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Early diagenesis and recrystallization of bone

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Abstract

One of the most challenging problems in paleobiology is determining how bone transforms from a living tissue into a fossil. The geologic record is replete with vertebrate fossils preserved from a range of depositional environments, including wetland systems. However, thermodynamic models suggest that bone (modeled as hydroxylapatite) is generally unstable in a range of varying geochemical conditions and should readily dissolve if it does not alter to a more thermodynamically stable phase, such as a fluorine-enriched apatite. Here, we assess diagenesis of alligator bone from fleshed, articulated skeletons buried in wetland soils and from de-fleshed bones in experimental mesocosms with and without microbial colonization. When microbial colonization of bone was inhibited, bioapatite recrystallization to a more stable apatite phase occurred after one month of burial. Ca-Fe-phosphate phases in bone developed after several months to years due to ion substitutions from the protonation of the hydroxyl ion. These rapid changes demonstrate a continuum of structural and bonding transformations to bone that have not been observed previously. When bones were directly in contact with sediment and microbial cells, rapid bioerosion and compositional alteration occurred after one week, but slowed after one month because biofilms reduced exposed surfaces and subsequent bioapatite lattice substitutions. Microbial contributions are likely essential in forming stable apatite phases during early diagenesis and for enabling bone preservation and fossilization.
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Keywords: Bioapatite; Bone diagenesis; Recrystallization; Geomicrobiology; American alligator

1. INTRODUCTION

Bone is a composite material consisting of organic (i.e., collagen, lipids) and inorganic (i.e., mineral) components. The mineralized fraction is a nonstoichiometric apatite phase, closest compositionally to hydroxylapatite (HAP) or carbonated HAP (Elliott, 2002; Olszta et al., 2007) $[(Ca)_{10-x}[(PO_4)_{6-x}(CO_3)_x](OH)_{2-x} \cdot 1.5H_2O]$ (Li and Pasteris, 2014). In life, flexibility of the apatite lattice for substitution permits bone to serve as a reservoir of Ca^{2+}, Na^{+}, and trace elements for biosynthesis (Bergstrom and Wallace, 1954; Green and Kleeman, 1991). Once removed from a living organism and deposited in an environment, the bone HAP lattice can potentially accommodate substitutions at all sites (e.g., Ca^{2+}, PO_4^{3-}, OH^{-}), which is facilitated by the rapid degradation of soft tissues surrounding and within bone Haversian canals through autolytic and biological activity (e.g., Carter et al., 2007; Cobaugh et al., 2015) and labile tissue removal, particularly by insects (e.g., Rodriguez and Bass, 1983). The remaining bone can then be altered during or after burial by diagenesis, which is the combination of physical and chemical alteration processes that act upon bone. Long-term preservation of bone as a fossil is achieved from the recrystallization of bone mineralogy and enrichment in rare earth and trace elements, like F^{-}, Fe^{2+}, Mn^{2+} (e.g., Hubert et al., 1996; Nielsen-Marsh and Hedges, 2000; Keenan, 2016).

Bone transformation into a fossil has previously been proposed to include processes and reactions that reduce

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HAP dissolution rates by changing mineral surface area to volume ratios (i.e., from increased crystallite size or structural ordering) (Kohn, 2008; Trueman et al., 2008) and enhancing ion transport and fluid migration from the degradation and removal of organics (Child, 1995; Kohn, 2008). These and other processes likely persist throughout fossilization (e.g., Suarez et al., 2010). Rates of bone recrystallization are estimated to occur "rapidly," within 30 thousand years (kyr) or less (Kohn, 2008); however, short-term (i.e., immediately following death) diagenesis studies are poorly represented in the literature and are restricted to bones examined on annual to millennial timescales (Nielsen-Marsh and Hedges, 2000; Trueman et al., 2004, 2008). Consequently, our understanding of the timescales of diagenesis, when bone bioapatite begins to recrystallize (Keenan, 2016), and specifically of short-term (i.e., several years, Trueman et al., 2008) to long-term (i.e., millions of years, Nielsen-Marsh and Hedges, 2000; Keenan et al., 2015) chemical and structural changes to bone is limited, despite extensive evaluation of major and trace element compositions of bones (e.g., Pate et al., 1989; Trueman and Benton, 1997; Koenig et al., 2009), reconstruction of isotopic records (e.g., Kolodny et al., 1996), and examinations of structural and developmental histories of bone through time (Olszta et al., 2007).

Short-term, early diagenesis of bone is expected to occur across a range of physiochemical conditions that are controlled by site-specific conditions, such as climate, precipitation, temperature, soil type, and grain size. In particular, soil and sediment type and grain size in contact with decomposing soft and hard tissues have the potential to influence ion exchange, fluid migration, oxygenation state, and will exert physiochemical controls on microbial communities. Moreover, autolytic and biological degradation of soft tissues should also alter decomposition-specific microenvironments, for example by potentially increasing or decreasing pH and altering oxygen availability and overall redox status due to localized anaerobic conditions (e.g., Carter et al., 2007; Cobaugh et al., 2015). As such, both site-specific and decomposition-specific conditions should interact to influence the availability of labile organic matter (i.e., collagen) for subsequent decay by soil and water microbial communities (e.g., Damann et al., 2015).

As a first step towards assessing site-specific controls on bioapatite recrystallization during the earliest stages of bone diagenesis, and in determining whether or not environmental (micro)biology affects bone mineral lattice structure, we evaluated the early diagenesis of bones from the American alligator (*Alligator mississippiensis*) in a wetland depositional environment with strong redox gradients (Elsey and Woodward, 2010) and explored the potential role of indigenous sediment microbial communities to diagenesis. We chose the modern alligator-wetland system because these crown-group archosaurs have occupied semi-aquatic environments since their divergence with avemetatarsalians (Gauthier, 1986) and there are extensive fossil archosaurian records (e.g., Syme and Salisbury, 2014) that could be used to draw comparisons with prior bone diagenesis research. We hypothesized that compositional changes to defleshed bone occur after only days to weeks, soon after the bone is exposed and starts to interact with the geochemistry and microbiology of a depositional environment. Bioapatite mineralogy and preservation have rarely been evaluated in the context of thermodynamic stability (Nielsen-Marsh and Hedges, 2000; Berna et al., 2004), and we generated thermodynamic models of bone HAP and phosphorus-bearing minerals and compared the output to long- and short-term experimental results. Annual (here defined as "long-term") diagenetic changes, including microbial controls that would affect bone preservation and fossilization (Child, 1995; Collins et al., 2002; Jans, 2008), were evaluated for up to three years from skeletal bone buried as complete carcasses. Short-term diagenesis of bone was assessed from days to weeks in laboratory mesocosms where bone was experimentally exposed to or excluded from indigenous soil microorganisms.

2. METHODS AND ANALYTICAL TECHNIQUES

2.1. Aqueous and sediment geochemical parameters used to populate thermodynamic models

At the Rockefeller Wildlife Refuge (RWR) in Cameron and western Vermilion Parishes, southwestern Louisiana (USA), silt to clay-sized sediment accumulated as overbank deposits in relic Mississippi River floodplains, and as laterally migrating beach-ridge complexes. Soils locally known as Creole clay are vertisols (Midkiff et al., 1995) that consist predominantly of mixed-layer smectite, mica, and quartz, confirmed with X-ray diffraction (XRD) (Table 1). Organic carbon content was determined in triplicate from loss on ignition (LOI) estimates (Wright et al., 2008; Wang et al., 2011, 2012). Soil pH was measured from 1:2 soil to deionized water slurries (Robertson et al., 1999).

The phosphorus sorption capacity of RWR clay minerals in the soil was determined from several representative samples along a depth profile from 15 to 45 cm depth (Table 2) (methods modified from Bache and Williams, 1971 and Lajtha et al., 1999). In brief, the target wet weight of each sample was calculated based on the ratio of wet to dry mass after drying soil at 105 °C for 24 h, with target wet weights ranging from 3.3 to 4.3 g. Wet soil was processed in triplicate. A stock solution of 0.01 M $CaCl_2{\cdot}2H_2O$ was used instead of 0.01 M KCl, and no chloroform was added. A phosphate stock solution with a concentration of 130 mg/L P as PO_4 was added to each sample (25 mL) in a 50 mL centrifuge tube (Falcon), and placed on a shaking platform (120 rpm) for 24 h. [P_T] was measured using ion chromatography (Dionex ICS-2100) of solutions gravimetrically filtered (Whatman 42) into acid-washed 50 mL syringes. Solutions were then filtered to 0.45 μm (Whatman) into glass IC sample vials and analyzed within 1–2 h of filtration.

Temperature, pH, and conductivity were measured in the field using standard electrode methods (APHA, 2005). Ion measurements utilized water samples filtered with 0.2 μm-PDVF filers (Millipore) in the field into pre-cleaned HDPE bottles, followed by analysis using ion chromatography (Dionex ICS-2100) (APHA, 2005). Cation sample bottles were HCl-washed and filtered

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