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Rare earth element systematics of fossil bone revealed by LA-ICPMS analysis

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Abstract

Intra-bone rare earth element (REE) fractionation trends were studied by LA-ICPMS analysis to put constraints on (1) the mechanisms controlling REE fractionation within fossil bones; (2) the relative timing of REE uptake in various parts of fossil bone and (3) the origin of REE in fossil bones. We have evaluated REE bone profiles across 54 fossil bones from a broad range of well-characterised taphonomic settings ranging in age from Triassic to early Medieval. REE patterns and concentration gradients are highly variable and intra-bone fractionation trends in $(La/Yb)_N$ vs. $(La/Sm)_N$ space of few specimens cover almost the entire range previously observed for bulk samples. Intra-bone variability of Ce anomalies, as well as variable Y/Ho and $(La/La^*)_N$ is also observed. Sometimes, diagenetic fluids with fractionated, HREE enriched compositions have entered the bone from the marrow cavity, producing secondary REE uptake profiles. Theoretical intra-bone fractionation trends, modelled using lattice strain theory, concur with most REE data but some trends cannot be modelled using realistic boundary conditions. This fact, as well as the occurence of positive and negative Ce anomalies within the same fossil sample, hint towards changing REE compositions of diagenetic fluids over the timescales of REE uptake. Because apparent Ce anomalies frequently evolve over bone profiles and Ce anomalies can be inherited from previous fractionation events, Ce anomalies are a highly ambiguous tracer for constraining ambient redox conditions. In general, bioapatite REE signatures may not always reliably reflect ambient taphonomic or redox conditions and diagenetic fluid compositions. Therefore REE patterns and Ce anomalies of fossil bones must be interpreted cautiously as they vary spatially within skeletal remains and are affected by intra-bone fractionation processes as well as changing compositions of the diagenetic fluid.

1. INTRODUCTION

Fossil bones and teeth are the most common remains of extinct vertebrates, which are preserved in sediments due to their high mineral content of bioapatite. The geochemical composition of these skeletal remains is commonly analysed to determine (1) ‘in vivo’ trace element and isotope compositions that are widely used to infer the diet, (thermo-) physiology, mobility and palaeoenvironment of extinct vertebrates (reviews in Koch, 1998, 2007; Kohn and Cerling, 2002); or (2) information about taphonomy and fossilisation processes (e.g., Kohn et al., 1999; Trueman et al., 2006; Kohn, 2008; Tütken and Vennemann, 2011; Brügmann et al., 2012). Because rare earth element (REE) concentrations of modern bones are in the lower ppt to ppb range (Kohn et al., 1999; Herwartz et al., 2011), while REE concentrations in fossil bones are many orders of magnitude higher (e.g., Kohn et al., 1999; Trueman and Tuross, 2002; Herwartz et al., 2011), ‘in vivo’ REE compositions are effectively overprinted. Hence, REE are ideal to study the taphonomic conditions of the fossilisation environment and have therefore

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