



Non-traditional isotope analysis of fossil bones and teeth – Preservation of biogenic compositions or diagenetic alteration?

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Bones and teeth are valuable geochemical archives of the life history and behaviour, as well as the habitat of extant and extinct vertebrates. The isotope compositions of the skeletal bioapatite records information about the animals diet, (thermo-)physiology and mobility as well as climate and environmental conditions. Isotope analysis of bones and teeth is thus increasingly used in ecological, forensic, anthropological, archaeological and palaeontological studies.

Besides traditional isotope systems ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$, $^{87}\text{Sr}/^{86}\text{Sr}$), non-traditional isotope systems such as $\delta^{44}\text{Ca}$ and Δ_{47} can yield additional information about the diet and thermophysiology of extinct vertebrates, respectively. Before investigating extinct vertebrates and ancient ecosystems, it is important to calibrate these new non-traditional isotope proxies on living vertebrates and well-characterized present-day ecosystems. Furthermore, it is crucial to understand the preservation of these chemical proxies in fossil skeletal remains. Studies in both these areas are currently underway and first results will be discussed.

Calcium isotopes ($\delta^{44}\text{Ca}$) in bones and teeth of living animals can yield information about their diet, and about the trophic level of these organisms within the local food chain. Calcium is the major element in bioapatite and, based upon current understanding, no significant alteration of biogenic appears to take place during diagenesis. Thus, $\delta^{44}\text{Ca}$ values provide a promising new proxy with high preservation potential for reconstructing diet of extinct vertebrates and for delimiting ancient food webs. The Ca isotope fractionation that occurs between diet and skeletal apatite remains comparatively poorly understood, however, and further work in this area is needed. Additionally, the Ca isotope compositions of living species with more varied dietary intake must be characterized to exploit fully the potential of Ca isotopes in evaluating diet of extinct taxa.

Clumped isotope (Δ_{47}) analysis of the ^{13}C - $^{18}\text{O}_{\text{excess}}$ in carbonate-containing enamel bioapatite of living vertebrates with different, known body temperatures yielded an Δ_{47} -temperature calibration that allows determining vertebrate body temperatures with an accuracy of 1-2°C (Eagle et al., 2010). Enamel Δ_{47} values can be preserved over millions of years, in principle, as Δ_{47} analyses of fossil teeth from Pleistocene mammoths as well as a Late Miocene rhinoceros and alligator imply body temperatures within error of those for modern taxa (Eagle et al., 2010). Clumped isotope thermometry is establishing itself as a promising new chemical thermometer for examining the thermophysiology of extinct vertebrates, such as dinosaurs. A note of caution is warranted, however, as the effects of diagenesis on Δ_{47} are not yet fully understood, and will need to be investigated in detail if this new and important tool is to fulfill its initial promise. In the meantime, a multi-proxy approach combining histological (transmitted light microscopy, $\mu\text{-CT}$), mineralogical (XRD, EMPA) and chemical ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, rare earth elements) indicators is recommended to characterize the enamel preservation and screen for diagenetic overprinting.

Rare earth elements (REE) are valuable chemical tracers for inferring the diagenetic conditions, as well as the time and place of fossilisation. Both intra-bone REE concentration profiles and unsuccessful attempts at radiometric Lu-Hf dating of bone provide clear evidence that fossil bones (and even teeth) behave as open systems with respect to REE and Hf over geological timescales of millions of years (Herwartz et al., 2011), rather than thousands of years, as previously been suggested.

Regrettably, the possibility of directly and reliably dating of fossil bone by Lu-Hf methods appears remote based upon current research and case studies. However, for materials that are relatively unaltered during fossilization, non-traditional isotope systems, such as $\delta^{44}\text{Ca}$ and Δ_{47} , are expected to contribute significantly to our understanding of the palaeo-diet and physiology of extinct vertebrates, and thus help to unravel some mysteries in palaeontology not amenable to study by long-established traditional means.

References:

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