; the available $^{14}$C dates, however, are much younger.

All dates for mammoth fossils from the Eurogeul region and adjacent area of the North Sea are older than c. 34,000 BP (Mol *et al*. 2008). According to Hijma *et al*. (2012), that would mean that these fossils must have been transported.

That seems impossible for a particular juvenile skull, known as NO 4513. This was dated 28,740 BP (GrA-50454) by means of fly pupae (Van der Plicht *et al*. in press). In addition, other finds from the Eurogeul such as large mammoth skulls including tusks must be in situ finds. Thousands of mammoth bones are collected, indicating the presence of articulated skeletons in the Eurogeul region. Following the geological analysis of Hijma *et al*. (2012), these mammoths must be younger than 30,000 BP. Such young dates have not been observed thus far in the Eurogeul and North Sea.

Based on these latest findings, apparently either mammoths lived longer (up till less than 30,000 years ago) in the Rhine/Meuse delta region than previously thought, or that the flies settled in the mammoth skull cavities much later than the mammoth's time of death.

As mentioned above, there is a second discussion item concerning the stratigraphic analysis of Hijma *et al*. (2012) and available $^{14}$C dates: those of marine mammals. Also here, the $^{14}$C dates are younger than expected. This fits in with other discussions on 'too young' $^{14}$C dates and their validity: shells. The datable fraction for these samples is their carbonate. Fossil corals and shells can recrystallize, enabling exchange of Carbon, including $^{14}$C. Foraminifera of Eemian age can produce dates significantly younger than 50,000 BP. This open system behaviour is also known to be species dependent (Nadeau *et al*. 2001; Busschers et al. in prep.).

This was already known in the early days of Radiocarbon. Olsson (1989) described that infinitely old shells date 33,700 BP, corresponding to 1.5% contamination with modern Carbon. This was observed in samples stored for a long time. Most contamination remains in the outer part of the shells.

In addition, note that also for shell dating the proper background for $^{14}$C dating (infinite age material) must be considered. Using anthracite easily yields similar interpretation problems as for fossil bones discussed above.

But all of this does not mean that obtaining good $^{14}$C dates for carbonate organisms are impossible, witness the very existence of the calibration curve intcal09. The fact that the calibration curve goes back to 50,000 years ago alone is proof of that.

The backbone of the calibration curve for the time frame discussed here (the later Pleistocene) is based on marine samples, in particular the unique and thoroughly measured dataset from the Cariaco Basin (off the coast of Venezuela). These are pristine planktonic foraminifera samples (Hughen *et al*. 2004). This means that for these carbonates, the $^{14}$C content has been measured without problems as discussed above, to even beyond 50,000 BP. Apparently these shells do *not* show open system behaviour. The Radiocarbon intcal committee has established unambiguous criteria for marine sample materials (Reimer *et al*. 2002).

The North Sea brings together many aspects of the subject of this paper: validity of $^{14}$C dates, degradation, open system behaviour, background questions, different behaviour of different sample materials, calibration, unknown geophysical aspects and, above all: context.

Truly interdisciplinary research no doubt will increase our understanding of this important heritage.

## 5. Beyond the $^{14}$C time scale

### *5.1 Schöningen*

Schöningen is a well-known Pleistocene site in Lower Saxony, Germany, about 90 km east of Hannover. It is an open-cast brown-coal mine that revealed ample paleontological and palaeolithic objects. Most spectacular is the find of 8 wooden spears with an age of 300-400,000 years (Thieme, 2007). Thousands of faunal bones have been collected over the years, which are being investigated in Leiden. The structural quality of some of the bones appeared very good, inspiring the author to test for the presence of collagen, with positive results. This spawned a study (financed by Leiden University Foundation (LUF)) to investigate the stable

isotopes $^{13}C$ and $^{15}N$ in collagen from selected bones. This was successful, and stable isotope ratios from 5 species (Bovidae, Cervidae, Elephantidae, Equidae and Rhinocertidae) were obtained from this remarkably old bone collagen (Kuitems et al. 2012).

Here we only mention a $^{14}C$ dating test we performed on the Schöningen bones. Of course the samples are an order of magnitude older than the $^{14}C$ dating range. But the excellently preserved collagen is of interest for background testing.

We have dated six Schöningen bone samples by AMS. Indeed, five samples showed dates >45-50,000 BP.

One bone dated 37,910 (+360-320) BP (GrA-49108). Detailed inspection showed that this particular bone consisted of fragments which were glued together. Glue (and some conservatives as well) is often collagen based. Apparently, we dated a mixture of bone collagen and glue collagen. This is confirmed by the peculiar $^{13}\delta$ value which is -33.73‰, whereas the other five bones showed more common values of around -21‰. Also the C content of the collagen was higher (54%) than the usual values for bone.

Extremely old bone collagen such as found in Schöningen is very rare. There are a handful of other sites known. Only the most extreme case is mentioned here: collagen has been extracted once from a Dinosaur bone (Bocherens *et al*. 1988).

### *5.2 Enrichment*

Enrichment of $^{14}C$ in samples (isotope separation, through which $^{14}C$ is concentrated in a fraction of the original sample) is a method to extend the possible age limit of $^{14}C$ dating.

The enrichment process has been used for very large samples using thermodiffusion of CO (Grootes et al. 1977). However background problems remain problematic.

A recent method applied in Groningen is based on ultra-centrifuge (originally developed for uranium enrichment for the nuclear power industry). These ultra high vacuum machines offer a very clean environment, and enable the direct enrichment of $CO_2$. This fact, together with extreme care in the other sample and standard preparation steps, resulted in a clear extension of the age limit. In a first test, enrichment was still relatively modest (about a factor of 2.5). Indeed the theoretical age extension of 7500 years was realised, as our background level before and after enrichment was virtually the same.

As a first demonstration of the possibilities of this enrichment technique, we dated a Khatanga mammoth, which (before enrichment) was on the edge of significantly different from background, resulting in a $^{14}C$ age of 50,800 (+950-850) BP (de Rooij *et al*. in prep.). The background variability level we achieved corresponds to a theoretical age limit of 63,000 BP.

The experiment to push the $^{14}C$ barrier back in time is shown to work in principle. However the complex nature of the laboratory procedures will not make this a feasible service as dating method.

## 6. Conclusions

The Radiocarbon dating method has developed during the last 60 years into a reliable dating method for organic sample materials. Since recently, the method has even become absolute for the complete dating range of 50,000 years by establishing the calibration curve known as intcal09.

The datable sample material includes fossil bone. More than any other material, this category is the subject of discussions concerning validity of the dates, in particular for the older part of the $^{14}C$ time scale.

In general, $^{14}C$ dating of fossil bone works well when the bone is of good quality, i.e. not degraded.

Not all problems have been solved but it is not justified to reject dates in general when they do not meet expectations.

Relatively new is the discovery that cremated bones, lacking organic materials, can be dated using the inorganic apatite fraction.

This contribution discusses difficulties, strategies and misinterpretations.

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