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Fractionation of rare earth elements within bone mineral: A natural cation exchange system

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ABSTRACT

The distribution of rare earth elements (REEs) within fossil bones is controlled by their partition coefficients between apatite and pore waters, and the rate of diffusion through the bone. Using simple theoretical models, we show that REEs are strongly fractionated from one another during diffusive transport and adsorption. Fractionation occurs due to the relative ease of substituting REE ions of differing ionic radius into the Ca sites in the apatite lattice, and the degree of fractionation is dependent on the rate of diffusion of ions within bone (and therefore the rate of recrystallisation). Variations in bone thickness, recrystallisation rate, and potentially pore water composition may all influence the relative distribution of REEs, and thus REE ratios within bones. Increases in bone thickness and reductions in either diffusion coefficients or the duration of REE uptake lead to enhanced fractionation of REEs in our model simulations. Interpretations of REE ratios in fossil bones either for palaeoenvironmental or taphonomic applications must consider how fractionation will influence REE ratios within bones, particularly when interpreting spatially resolved analyses within single bones.

1. Introduction

Bone is a composite material composed of nanometre-sized crystals of bioapatite contained within a collagenous protein matrix. After death, as bone crystals are exposed following hydrolysis of collagen, a wide variety of metals contained within the surrounding pore water are sorped onto the crystal surfaces. The uptake of these metals from the local burial environment into bone after death potentially allows the trace element composition of ancient bone to be used to investigate aspects of the burial environment and taphonomy (e.g., Grandjean et al., 1987; Plummer et al., 1994; Williams et al., 1997) and forms the basis of uranium-series and ESR dating of archaeological bone (Millard and Hedges, 1996; Pike et al., 2002).

The rare earth element (REE) composition of fossil bones and teeth has received particular attention as the relative abundances of REEs can be used to study conditions in the surrounding environment (Metzger et al., 2004; Suarez et al., 2010; Trueman et al., 2006; Williams et al., 1997) as a proxy for ancient seawater (e.g., Elderfield and Pagett, 1986; Goldberg et al., 1963; Scher and Martin, 2006; Via and Thomas, 2006; Wright et al., 1984) and to assess the degree of post-mortem movement and mixing in bone assemblages (e.g., Staron et al., 2001; Trueman, 1999; Trueman and Benton, 1997; Trueman et al., 2003). All of these applications rely on the assumption that the measured REE composition of a fossil bioapatite reflects that of surrounding pore waters with relatively little, or at least consistent, fractionation.

Increasingly, spatially resolved analytical techniques such as laser ablation ICP-MS are being used to measure the distribution of trace elements in fossil bone mineral (e.g., Herwartz et al., 2011; Janssens et al., 1999; Koenig et al., 2009; Trueman and Tuross, 2002; Williams et al., 1997) and it is clear that not only do absolute concentrations of REEs decrease with depth into bone cortex, but also the relative concentrations of REEs are not consistent throughout the thickness of bone: REEs are fractionated from one another during transport and uptake within bone. The observed variations in absolute and relative concentrations of REEs within fossil bones could potentially reflect changing pore water conditions during the timescale of trace element uptake. However, partition coefficients for REEs between water and bioapatite vary systematically with ionic radius, such that fractionation of REE would be expected under both equilibrium and disequilibrium conditions (Reynard et al., 1999; Trueman and Tuross, 2002). To interpret spatial variation in the REE element content of a fossil bone, it is therefore important to establish the nature and extent of fractionation expected under differing depositional conditions.

Here we take a theoretical approach to model fractionation of REEs during diagenetic incorporation into bone. We focus on bone, but the principles applied extend to root material in teeth and also to dentine, although in the case of dentine, extra complexities may occur due to the geometry of the dentine–enamel boundary and direction of trace element uptake. We then compare theoretical results with measured

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REE compositions and discuss the implications for geochemical analyses of ancient bone.

2. Nature of bone mineral and fossilisation

Bone mineral is composed of carbonated calcium phosphate minerals belonging to the apatite group. It has a range of lattice substitutions and a non-stoichiometric composition, such that assigning bone mineral to a particular mineralogical form (e.g., dahllite) may lead to false impressions of homogeneity and well-ordered crystal chemistry. The size and shape of bone mineral crystallites are on the order of tens of nanometres in length and breadth, and 1–10 nm in thickness (Elliott, 2002; Rubin et al., 2003; Weiner and Price, 1986). Bone crystallites are amongst the smallest of all biomineralised crystals, and their chemistry is dominated by their surface area/mass ratio and high degrees of lattice strain. The mineral component of bone is thermodynamically metastable and once exposed to pore-waters, bone crystallites will react, either dissolving or spontaneously recrystallising, increasing mean crystal sizes (Berna et al., 2004; Moradian-Oldak et al., 1991; Trueman et al., 2004). Bone mineral is held within and upon a protein matrix principally composed of collagen. Collagen prevents interaction at the surfaces of bone crystals, but as collagen degrades post-mortem, these crystal surfaces are exposed and available for element exchange with pore waters. During early diagenesis, the concentration of many trace elements increases in bone crystals, reflecting the high adsorption capacity of bone crystals. The reactivity of bone crystals also sets a requirement for long-term preservation. For bone to survive into deep time, crystals must grow, reducing their surface area and crucially, limiting inter-crystalline porosity. 'Fossilisation' of bone can be considered as the coincident degradation of collagen and growth or recrystalliation of bioapatite crystals. Diagenetic recrystallisation is complete once the inter-crystalline porosity originally occupied by collagen is closed. At this point, the rate of interaction between bone and pore waters and further exchange of trace elements is greatly reduced (Kocsis et al., 2010).

Trace elements are supplied to bone from the surrounding pore waters via both the vascular network and the pore spaces left by collagen degradation. Buried bone is generally saturated with water, thus allowing diffusion of trace elements through these interconnected, water-filled pore spaces. Trace elements are removed from pore waters by sorption onto exposed crystallite surfaces. Two models are therefore needed to study the distribution of trace elements such as the REEs in bone, a model predicting the adsorption affinity of exposed bone crystals for each REE, and a model describing the diffusion of REEs through bone as a function of time.

3. Theory

3.1. Modelling adsorption coefficients for REEs between bone and pore water

The extent of adsorption of REEs onto apatite crystals (partition coefficients defined as $[REE]_{apatite}/[REE]_{fluid}$ at equilibrium where [] denotes concentration) can be predicted from the lattice strain partitioning model of Blundy and Wood (1994). In this model the equilibrium partitioning behaviour of cations between a mineral and a liquid at a particular temperature, pressure, and composition of interest can be explained by a version of the Brice (1975) equation, in which the size and elasticity of crystal lattice sites play a major role.

$$D_i(P,T,X) = D_o(P,T,X) \; x \; \exp\left[\frac{-4\pi E N_A\left[r_o/2(r_i-r_o)^2 + 1/3(r_i-r_o)^3\right]}{RT}\right] \quad (1)$$

where D_i is the partition coefficient and D_o is a "strain compensated partition coefficient" that describes cation substitution where the substituent ion radius (r_i) is equal to the radius of the ion site (r_o). E is the Young's modulus of the cation site, N_A is Avogadro's number, R is the gas constant and T is temperature in Kelvin.

Eq. (1) demonstrates that the ease with which mis-matched cations of equal ionic charge can be accommodated into the crystal lattice site is controlled by a measure of the strain imposed on the crystal lattice as a consequence of the substitutions – expressed by the Young's modulus. Higher values of Young's modulus indicate that mismatched ions cannot be accommodated readily in a lattice site and therefore reflect a high potential for fractionation based on differences in ion radius. Eq. (1) was derived to model equilibrium partition coefficients, but effectively describes any ion substitution either within a crystal lattice (modeling a true partition coefficient) or at a crystal surface (effectively modeling an adsorption coefficient). In the case of bone crystals, adsorption occurs preferentially at Ca sites on the crystal surface (Koeppenkastrop and DeCarlo, 1992). Adsorption of REEs onto bone crystals is therefore also crystal chemical controlled and can be modelled via strain-compensated partition models. We use Eq. (1) to estimate adsorption coefficients for REEs between bioapatite and water. Ion radii were taken as values in VI fold co-ordination. We use a value of 1×10^6 as a reasonable first approximation for ideal strain-free adsorption D_o. This value is taken from experimental determination of adsorption coefficients between water and authigenic francolite from Koeppenkastrop and DeCarlo (1992) and is of the same order as experimentally determined partitioning of U between bone mineral and water (Millard and Hedges, 1996).

The Young's modulus for incorporation of trivalent REE ions onto the Ca lattice sites in bioapatite is unknown but has been estimated from the experimental adsorption data of Koeppenkastrop and DeCarlo (1992) at c. 90 GPa (Reynard et al., 1999). The Young's modulus value for REE partitioning into apatite at high temperatures has been estimated as between 340 GPa and 520 GPa (Trueman and Tuross, 2002).

3.2. Modelling the distribution of trace elements in bone

Millard and Hedges (1996) extended the solutions to diffusion equations provided by Crank (1975) to develop a diffusion–adsorption (DA) model predicting the distribution of U within a bone as a function of time. In their simplest form, DA models assume bone to be a finite slab with a homogenous and constant porosity. Trace elements are supplied to bone from the external margins, and the initial concentration of elements within bone is assumed to be zero. In this case, the concentration (Z) of a given element at any point (x) in the bone is a function of the diffusion coefficient modified to reflect the pore size distribution (D), the adsorption (partition) coefficient (R) and the time since initiation t:

$$Z = pRC1\left(1-\tfrac{4}{\pi}\sum\frac{(-1)^n}{2n+1}\exp\left[\frac{-D(2n+1)^2\pi^2 t}{(R+1)4l^2}\right]\cos\left[\frac{(2n+1)\pi x}{2l}\right]\right) \quad (2)$$

where ϕ = porosity, C = the concentration of the element in the surrounding pore water, l = half of the thickness of the bone.

This expression is simplified by working with a set of reduced, dimensionless variables:

$$Z' = Z/\phi RC_1 \quad (3)$$

$$x' = x/l \quad (4)$$

$$t' = tD/(R+1)l^2 \quad (5)$$