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Timescales and mechanisms of REE and Hf uptake in fossil bones

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Abstract

Rare earth element (REE) patterns of fossil bones and teeth are widely used as proxies for provenance, taphonomy, and palaeoenvironment. In order to investigate if fossil bones behave as closed systems over geologic time, REE profiles were analysed by LA-ICPMS along cross sections of 54 bones from various well-characterised and well-dated settings. These include terrestrial and marine diagenetic environments, covering Early Triassic to Holocene ages. In general, all fossil bones exhibit the highest REE concentrations at the outer rim, gradually decreasing by up to four orders of magnitude toward the inner bone cortex. Intra-bone REE concentration gradients decrease significantly from Quaternary via Tertiary to Mesozoic specimens, suggesting long term REE uptake and open system behaviour of fossil bone. This view is further corroborated by ^{176}Lu–^{176}Hf dating of selected samples, all yielding significantly younger ages than the known chronostratigraphic ages. Hence, there is clear evidence for long term open system behaviour of fossil bones with respect to REE, which is in marked contrast to currently accepted models suggesting that REE uptake is only early diagenetic. Although unexpected, statistically significant four to seven point isochrons are observed for four fossil dinosaur bone samples and one Upper Triassic *Mastodonsaurus* tooth with MSWDs ranging from 0.083 to 4.5. Notably, mobility of Lu alone cannot account for the observed age patterns. Assuming constant Lu uptake rates over time, the radiometric ages should only be as low as half of the chronostratigraphic age. However, a six-point isochron defined by subsamples of a single Upper Triassic *Mastodonsaurus* tooth yields an age of 65.2 ± 1.1 Ma (MSWD = 0.68), much younger than half of the stratigraphic age (ca. 234 Ma). Hence, Hf must also undergo late diagenetic exchange. Likely mechanisms to account for the presence of statistically meaningful isochrons as well as for the late diagenetic exchange of both REE and Hf are diffusion, adsorption, and dissolution–reprecipitation processes.

1. INTRODUCTION

1.1. Mechanisms of fossilisation

Fresh bone is composed of nm-sized crystals of non-stoichiometric hydroxy-carbonate apatite, embedded in a protein matrix of collagen (e.g. Pfretzschner, 2004; Wopenka and Pasteris, 2005; Pyzalla et al., 2006; Pasteris et al., 2008). In general apatite crystallites are plate-like and range from a few nm in thickness, to tens of nanometres in breadth and length (e.g. Rubin et al., 2003; Dumont et al., in press). These crystallites are thermodynamically metastable and thus either dissolve or recrystallise when exposed to the environment (e.g. Berna et al., 2004). The timescales of these processes are largely dependant on the dynamics of post mortem collagen decay (e.g. Trueman and Tuross, 2002; Tütken et al., 2008). Under favourable conditions, the non-stoichiometric hydroxy-carbonate apatite is transformed into thermodynamically stable flourapatite by a dissolution–reprecipitation process (Pasteris and Ding, 2009), which is the prerequisite for the fossil to survive into deep time. Crystallinity and crystal size are usually increased during the fossilisation stage (Trueman and

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