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Lu–Hf isotope systematics of fossil biogenic apatite and their effects on geochronology

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Abstract

Reliable methods for direct dating of biogenic apatite from pre-Pleistocene fossils are currently not available, and recent attempts using the Lu–Hf decay system yielded highly inaccurate ages for both bones and teeth. The geological processes accounting for this poor accuracy of Lu–Hf chronometry are not yet understood. Here we explore Lu–Hf systematics in fossil bones and teeth in detail, by applying five different sample digestion techniques that are tested on bones and composites of bone and sediment. Our current dataset implies that dissolution methods only slightly affect the resulting Lu–Hf ages, while clear differences between the individual digestion techniques became apparent for element concentrations. By analysing the insoluble leftovers from incomplete sample dissolution, four main 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; 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 Zr(Hf)-phase must have been precipitated within the fossil bone sample at a late stage of burial history, thereby incorporating radiogenic ¹⁷⁶Hf released from apatite surfaces over geological timescales.

A second focus of our study is the effect of different sediment matrices and of crystal size on the preservation of pristine Lu–Hf isotope compositions in bioapatite. Because near-depositional Lu–Hf ages of phosphate fossils have previously been reported for the London Clay (England) and a calcareous marl from Tendaguru (Tanzania), we herein investigate specimens fossilised in carbonate matrices (calcareous marl from Oker, Germany; carbonate concretions from the Santana Formation, Brazil; carbonate from the Eifel, Germany) and argillaceous matrices with low permeability (oil shale of Messel, Germany; Posidonienschiefer of Holzmaden, Germany). Materials analysed from these localities include bones, teeth, conodonts, as well as coproliths and diagenetic minerals (siderite, montgomeryite and messelite). 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. Low ¹⁷⁶Lu/¹⁷⁷Hf ratios in all materials from the Middle Eocene Messel oil shale (e.g., bones, fish scales, sediment, siderite) result in poor age precision and an age that is near-depositional due to this large analytical error. In agreement with previous results, all other ages determined here for both bones and teeth are by far younger than respective chronostratigraphic ages.

A model illustrating the behaviour of Lu and Hf over time, with respect to the fossilisation process is presented, which accounts both for the formation of a late diagenetic radiogenic Zr(Hf) phase and long term open system behaviour. The continuous Lu–Hf element exchange between the fossils and the embedding sediment is probably related to the nm-scale crystal

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