Palaeogeography, Palaeoclimatology, Palaeoecology 416 (2014) 4–16

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

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

Trace elements and their isotopes in bones and teeth: Diet, environments, diagenesis, and dating of archeological and paleontological samples

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ARTICLE INFO

Article history:
Received 24 March 2014
Received in revised form 10 July 2014
Accepted 31 July 2014
Available online 9 August 2014

Keywords:
Trace elements
Biogenic apatite
Diet
Environment
Diagenesis
Dating

ABSTRACT

Fossil biogenic apatites display trace element (TE) compositions that can record environmental and biological signals, give insights into past water compositions, or be used for dating paleontological and archeological bones and teeth. Processes of TE incorporation into apatites of skeletal phosphatic tissues are described, ranging from those active in living organisms to those active during diagenesis. Abiotic incorporation mechanisms have been modeled theoretically and experimentally and include crystallographic controls on TE partitioning coefficients, inorganic surface adsorption and adsorption mediated through chelation and diffusion–adsorption processes, each leading to specific fractionation patterns. Predictions from models and experiments have been tested against TE concentration and isotopic composition data on remains of contemporary wild or raised animals and on fossils of various ages and environments. In living organisms, TEs incorporated in apatite are separated in two categories, non-essential elements whose concentration is compared to that of an essential element with similar behavior (e.g. Sr/Ca) to reconstruct trophic chains, and essential elements whose isotopic ratios are used to trace metabolic activity, diet, etc. In fossils, elements are incorporated during diagenesis, such as rare earth elements (REEs), and trace diagenetic processes ranging from very early quantitative adsorption likely mediated by chelators, protracted diagenesis through inorganic adsorption and fractionation through diffusion–adsorption, to low-grade metamorphism associated with intense redistribution under crystal-chemical control. These different steps are also identified as steps of radionuclide incorporation. Only samples where the earliest steps can be deciphered are useful for determining stratigraphic and archeological ages. Other samples will date late diagenetic events that have obliterated the paleoenvironmental signals, but may be of geological significance, e.g. tectonic events.

1. Introduction

TEs have long been known to enter bio-apatites of the exo- and endo-skeletons of organisms during their life (Stoeltzner, 1908; Hodges et al., 1950) and during the *post mortem* fossilization processes (Arrhenius et al., 1957; Parker and Toots, 1970). Their concentrations and stable isotopic compositions contain information firstly on intensive and extensive parameters of the environment during the life of the organisms, such as temperature, water composition, food and place in the trophic chain, and secondly on conditions, timing and extent of diagenetic alteration of this paleoenvironmental signal. Understanding the mechanisms of TE incorporation and the thermodynamics and kinetics at work during those processes is essential for separating the information pertinent to paleoenvironmental conditions from that relating to the diagenetic history.

Elements like the alkali-earth (Mg, Sr, Ba) are incorporated in significant amounts during life, and divalent metals (Zn, Cu, Fe) at lower levels. These elements will typically be used to trace the environmental and biological signals. Elements like REE and high-field strength elements (Hf, U, Th) are incorporated post-mortem, and trace diagenetic processes from early on in water-rich unconsolidated sediments to low-grade metamorphism. Lu, Th and U are used for dating provided that they can be linked to diagenetic events that took place in a relatively short time interval after the death of the organism.

Different laws govern incorporation of TEs depending on their nature and on the mechanism of uptake by fossils. Properties of the bulk crystal influence the partitioning of TEs with biological or environmental fluids when recrystallization is important during the growth of the skeleton or

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http://dx.doi.org/10.1016/j.palaeo.2014.07.038
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in case of dissolution–precipitation during fossilization. Interactions with mineral surfaces can also play an important role at each of these stages. Interaction with organic molecules is an overlooked mechanism that may explain features of element partitioning in vivo or at early diagenetic stages when part of the organic fraction of the skeletons is preserved or when fluids are rich in chelating organic agents due to biological activity in soils and sediments.

In addition to the direct crystal-chemical effects, partitioning can occur due to kinetic controls on dissolution, precipitation, and transport of the elements in the complex skeleton structure. This implies a complex interplay of aqueous transport in mesoscale pores, diffusion at wetted grain boundaries, diffusion and concentration-controlled dissolution or precipitation, and buffering or intermittent interaction with the diagenetic fluid. Quantification of these phenomena is essential for deciphering potential alteration of the paleoenvironmental signal and for interpreting ages provided by radiogenic isotopic measurements.

Various incorporation mechanisms lead to specific partitioning and composition patterns in fossils that can be assessed by thermodynamic modeling or experimental investigations. We discuss here theoretical and experimental evidence of activity of these different processes, and their consequences on the interpretation of the fossil record in terms of biological signals, paleoenvironments, dating, and diagenetic processes.

2. Mechanisms of TE incorporation in apatite: theoretical and experimental constrains

2.1. Partitioning between aqueous fluids and crystals

Partitioning of divalent cations is defined by the chemical equilibrium expressing divalent cation (Me^{2+}) exchange between apatite and aqueous solutions:

$$\mathrm{Me}^{2+}(\mathrm{aq}) + \text{Ca-apatite}(\mathrm{ss}) = \mathrm{Ca}^{2+}(\mathrm{aq}) + \text{Me-apatite}(\mathrm{ss}), \tag{1}$$

where (aq) and (ss) refer to the aqueous solution and to the solid solution, respectively, with the associated equilibrium constant:

$$K_D\left(\frac{\mathrm{Me}^{2+}}{\mathrm{Ca}}\right) = \frac{\frac{X_{\text{Me-apatite}}}{X_{\text{Ca-apatite}}}}{\frac{m_{\mathrm{Me}^{2+}}}{m_{\mathrm{Ca}}}} = \frac{K(T)_{\text{Ca-apatite}}}{K(T)_{\text{Me-apatite}}}\frac{\lambda_{\text{Ca-apatite}}}{\lambda_{\text{Me-apatite}}}\frac{\gamma_{\mathrm{Me}^{2+}}}{\gamma_{\mathrm{Ca}}}, \tag{2}$$

where X is the molar fraction in apatite solid solution, m the molality in water, λ the activity coefficient of the component in the solid solution, $K(T)$ the solubility product of the end-member at temperature T, and γ the ion activity in the aqueous solution, whose ratio in water is assumed to be equal to unity in the following. The activity coefficients in a regular solid solution model are described by Margules parameters and can be approximated by the elastic energy due to the deformation of the host crystal lattice around the substituted cation (Brice, 1975):

$$W_{G_{ji}} = 4\pi \mathrm{N_A} E\left[\frac{r_i}{2}\left(r_j - r_i\right)^2 + \frac{1}{3}\left(r_j - r_i\right)^3\right], \tag{3}$$

where N_A is the Avogadro number, E the Young's modulus of the crystal, r_i the ionic radius of the cation normally occupying the site in the i compound (Ca in apatite), and r_j the ionic radius of the substituted cation in compound j. Elasticity of hydroxyapatite gives $E = 114 \pm 2$ GPa (Gilmore and Katz, 1982; Bass, 1995). Numerical applications with 6- to 9-fold coordination ionic radii (Shannon, 1976) give similar results. The elastic energy is assumed constant over the pressure and temperature interval of interest. Using slightly different boundary conditions leads to different equations (Nagasawa, 1966; Gnanapragasam and Lewis, 1995) and to differences in the substitutions energies in the order of ±10%. Apatite solid solution properties were also accurately modeled from interatomic and first-principles calculations (Rabone and De Leeuw, 2006; Kawabata and Yamamoto, 2010; Almora-Barrios et al., 2013).

At low concentrations ($X_{\text{Me-apatite}} \ll 1$) like those of TEs in biogenic apatites, Eq. (2) reduces to:

$$K_D\left(\frac{\mathrm{Me}^{2+}}{\mathrm{Ca}}\right) = \frac{K(T)_{\text{Ca-apatite}}}{K(T)_{\text{Me-apatite}}} \exp\left(-W_{G_{\mathrm{MeCa}}}/\mathrm{R}T\right) = \exp\left(-\left(G_{ideal} + W_{G_{\mathrm{MeCa}}}\right)/\mathrm{R}T\right), \tag{4}$$

where the term $\exp(-\Delta G_{ideal}/\mathrm{R}T)$ is the free enthalpy change of reaction (1), equivalent to the ratio of end-member solubility products. Unlike carbonates, solubility products and thermodynamic data for end-member apatites are scarce (Jemal et al., 1995). When no data are available for the solubility and enthalpy of formation of the end-members, it is assumed that the elastic energy term dominates partitioning, i.e. $\Delta G_{ideal} \ll W_{G_{\mathrm{MeCa}}}$. Promising ways for obtaining enthalpies of formation and substitution energies are first-principles calculations (Almora-Barrios et al., 2013) and atomistic modeling (Rabone and De Leeuw, 2006).

For heterovalent substitutions, the equilibrium reaction becomes complex since complementary substitutions are necessary to maintain charge balance in the crystal. Typically, substitution of the trivalent elements of the important rare-earth series requires compensation by Na^+ for Ca^{2+} in an adjacent site, or yet more complex substitution scheme involving carbonate groups, fluorine (Yi et al., 2013). In that case, most thermodynamic data required for calculating the equilibrium constant are not available. Among a series of elements with the same charge and substitution scheme, the pattern of equilibrium constants, or of distribution coefficients, can be approximated by combining Eqs. (3) and (4) (Blundy and Wood, 1994, 2003):

$$K_D = K_D^0 \exp\left(-4\pi \mathrm{N_A} E_{eff}\left[\frac{r_0}{2}\left(r_j - r_0\right)^2 + \frac{1}{3}\left(r_j - r_0\right)^3\right]/\mathrm{R}T\right), \tag{8}$$

where E_{eff} is the effective Young's modulus and r_0 is the optimum radius for maximum equilibrium constant $K_D{}^0$, all of which will depend on the charge of the considered series of elements. These parameters can be adjusted to experimental data such as partition coefficients between minerals and liquids (Blundy and Wood, 1994) and lead to parabola-like curves whose position and curvature depends on the charge of the element (Fig. 1). This approach was so far only applied to rare-earth elements in apatite (Fig. 2), where relative partition coefficients were extrapolated from magmatic temperatures around 800 °C (Fujimaki, 1986) to low temperatures appropriate to fossil diagenesis (Reynard et al., 1999).

2.2. Surface adsorption, complexation, and chelation

The chemical equilibrium used above applies to systems where solution–precipitation and diffusion in solids are fast enough to allow equilibration between the fluid composition and bulk composition of crystals. This is usually far from being the case in living organisms and in low temperature sedimentary environments. Equilibrium (1) may in this case be replaced by local equilibrium between the ions in solution and ions adsorbed on the apatite surfaces. The crystal surface composition is incorporated in the crystal during its growth with equilibrium constants that can differ strongly from those of equilibrium (1) between a bulk mineral solid solution and aqueous solutions. Direct measurement of surface composition in equilibrium with a fluid is difficult, and few data on surface speciation are available (Rimbert et al., 1982). The thermodynamics of this local equilibrium may be discussed from the difference between effective fractionation as measured on experimentally grown crystals and equilibrium (1). Surface adsorption energies and associated equilibrium constants can be obtained from first-principles calculations that were so far applied to Mg incorporation in