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Radiocarbon and mammoth bones: What's in a date

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ABSTRACT

The Radiocarbon dating method has developed into a reliable dating method for organic sample materials. The latest calibration curve released enables numerical dating covering the complete dating range of the method. However, the category of fossil bones is the subject of discussion concerning validity of the dates, in particular for the oldest part of the ^{14}C timescale. This is a complex interplay of sample material integrity, contamination issues and proper blanks. In practice, a safe upper limit for ^{14}C dates of bone material appears to be 45,000 BP (50,000 calBP).

1. Introduction

The Radiocarbon (^{14}C) dating method has contributed significantly to many disciplines studying the past, as it provides a physical yardstick of time (Libby, 1952). Organic samples such as charcoal, bone, wood, peat, shells, and plant remains can be directly dated to about 50,000 years ago. Since the conception of the method in the 1950s, it has continuously been improved; the most significant improvements being the introduction of AMS (Accelerator Mass Spectrometry) enabling small sample analysis (Tuniz et al., 1998), and the establishment of a calibration curve for the complete dating range (Reimer et al., 2013).

Many chronological questions have been solved by Radiocarbon dating over the years. However there always have been debates concerning the acceptance of ^{14}C dates, in particular in archaeology (Renfrew, 1999). These continue to the present day – witness, to mention just one prime example, the dating of the Santorini/Thera volcanic explosion (Antiquity, 2014).

In this contribution, the focus will be mainly on a specific category of ^{14}C dating most relevant for paleontologists researching Late Pleistocene mammal remains: bones, in particular from its most iconic representative, the woolly mammoth. Also here are sometimes vehement discussions concerning validity of dates, sample quality and methodology. This is triggered by relatively recent developments of the ^{14}C method, in particular the introduction of AMS and sample treatment improvements including the ultrafilter method. The latter was coined a "revolution for Palaeolithic archaeology" (Mellars, 2006) but is the subject of debate (Hüls et al., 2009) and to extensive testing using palaeontological bone (e.g., Fiedel et al., 2013).

It is important to note that bone is perhaps the most difficult (or sensitive) material to date by ^{14}C, in comparison 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; Vartanyan, 2013).

There is a variety of 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). However, there is not a simple one-to-one correlation between these.

The danger of circular reasoning is present. When an improvement in the method produces dates that fit expectations of the user (usually in the older direction), that does not necessarily mean that the dates are then correct. Also, when 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. The purpose of this contribution is to review present knowledge and enable the ^{14}C user community to be better able to judge the validity of bone dates, in particular near the detection limit of the method.

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2. The Radiocarbon timescale

Originally (during the early 1950s), ^{14}C dates were reported in BP (Before Present), just as it 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 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 halflife value of 5568 years, as determined by Libby was used.

It was soon discovered that there were problems 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 halflife has later been accurately determined as 5730 years. 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 (oxalic acid). The value of this reference is standardized to a specific activity and reference year (1950)
2). It is corrected for fractionation using the $^{13}C/^{12}C$ ratio of the sample to an agreed standard value
3). The ^{14}C age is calculated using the original halflife (5568 years)
4). The ^{14}C age is reported in the unit "BP".

Thus, the ^{14}C timescale is defined. Note that this timescale is "elastic" because of natural variations in the ^{14}C content of nature. The defined ^{14}C timescale needs to be connected to the calendar timescale by calibration. This calibration automatically takes into account natural ^{14}C variations and the halflife uncertainty. The only uneasy element in this definition is BP, which does not mean Before Present in the literal sense. However, the use of this term has been so widespread that all attempts to change it have failed.

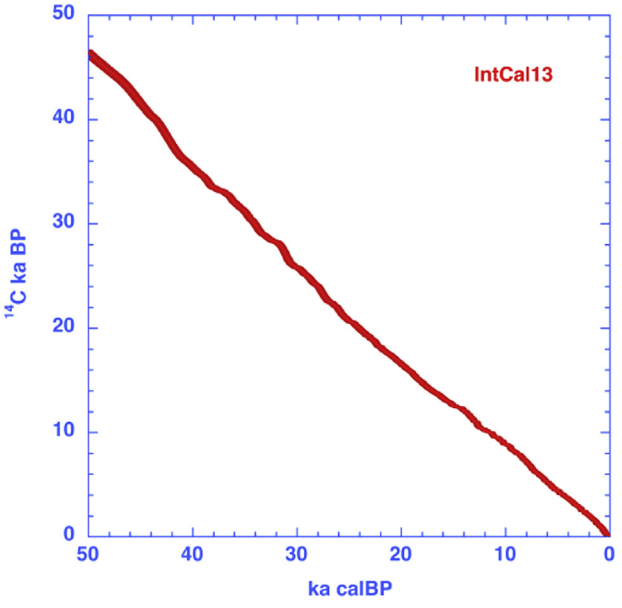

Fig. 1. The calibration curve Intcal13 (Reimer et al., 2013), showing the relation between Radiocarbon years (BP, vertical) and calendar years (calBP, horizontal).

Calibration of the ^{14}C timescale 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., 2013). This calibration curve Intcal13 is shown in Fig. 1. The older part of the curve is derived from U-series dated corals and foraminifera, and from laminated sediment from Lake Suigetsu, Japan (Bronk Ramsey et al., 2012). The ^{14}C ages are shown in BP, and the calendar timescale in calBP. The latter is defined as years relative to 1950 AD, i.e. calBP = 1950 − AD (Mook and van der Plicht, 1999).

3. ^{14}C methodology

3.1. Sample treatment

Before the actual ^{14}C measurement, sample materials have to be chemically pretreated in order to isolate the datable fraction, and to remove contaminants (Mook and Streurman, 1983). Bone dating proved to be difficult in the early days of Radiocarbon. Dating of "bulk" carbon was practiced, 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. However, 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. Nevertheless, carbonate dating usually gives good dates for teeth and tusks, simply because they are more resistent to degradation and less sensitive to exchange of Carbon with the environment.

The main quality parameters for bone collagen isotopic analysis are the Carbon and Nitrogen content. Their values should be higher than ~30% and 12%, respectively, while the acceptable range for the C/N ratio (normalized for the atomic mass ratio 14/12) is 2.9–3.6 (DeNiro, 1985; van Klinken, 1999). These values are based on those of fresh animal bone.

Additional collagen quality information is provided by the stable isotopes ^{13}C and ^{15}N. Their numbers are expressed in so-called delta values $\delta^{13}C$ and $\delta^{15}N$, which are defined as: $\delta X = (R_{sample}/R_{standard}) - 1 \times 1000‰$, where X stands for ^{13}C or ^{15}N and R stands for $^{13}C/^{12}C$ or $^{15}N/^{14}N$.

For bone collagen, the $^{13}\delta$ values are generally in the range −18 to −22‰ (Mook and Streurman, 1983). Impurities generally result in lower $^{13}\delta$ values, as the insoluble compounds have $^{13}\delta$ values of −22 to −29‰. Note that the stable isotope ratios $^{13}\delta$ and $^{15}\delta$ for bone collagen also depend on the food source of the organism (Kohn, 1999). This is not further discussed here.

Bones which are degraded show deviating collagen quality parameters. Their dating results are often questionable. 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 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