Available online at www.sciencedirect.com

ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology 249 (2007) 90 – 102

PALAEO

www.elsevier.com/locate/palaeo

Burning and boiling of modern deer bone: Effects on crystallinity and oxygen isotope composition of bioapatite phosphate

L.E. Munro [a,*], F.J. Longstaffe [a], C.D. White [b]

[a] *Department of Earth Sciences, The University of Western Ontario, London, ON, Canada N6A 5B7*
[b] *Department of Anthropology, The University of Western Ontario, London, ON, Canada, N6A 5C2*

Received 26 July 2006; received in revised form 2 January 2007; accepted 15 January 2007

Abstract

The extent of preservation of stable isotope compositions in biomaterials exposed to burial and weathering continues to be a topic of some debate. Changes in the isotopic composition of archaeological bones and teeth during recrystallization are often suspected, but difficult to prove. Here, we examined the effects of heating (burning, boiling) on the isotopic composition of phosphate oxygen ($\delta^{18}O_p$) in bone bioapatite from two modern White-Tailed deer (*Odocoileus virginianus*). Our experiments simulated cooking and refuse disposal practices, which have affected many archaeological samples. Original values for $\delta^{18}O_p$ were preserved at <300 °C. At higher temperatures, values were lowered by as much as 7‰ from primary compositions. Only small changes in crystallinity (measured using FTIR and XRD) were observed from 25 to 675 °C, despite large shifts in $\delta^{18}O_p$ above 300 °C. Original values for $\delta^{18}O_p$ were preserved only at FTIR CI ≤2.5–2.7. XRD CI values were not sensitive to changes in $\delta^{18}O_p$ below ~625 °C.

Keywords: Bioapatite; Stable isotopes; Heating; Recrystallization; Diagenesis

---

1. Introduction

The structure and chemical composition of bone can be altered after death by natural processes such as weathering, dissolution, precipitation, microbial remodeling, mineral replacement, ionic substitution, recrystallization and isotopic exchange (Pate and Hutton, 1988; Collins et al., 2002; Hedges, 2002; Lee-Thorp, 2002; Trueman and Martill, 2002). Such alteration (commonly referred to as diagenesis) can affect the preservation of isotopic compositions in bone, limiting their usefulness as a tool for reconstruction of climate, diet and mobility of humans and other organisms. Structural carbonate and co-existing phosphate in bone bioapatite have been used in such examinations of ancient biological systems. The behaviour of stable carbon and oxygen isotopes in structural carbonate from bone bioapatite has been most intensively investigated (e.g., Iacumin et al., 1996; Wright and Schwarcz, 1996; Kohn and Cerling, 2002; Lee-Thorp, 2002; Munro et al., submitted for publication) on the assumption that bioapatite carbonate is less resistant to exchange than phosphate. Here, we use two modern White-Tailed deer (*Odocoileus virginianus*) specimens to study oxygen isotope exchange of phosphate in bone bioapatite during burning and boiling, which are *post-mortem* processes that can arise from human activity.

---

* Corresponding author. Fax: +1 613 567 6738.
E-mail address: lisa_m11@hotmail.com (L.E. Munro).

0031-0182/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.palaeo.2007.01.011

Most literature concerning oxygen isotopic modification of bioapatite has focused on changes arising from weathering and secondary mineralization. However, bones are sometimes obtained from contexts where they are likely to have been heated, e.g., middens or near hearths (Shipman et al., 1984; Brain and Sillen, 1988; Nicholson, 1993; Stiner et al., 1995; Taylor et al., 1995; Shahack-Gross et al., 1997; Balter, 2001; Roberts et al., 2002). Burning or boiling has the potential to cause modification of the original oxygen isotope composition of bone bioapatite. In this study, the structural and oxygen isotopic effects on bone subjected to such heating is examined using experiments that mimic cooking and waste disposal practices relevant to archaeological contexts.

Because thermal alteration is assumed to cause changes in composition, burnt bones are generally rejected as suitable material for isotopic studies. Studies of burnt bone have mostly involved physical characteristics, i.e., colour, and morphological and histological assessments (Shipman et al., 1984; Grupe and Hummel, 1991; Nicholson, 1993; Stiner et al., 1995). There have also been investigations of crystallinity, staining, chemical composition, amino acid biochemistry and differential-thermogravimetric changes (Shipman et al., 1984; Brain and Sillen, 1988; Grupe and Hummel, 1991; Nicholson, 1993; Taylor et al., 1995; Stiner et al., 1995; Person et al., 1996; Reiche et al., 2000; Pasteris et al., 2001).

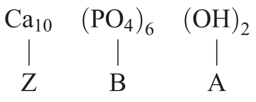
Three earlier reports are of special interest. Shemesh (1990) suggested that *post-mortem* shifts in the oxygen isotope composition of bioapatite were mirrored by changes in crystallinity and proposed that peak sharpness obtained from Fourier Transform infra-red (FTIR) patterns could be used as a Crystallinity Index (CI). Person et al. (1996) studied the effects of burning on crystallinity, comparing experimentally heated bone with archaeological bones. They found that the bone bioapatite crystallinity index, as measured using powder X-ray diffraction (XRD), could be used to monitor the extent of diagenesis. Lindars et al. (2001) examined pretreatment methods for removal of rapidly exchangeable, non-phosphate oxygen from bioapatite in advance of laser-fluorination isotopic analysis. Their experiments included measurement of the phosphate oxygen isotope composition ($\delta^{18}O_p$) of bone heated to 100–1000 °C in 100 °C increments. They observed that $\delta^{18}O_p$ varied with temperature.

We have built on these earlier studies by characterizing changes in bone $\delta^{18}O_p$ during burning and boiling. We have also re-evaluated the temperature and crystallinity index thresholds for preservation of original phosphate oxygen isotopic compositions in heated bones. Munro et al. (submitted for publication) have described the behaviour of bioapatite structural carbonate in the same samples.

2. Background

Bone comprises ~30% organic matrix, interwoven with a framework of ~70% poorly crystallized mineral matter composed primarily of calcium phosphate with a carbonated hydroxyapatite-like structure (Posner et al., 1984; Sillen, 1989). This bioapatite resembles inorganically formed varieties of apatite, called francolite and dahllite (Posner et al., 1984; Skinner, 1989; Krueger, 1991). Bioapatite differs from these phases in its lack of stoichiometry, its small plate-like crystals (averaging 10–50 nm), and its structural disorganization (Boskey and Posner, 1984; Glimcher, 1984; Sillen, 1989; Skinner, 1989; Person et al., 1995; Lee-Thorp, 2000; Surovell and Stiner, 2001; Berna et al., 2004; Trueman et al., 2004). Because of its small crystal size, high surface area and high substitution rate, bioapatite is very soluble and highly reactive (Posner et al., 1984; Sillen, 1989; Ayliffe et al., 1994; Bigi et al., 1997; Lee-Thorp, 2000, 2002; Berna et al., 2004). These qualities lead to the enzyme-mediated equilibrium relationship between bioapatite phosphate and body water during metabolism, and facilitate *post-mortem* alteration by surrounding fluids (Sillen, 1989; Lee-Thorp, 2000, 2002).

Hydroxyapatite has the chemical formula of $Ca_{10}(PO_4)_6(OH)_2$ (Michel et al., 1995; Wright and Schwarcz, 1996). Bioapatite has been described as:



$$\underset{\substack{|\\ Z}}{Ca_{10}}\quad \underset{\substack{|\\ B}}{(PO_4)_6}\quad \underset{\substack{|\\ A}}{(OH)_2}$$

where Z = Ca^{2+}, Na^+, Mg^{2+}, Sr^{2+}, K^+; B = PO_4^{3-}, CO_3^{2-}, HPO_4^{2-}; $P_2O_7^{4-}$, and A = OH^-, CO_3^{2-}, F^-, Cl^-, H_2O (LeGeros and LeGeros, 1984; Michel et al., 1995). Its structure is modified from that of hydroxyapatite mostly by Type-B substitution of carbonate (CO_3^{2-}) for the phosphate group (PO_4^{3-}) (Shemesh, 1990; Krueger, 1991; Wright and Schwarcz, 1996). Type-A substitution of CO_3^{2-} for hydroxyl (OH^-) groups is uncommon (Wright and Schwarcz, 1996; Pasteris et al., 2001). Additional CO_3^{2-} or bicarbonate (HCO_3^-) can also be adsorbed to crystal surfaces during weathering and diagenesis (Wright and Schwarcz, 1996; Lee-Thorp, 2000, 2002).

In "average" bioapatite, phosphate comprises ~35 wt.% oxygen, carbonate ~3.3 wt.% oxygen, and hydroxyl ≤1.6 wt.% oxygen (Cerling and Sharp, 1996). Thus, the