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Investigating inherent differences in isotopic composition between human bone and enamel bioapatite: implications for reconstructing residential histories

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ABSTRACT

In archaeological research, human bone and enamel bioapatite isotopic compositions are commonly used to reconstruct residential and dietary histories. In doing so, enamel and bone bioapatite are implicitly treated as isotopically equivalent, but recent research has determined that carbonate–carbon and –oxygen isotopic compositions of these two tissues may be offset by several per mil. Here, we compare the isotopic compositions of co-forming bone and enamel from juvenile humans. We also assess the impact of a standard pre-treatment procedure for the removal of organic matter and exogenous carbonates on carbon- and oxygen-isotope compositions and on bioapatite crystallinity and carbonate content. Pre-treatment procedures had minimal effect on both enamel and bone carbon and oxygen isotopic compositions (±0.4–±0.9‰) and bioapatite crystallinity, and effectively removed exogenous carbonates. The offset between enamel and bone phosphate–oxygen isotopic compositions is relatively small (±0.7 ± 0.5‰). The offsets for carbonate–oxygen (+1.4 ± 1.0‰) and –carbon (+4.3 ± 1.2‰) are larger, and enamel is consistently ^{18}O- and ^{13}C-enriched relative to bone. Interpreted conservatively, phosphate–oxygen isotopic data from paired enamel and bone remain suitable for determining residential history, whereas the isotopic compositions of carbonate–oxygen and –carbon from enamel and bone bioapatite are inherently different and cannot be compared uncritically.

1. Introduction

Carbonate–carbon and –oxygen and phosphate–oxygen isotopic analyses of bioapatite from bone and tooth enamel are widely used in archaeological and palaeoenvironmental studies to investigate seasonality, mobility, and climate change, and to reconstruct palaeodiet and the ecology of past ecosystems. In archaeological research, human bone and enamel samples are commonly used to investigate changes in drinking water source ($\delta^{18}O_p$ and $\delta^{18}O_{sc}$) and to infer changes in place of residence based on natural variability in environmental water isotopic composition (*inter alia* Buzon et al., 2012; Chenery et al., 2010; Dupras and Schwarcz, 2001; Fricke et al., 1995; Hewitt, 2013; Knudson, 2009; Knudson et al., 2009; Mitchell and Millard, 2009; Perry et al., 2009; Schwarcz et al., 1991; Smits et al., 2010; Webb, 2010; Webb et al., 2013; White et al., 1998, 2000, 2002, 2004a, 2004b, 2007). This research is based on the well-established relationship between the oxygen-isotope compositions of mammalian body tissues and consumed water, including drinking water and, to a lesser extent, food water and respired oxygen (Bryant and Froelich, 1995; Luz and Kolodny, 1985; Stuart-Williams and Schwarcz, 1997). Drinking water oxygen-isotope values ($\delta^{18}O_{dw}$) reflect the isotopic composition of environmental water, including both meteoric and recycled water (Luz and Kolodny, 1985; Stuart-Williams and Schwarcz, 1997), and this isotopic ratio is incorporated into body tissues (adjusted by a metabolic fractionation factor). Carbon-isotope data ($\delta^{13}C_{sc}$) are further used to reconstruct diet and dietary change between childhood and adulthood, and, with carbon- and nitrogen-isotope compositions of protein, can be used to create a more informative dietary reconstruction. The $\delta^{13}C_{sc}$ values of bioapatite reflect the total macronutrient content of diet, in contrast to $\delta^{13}C$ values of collagen, which reflect the isotopic composition of dietary protein. Natural isotopic variability in carbon-isotope compositions begins at the base of the food web, where different plants discriminate

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against ^{13}C to differing degrees based on photosynthetic pathway (i.e., C_3 versus C_4 plants). This variability is transmitted through the food web and is ultimately reflected in the $\delta^{13}C_{sc}$ values of consumers (Ambrose and Norr, 1993; DeNiro and Epstein, 1978; Howland et al., 2003; Jim et al., 2004; Kellner and Schoeninger, 2007; Tieszen and Fagre, 1993).

Isotopic studies make valuable contributions to understanding migration and residential histories in archaeological societies and in the hominid evolutionary past. There are numerous ways in which isotopic data can inform residential mobility by, for example, assessing relative isotopic variability within a sample, comparing human isotopic data to environmental or geological baseline data, or comparing multiple or paired tissues from the same individual to create a residential history. The validity of comparing isotopic data from paired bone and enamel samples from one individual, or the comparison of bone and enamel isotopic values among different individuals, rests on the assumption that the bioapatite in enamel and bone records $\delta^{13}C_{sc}$, $\delta^{18}O_{sc}$ and $\delta^{18}O_p$ values in a similar fashion and that there are no differences in fractionation between the two tissues. Recent research involving pigs has demonstrated that there are large, consistent offsets in carbonate–oxygen and –carbon between enamel and bone forming at the same time (+2.3‰ for $\delta^{13}C_{sc}$, +1.7‰ for $\delta^{18}O_{sc}$; Warinner and Tuross, 2009). An offset of similar magnitude was not, however, found in a controlled growth and feeding study of rats (Luz and Kolodny, 1985) for phosphate-oxygen isotopic compositions. Instead, a minor and inconsistent offset of ±0.5 ± 0.6‰ was determined. Here, our objectives are to assess the inherent offset between enamel and bone bioapatite isotopic compositions for both phosphate-oxygen and carbonate-carbon and -oxygen in humans. More specifically, we will compare paired bone and enamel isotopic data from children less than 12 years of age in order to estimate the expected offset between tissues growing at approximately the same time under 'normal' conditions of growth and food and water consumption. We use Fourier Transform Infrared spectroscopy (FTIR) to monitor changes in bioapatite structure related to diagenesis, and to detect any anomalous materials (e.g., calcite) in the samples. We will also assess the impact of a common pre-treatment protocol for the removal of organic material and secondary carbonates on carbonate isotopic data and FTIR parameters.

2. Background

2.1. Research design

The individuals selected for this study were juveniles less than 12 years of age, chosen with the objective of minimising inter-tissue differences caused by bone and enamel mineralisation occurring during different periods of an individual's lifetime. Tissues forming at different times during an individual's life could induce isotopic differences that result from changing patterns of water and food consumption as adults relative to childhood, rather than inherent biological differences. For children aged 4–6 years, 1st molars and associated bone were sampled. Any influence on oxygen-isotope compositions resulting from breastfeeding is expected to be represented in both bone and 1st molar enamel for the younger children, so no adjustment was made to compensate for ^{18}O-enrichment of tissues formed before weaning (as in White et al., 2000, 2004b). For slightly older children (aged 4–12 years), 2nd molars and associated bone were sampled. All teeth selected had well-mineralised crowns and partially or fully formed roots. Bone turnover occurs at a rate of 10–30% per year for adolescents (Hedges et al., 2007) and as high as 100% per year for very young children (Nanci et al., 2003); thus, although the period of time represented by bones and teeth does overlap, the tissues may not be entirely co-forming. An additional important consideration is that all of the children died at a young age from unknown disease processes or stressors, which could have impacted their metabolism in unknowable ways.

2.2. FTIR parameters

FTIR spectroscopy is routinely used to assess post-mortem recrystallization, deposition of secondary carbonates, and the ratio of carbonate to phosphate present in bone and enamel samples. Although this methodology does not directly assess biochemical preservation, FTIR does describe the bioapatite structure and detects aberrant materials, such as calcite, adsorbed from the burial environment. Commonly used parameters included in this study are crystallinity indices (CI) and carbonate-phosphate ratios (CO_3/PO_4), as well as B-carbonate on phosphate indices (BPI), used to assess substitution of carbonate for type B trivalent phosphate ions, and weight percent carbonate content (LeGeros, 1991; Pucéat et al., 2004; Sponheimer and Lee-Thorp, 1999; Shemesh, 1990; Surovell and Stiner, 2001; Weiner and Bar-Yosef, 1990; Wright and Schwarcz, 1996).

Crystallinity indices were determined using the following formula: $[605_{ht} + 565_{ht}] / 590_{ht}$, where 'ht' represents the height of the bands or valleys at the positions specified. Crystallinity indices for fresh bones are approximately 2.8–3.0, and typically range from 3.5–4.8 for archaeological samples. A crystallinity index that is higher than 4.3 suggests extensive recrystallization, and therefore poor bioapatite preservation (Stuart-Williams et al., 1998; Wright and Schwarcz, 1996). Carbonate/phosphate (CO_3/PO_4) ratios are calculated as follows: $1415_{ht}/1035_{ht}$; typically, modern bones have CO_3/PO_4 ratios of ~0.5 and unaltered enamel has a slightly lower ratio (Smith et al., 2007; Wright and Schwarcz, 1996). Archaeological material that has lower CO_3/PO_4 ratios is assumed to have lost carbonate to the burial environment, whereas higher CO_3/PO_4 ratios suggest addition of secondary carbonate from the burial environment (Smith et al., 2007). BPI is calculated as: $1415_{ht}/605_{ht}$ and describes B-site carbonate content. Using the BPI, weight % carbonate can be estimated using the following equation: 10 * BPI+0.7 (LeGeros, 1991), and this estimate provides a more intuitive description of the presence of carbonate in the sample. Using this formula, unaltered bone should contain ~7.4 wt.% carbonate and enamel ~3.5 wt.% carbonate (LeGeros, 1991). Spectra were also visually inspected for aberrant peaks, particularly near 710 cm^{-1}, which indicate the presence of calcite, and a shoulder at 1096 cm^{-1}, which indicates that francolite may have formed. Based on Garvie-Lok et al. (2004), CI and CO_3/PO_4 ratios should not change significantly with pre-treatment. The BPI and wt. $\%CO_3$ estimates will likely decrease for some samples due to the removal of secondary/adsorbed carbonate.

2.3. Impact of pre-treatment procedure on carbonate–oxygen and –carbon isotopic compositions

Bone and enamel destined for carbonate-carbon and –oxygen isotopic analysis are typically subjected to some form of pre-treatment protocol, the objective of which is to remove organic matter, as well as adsorbed carbonate and exogenous carbonate-containing material. It is believed that adsorbed carbonate, which adheres to the surface of bioapatite mineral[1] is likely to be contaminated both by exogenous carbonates (e.g., calcite) from the burial environment and through isotopic exchange and bioapatite

[1] As opposed to structural carbonate, which substitutes *in vivo* in either the OH^- or PO_4^{3-} positions of bioapatite ($Ca_{10}(PO_4)_6(OH)_2$).