Palaeogeography, Palaeoclimatology, Palaeoecology 416 (2014) 168–178

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

Bone and enamel carbonate diagenesis: A radiocarbon prospective

Antoine Zazzo

CNRS/Muséum national d'Histoire naturelle, Département Ecologie et Gestion de la Biodiversité, USM 303/UMR 7209 du CNRS - Archéozoologie, Archéobotanique: Sociétés, Pratiques et Environnements, case postale 56, 55 rue Buffon, F-75231 Paris cedex 05, France

ARTICLE INFO

Article history:
Received 27 January 2014
Received in revised form 5 May 2014
Accepted 7 May 2014
Available online 16 May 2014

Keywords:
Bone apatite
Dentine apatite
Enamel apatite
Radiocarbon dating
Diagenesis
Stable isotopes

ABSTRACT

The debate regarding the susceptibility of bone and enamel carbonate to preserve in vivo carbon isotope ratios is as old as paleodietary research. After more than three decades of controversy, a consensus seems to have been reached, and archeological bone apatite is generally considered suitable while enamel has become the gold standard for pre-Quaternary studies. But the absence of a quantitative diagenetic test to assess the preservation of bone and enamel carbonate $\delta^{13}C$ values is problematic. Here, radiocarbon (^{14}C) dating is used as a tracer, to quantify carbon isotope exchange in bone, dentine and enamel carbonate during early diagenesis. Samples covering most of the range of radiocarbon dating and coming from different burial environments and climates were dated. When possible, enamel, dentine and bone from the same individuals were selected. All tissues record an uptake of modern carbon leading to a change in the radiocarbon age of the sample which becomes significant after about 8000 BP. In some of the sites, enamel is older than bone or dentine carbonate from the same individual, while in others, the contrary is observed. An intermediate case where identical ^{14}C ages were measured between bone carbonate and enamel was also observed, suggesting either a lack of alteration, or similar degree of C-isotope exchange for the two tissues. Overall, no systematic ^{14}C difference was found between bone, dentine and enamel from the same individual suggesting that differences in crystallinity or porosity do not play a major role during the early stage of bone and enamel diagenesis and that $\delta^{13}C$ values measured in bone apatite are as reliable as in enamel at least for the past 40,000 yr.

1. Introduction

The debate regarding the susceptibility of bone and enamel carbonate to preserve in vivo carbon isotope ratios is as old as paleodietary research. More than 30 yr ago, Sullivan and Krueger (1981) concluded that in the case of material over a few thousands of years old, suitably pretreated bone apatite yielded reliable $\delta^{13}C$ values which were offset from those obtained from collagen. Their conclusion was quickly challenged by Schoeninger and DeNiro (1982) who found variable spacing between collagen and apatite and concluded that bone apatite was altered. It was later discovered that the collagen–apatite spacing is naturally variable, and that this criterion cannot be used as a test for validity of bone apatite $\delta^{13}C$ values (Krueger and Sullivan, 1984; Lee-Thorp et al., 1989). A more balanced view was reached a decade later. Based on the observation that expected isotopic differences between grazers and browsers in mixed C_3–C_4 environments were maintained, it was concluded that alteration of the isotopic signal becomes significant only for very old (>100,000 yr) bone samples (Lee-Thorp and van der Merwe, 1987; Lee-Thorp, 2000; Lee-Thorp and Sponheimer, 2003). A similar conclusion was reached by Wang and Cerling (1994) based on the predictions of a water–rock interaction model and stable isotope analysis of Oligocene bone and tooth apatite from South Dakota. These studies also emphasized that fossil enamel is more likely to preserve its primary $\delta^{13}C$ value due to its lower organic content, porosity and surface area and higher crystallinity. As a result, most stable isotope studies performed on older (paleontological) material in particular, shifted entirely to enamel which became the gold standard for pre-Quaternary research. For a more recent material, a quick literature review shows that the message sent by Lee-Thorp and van der Merwe (1987) has been very well received by the archeologist community and bone apatite $\delta^{13}C$ values are now regularly published and discussed in terms of paleodiets (i.e., Ambrose et al., 2003; Harrison and Katzenberg, 2003; Lösch et al., 2006; Clementz et al., 2009; Gil et al., 2009; Tykot et al., 2009; Lanehart et al., 2011). This long-lasting interest in bone apatite is partly explained by the limitations of enamel as a support for paleodietary research. First, unlike bone which turns over continuously and preserves the record of the last years of an individual (Hedges et al., 2007), enamel is essentially mineralized during childhood (Scheuer and Black, 2000) and cannot be used to track the long-term dietary history of individual adults. Second, sampling of bone carbonate in conjunction with bone collagen is extremely informative because it provides a way to tease out the contribution of the protein and carbohydrates to the diet due to the different routing of these macronutrients (Krueger and Sullivan, 1984) and can therefore help describe in more details the human or animal diet (i.e., Katzenberg and Weber, 1999; Katzenberg

E-mail address: zazzo@mnhn.fr.

http://dx.doi.org/10.1016/j.palaeo.2014.05.006
0031-0182/

et al., 2012). This variability has also been used in ecology to clarify the position of an animal species within the food chain (Clementz et al., 2009). The majority of the researchers working with relatively recent (Holocene) samples are confident in interpreting bone carbonate isotope values in terms of paleodiets and many of them do not feel the need to test for diagenetic alteration (Ambrose et al., 2003; Harrison and Katzenberg, 2003; Lösch et al., 2006; Tykot et al., 2009). Sometimes, the possibility that diagenesis might have altered the isotope signal is not even mentioned (Katzenberg and Weber, 1999; Gil et al., 2009; Lanehart et al., 2011). In this respect, it is quite ironic to notice that even authors who were initially very critical about the use of bone apatite $\delta^{13}C$ values do not even discuss this possibility anymore (i.e., Schoeninger and DeNiro, 1982 vs. Kellner and Schoeninger, 2007).

Several diagenetic tests have been proposed in the literature (for a complete review, see Kohn and Cerling, 2002). Relevant to carbon isotope values, comparison with values expected for animals of known diets coupled with isotope analysis of cement are helpful but only gives a semi-quantitative estimate of possible diagenetic shifts (Lee-Thorp and van der Merwe, 1987; Lee-Thorp, 2000). The spacing between $\delta^{13}C$ measured in bone apatite and collagen has also been proposed, but as observed, this value can be quite variable which reduces the use of this test to animals with known and predictive diets (thus excluding humans). Finally, crystallinity indexes, measured by Fourier-transform infrared spectroscopy (FT-IR) or X-ray diffraction (XRD) have also been proposed to identify post-mortem recrystallization possibly associated with isotope exchange (Person et al., 1995; Wright and Schwarcz, 1996; Dupras and Schwarcz, 2001; Prowse et al., 2004; Katzenberg et al., 2009; Shin and Hedges, 2012). These indexes are, however, of limited value because modification of the splitting factor measured by FT-IR (through dissolution of the more soluble crystallites for example) does not necessarily imply isotopic exchange. Similarly, the tests consisting of comparing $\delta^{13}C$ values of ancient vs. modern herbivores are only semi-quantitative because there is an inherent variability in the isotope values of the plants ingested (i.e., within the C_3 and C_4 photosynthetic pathways) so it is not possible to decide whether the variability measured in fossils is biogenic (due to individual dietary differences), or to different amounts of isotope exchange during fossilization. So, there is a need to develop a quantitative diagenetic test in order to ensure that bone apatite $\delta^{13}C$ value has not significantly shifted from its original value.

In a previous study, Zazzo and Saliège (2011) proposed a series of quantitative diagenetic tests to evaluate the reliability of bone apatite ^{14}C ages. These tests were based on the comparison of bone apatite ^{14}C ages with the age measured on a contemporary reference material offering good resistance to diagenetic alteration. Collagen extracted from the same bone, when preserved, best meets the quality criterion of contemporaneity, followed by material found in close association (collagen from other bones, charcoal, seed, etc.). In arid environments, the congruence of ages demonstrated the lack or very limited influence of carbon isotope exchange, while in temperate environments the divergence of ages indicated an alteration of the apatite fraction. However, this meta-analysis relied partly on dates taken from the literature, or on dates produced before the advent of the AMS technique. Moreover, the differential preservation of bone vs. enamel apatite could not be evaluated because most of the dates presented in Zazzo and Saliège (2011) were performed on bone apatite. Before the advent of AMS, enamel dating was simply not feasible due to the small size of teeth, and the limited content of inorganic carbon. There have been very few published examples since, which made it difficult to compare the relative resistance of enamel versus bone or dentine apatite. The first systematic trial compared enamel to bone collagen for Pleistocene mammals from the UK and South Africa and showed that enamel was not immune to isotopic exchange (Hedges et al., 1995a).

This study presents a comprehensive series of new AMS ^{14}C dates performed on archeological bioapatites. It aims to re-examine the stability of bone and enamel carbonate $\delta^{13}C$ value during early diagenesis using ^{14}C dating as a tracer of carbon isotope exchange. When possible, the resistance of bone apatite will be compared to that of dentine and enamel apatite from the same specimen. Radiocarbon is a powerful tool to look at diagenetic alteration of bone and enamel carbonate because the $^{14}C/^{12}C$ ratio is about ten orders of magnitude lower than the $^{13}C/^{12}C$ ratio. Minute amounts of exogenous carbon can significantly alter the $^{14}C/^{12}C$ ratio before the $^{13}C/^{12}C$ ratio is modified. This approach was recently used by Shin and Hedges (2012) to examine the reliability of a density-based separation technique. Divergence from expected ages will be quantified by comparing the apatite age to the age measured on collagen from the same specimen when preserved, or associated material.

2. Material

Table 1 presents a list of the archeological samples analyzed in this study. Most of the samples were prepared over the last 5 yr or so by the author, alone or in collaboration with J.-F. Saliège. While most of the data are original, others come from previously published papers (Sereno et al., 2008; Beech et al., 2009; Paris and Saliège, 2010; Vigne et al., 2011; Zazzo et al., 2012, 2013, 2014) but are summarized here for convenience. Samples cover a large spatial distribution and come from temperate (i.e., France), Mediterranean (i.e., Cyprus), subtropical (i.e., Thailand, Borneo) and arid (i.e., Niger, Sudan) environments. They also cover a large chronological distribution, from the Medieval Period (i.e., Kumbi Saleh) to the Upper Paleolithic (i.e., Abri Pataud) with the highest density of samples dating between 0 and 15,000 BP. This dataset was complemented by bioapatite dates produced by other teams and available from the literature (Hedges et al., 1995a; Cherkinsky, 2009; Cherkinsky et al., 2013). Only samples for which at least two different fractions from the same individual were dated and for which analytical methods were comparable were included in the dataset.

Table 1 also presents the list of reference ages against which the apatite age can be compared. Reference ages were ranked according to their quality. High-quality reference ages (QR1) were obtained through the direct dating of the collagen fraction of the same individual. Medium-quality reference ages (QR2) were obtained through the dating of associated material from the same level (i.e., charcoal, shell, or collagen from another specimen) was dated. Poor-quality reference age (QR3) refers to the cases where associated material was not available and where the age of the archeological sample was indirectly estimated by the dating of artifacts stratigraphically situated above (*terminus ante quem*, TAQ) or below (*terminus post quem*, TPQ). Samples which lacked reference age were ranked QR4.

3. Sample preparation and analysis

Samples processed before 2010 were prepared at the LOCEAN Lab (Univ Pierre et Marie Curie, Paris VI) and are labeled "P", or "Pa". Samples processed after 2010 were prepared at the radiocarbon lab of the MNHN (Muséum national d'histoire naturelle) and are labeled "Muse". For bone and enamel apatite, a modified version of the pretreatment protocol described in Krueger (1991) and Balter et al. (2002) was used (referred to as treatment B in the text), as this protocol was shown to remove efficiently most of the diagenetic carbon. Bone apatite (1–2 g) was finely (<160 μm) powdered then pretreated for about 20 h (17–24 h) at room temperature in 100 ml 1 N acetic acid under weak vacuum. The same protocol was also applied to enamel (referred to as Treatment B in the text). The evolution of fine gas bubbles usually slows down drastically after 1 h, and stops after 10+ h, suggesting that all secondary calcite as well as the smallest apatite crystals have been dissolved by then. Bone samples still containing organic matter were oxidized prior to the acid treatment using NaOCl 1–2% for 2–3 days or until degassing stops. A less aggressive pretreatment protocol was also tested on a small enamel subsample from two sites in