

Isotopes in vertebrate bioapatite: proxies for climate, pCO₂ and diet

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Vertebrates integrate bioavailable elements in their skeletal tissues taken up from the environment via air, water and food. Bones and teeth archive isotope signatures of these elements over the timespan of tissue formation and/or remodelling. This enables the reconstruction of diet ($\delta^{13}\text{C}$, $\delta^{44/42}\text{Ca}$), climate ($\delta^{18}\text{O}$), body temperature (Δ_{47}), atmospheric pCO₂ ($\Delta^{17}\text{O}$) and habitat ($\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$) from vertebrate fossils. Bioapatite of fossil hard tissues, especially enamel, can preserve original isotope compositions over geological time scales. The isotopes of the two major elements (Ca, O_(PO₄)) in bioapatite are least biased by diagenetic alteration.

$\delta^{18}\text{O}_{\text{PO}_4}$ of terrestrial and aquatic vertebrates is a proxy for meteoric and ambient water $\delta^{18}\text{O}$ values, respectively. Enamel $\delta^{18}\text{O}_{\text{PO}_4}$ values of fossil large mammals were used to infer the terrestrial palaeoclimate during the last 35 million years for Central Europe. Reconstructed air temperatures agree well with other climate proxy data. The ^{17}O -anomaly ($\Delta^{17}\text{O}$) of air oxygen is a proxy for atmospheric pCO₂. This anomalous $\Delta^{17}\text{O}_{\text{air}}$ is partially recorded in bioapatite $\Delta^{17}\text{O}_{\text{PO}_4}$ of small mammals (<1kg) with a high metabolic rate and thus O₂ consumption. It is preserved in fossil teeth and $\Delta^{17}\text{O}_{\text{PO}_4}$ can be used as a new proxy for palaeo-pCO₂ reconstructions and to monitor diagenetic alteration of bioapatite $\delta^{18}\text{O}_{\text{PO}_4}$ values.

Calcium isotopes ($\delta^{44/42}\text{Ca}$) are a very promising deep time diet proxy for fossil vertebrates with a high preservation potential, even in fossil bones. $\delta^{44/42}\text{Ca}$ values enable us to determine the consumption of plant versus animal tissues and decrease systematically with each trophic level along the foodchain. We found a trophic level effect of $\sim 0.4\text{‰}$ between bones of extant African mammalian herbivores ($-0.46 \pm 0.14\text{‰}$) and carnivores ($-0.89 \pm 0.14\text{‰}$). Ant/termite-feeding mammals ($0.04 \pm 0.16\text{‰}$) have higher $\delta^{44/42}\text{Ca}$ values than both herbivores and carnivores. Whether Ca isotopes are indeed a new geochemical proxy for insectivory is currently being investigated. Using Ca isotopes past diets of extinct vertebrates and fossil food webs can be reconstructed to identify apex predators. T-Rex and sympatric herbivorous dinosaurs display a similar trophic level effect as extant mammals. Preliminary $\delta^{44/42}\text{Ca}$ data for the Eocene terror bird (*Gastornis*) are more in accordance with a herbivorous diet.

Developing speciation codes and thermodynamic data for non-isothermal and non-isobaric systems: applications to CO₂ sequestration

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Geochemical models typically simulate geochemical processes using thermodynamic data sets of equilibrium constants calculated 0.01-300°C along the steam saturation curve. This approach is sufficient for a broad range of geologic conditions, as long as the data has been calibrated against calorimetric, field, and experimental measurements. However, some commonly utilized data and methods result in unacceptable uncertainties. Notably, longstanding inconsistencies in the aluminum mineral and aqueous species data that are included in many thermodynamic datasets have not been sufficiently resolved. Moreover, simulations of key geologic processes, such as geologic CO₂ sequestration and hydrothermal alteration, are challenging due to the limited T-P range of the data sets.

In this contribution, we correct some of these problems by taking account of recent innovations that enable acquisition of formatted datasets at any T and P within the limits of the thermodynamic equations of state [1]. This is only a short-term measure, however, because modern computers permit development of a new generation of speciation codes that dynamically calculate equilibrium constants at the modeled T-P conditions. These codes will be particularly useful in large-scale, non-isothermal, and non-isobaric reactive transport models. To this end, we develop and use an integrated thermodynamic-speciation code that relies only on standard state thermodynamic properties and equation of state parameters to dynamically calculate mineral-brine-CO₂ interactions. The code incorporates a new, calibrated, internally consistent thermodynamic data set for key aluminum minerals and aqueous species as well as literature data for other minerals and aqueous species. Compared with experiments involving a) thermally-driven dolomite dissolution and precipitation and CO₂ exsolution, and b) arkose alteration under elevated T, P, pCO₂ conditions, the data and integrated speciation code perform well and provide a new opportunity to kinetically evaluate whole-rock dissolution and precipitation reactions.

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