

Fossil bones in persistent action – uptake, loss and redistribution of REE and Hf

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Recent approaches to directly date biogenic apatite via Lu-Hf have resulted in highly inaccurate ages for both bones and teeth [1; 2; 3]. To investigate the cause for these ambiguous Lu-Hf ages we have performed measurements on bones from different geological matrices and also tested different analytical protocols.

In terms of method development, we investigated the effect of five different dissolution techniques that were tested on bones as well as bone and sediment composites. By also analysing the insoluble leftovers from different sample digestion protocols, four reservoirs of Hf in fossil bones were identified: (1) a radiogenic end-member associated with apatite; (2) an unradiogenic end-member represented by the authigenic minerals or the embedding sediment; (3) a highly unradiogenic end-member that can be attributed to detrital zircon in the sediment; and (4) a moderately soluble phase (probably a Zr(Hf)-phosphate) that yielded very low Lu/Hf but a highly radiogenic Hf isotope composition at the same time. This phase is clearly of late diagenetic origin, as it comprises a significant portion of radiogenic ^{176}Hf that was produced within the sample over geological timescales. However, our current dataset implies that such mineral phases and the biases introduced by different dissolution methods only slightly affect the Lu-Hf ages.

Using the most appropriate digestion technique (HCl-HF-HClO₄ table-top), the role of different sediment matrices and of crystal size for preservation of pristine Lu-Hf isotope compositions in bioapatite were further investigated. In addition to previously published examples [1; 3], near-depositional Lu-Hf ages were obtained for a bony fish sample (*Notelops brama*) encapsulated in an early diagenetic carbonate concretion from the Early Cretaceous Santana Formation, Brazil and for conodonts from a Middle Devonian carbonate from the Eifel, Germany. The analysed materials from the Middle Eocene Messel oil shale (e.g., bones, fish scales, sediment, siderite) yielded surprisingly low $^{176}\text{Lu}/^{177}\text{Hf}$ ratios, and therefore the age for Messel might only be near-depositional due to the large age uncertainty. In agreement with previous results, all other ages determined for both bones and teeth are by far younger than respective chronostratigraphic ages. The reason for the apparently continuous Lu-Hf element exchange between the fossils and the embedding sediment is probably the nm-scale crystal size of fossil bones, dentine and also of enamel that generates large surface areas, facilitating sorption/desorption processes and open system behaviour.

As evident from our data, radiogenic ^{176}Hf is in most cases lost to the host sediment over prolonged timescales. Hence, element diffusion processes must operate rather efficiently even after pore spaces have been filled with diagenetic minerals. Consequently, REE can be scavenged from the host sediment at any time during burial and it is by no means justified to assume an entirely early diagenetic incorporation of the REE in fossil bones and teeth [e.g. 4], even if millennial timescales of REE uptake are suggested by diffusion modelling [e.g. 5].

[1] Barfod et al. (2003) *Chem. Geol.* **200**, 241-253; [2] Kocsis et al., (2010) *Geochim. Cosmochim. Acta* **74**, 6077-6092; [3] Herwartz et al., (2011) *Geochim. Cosmochim. Acta* **75**, 82-105; [4] Trueman and Tuross (2002) *Mineral. Soc. Am. Rev. Mineral. Geochem.* **48**, 489-521; [5] Kohn (2008) *Geochim. Cosmochim. Acta* **63**, 2737-2747.