

Trace element and REE distribution in fossil bone implications for Lu-Hf dating of diagenesis

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Fresh bone is composed of nm-sized hydroxyapatite crystals which are embedded in a protein matrix of collagen. During early diagenesis, collagen decomposes rapidly and bone porosity is usually filled by recrystallizing apatite and additional secondary mineral phases. Trace metals such as REE are incorporated at high concentrations into bone apatite during early diagenetic recrystallisation, which occurs rapidly within 10^1 to 10^4 years post mortem. Especially REE and U are important elements to constrain the taphonomy, reworking, and age of fossil bone. The Lu-Hf system can potentially be used for direct radiometric dating of fossil bones and teeth (Barfod et al., 2003), however, only if the fossil bone behaved as a closed system over geologic timescales after the initial early diagenetic REE uptake.

To determine the element mobility during diagenesis, REE and trace element profiles across the cortex of fossil bones, mostly from dinosaurs, were measured with LA-ICP-MS. Altogether 39 bones from different well-characterized and -dated terrestrial and marine diagenetic settings of Permian to Pleistocene age were analyzed. Most of these bones have high REE concentrations at the outer bone rim, gradually decreasing by a factor of 10^1 - 10^3 toward the inner bone. While sub-fossil Pleistocene mammal bones with REE enriched outer rims still have low REE in the central cortex contents similar to fresh bones, Mesozoic dinosaur bones have several orders of magnitude higher REE concentrations. Some of the dinosaur bones even display a flat and homogeneous REE distributions across the bone cortex, probably due to an intense diagenetic alteration or late diagenetic REE diffusion/recrystallisation. This suggests open-system behaviour at least for some bones. Lu-Hf-dating of some of the bones is currently performed to date diagenesis.

Intra-bone REE patterns display an increasing depletion of MREE towards the central bone cortex, likely due to MREE scavenging during intra-bone transport. Y/Ho and Zr/Hf ratios are markedly higher than chondritic ratios. Ratios of Zr/Hf (up to 600) are relatively similar across the bone cortex. In contrast, Y/Ho usually increase from chondritic ratios (28) along the rim to ratios of up to 200 in the center, decreasing again towards the marrow cavity.

Non charge radius controlled behaviour of trace elements, resulting in differing chemical bonding properties, might be responsible for the observed REE and trace element distribution patterns in fossil bones.

References

Barfod, G.H., Otero, O., Albarède, F., 2003. Phosphate Lu-Hf geochronology. *Chemical Geology* 200, 241–253.

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