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Readdressing the calibration of the 'clumped isotope' paleothermometer for bioapatites

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Bioapatites ($Ca_5(PO_4,CO_3)_3(OH,F)$) form the main constituent of bones, teeth and fish scales. The magnitude of oxygen isotope fractionation between phosphate or structural carbonate inside the bioapatite and body water reflects the body temperature. In this respect, the oxygen isotopic composition of biogenic apatite has often been analyzed to constrain past ocean temperatures as well as body temperatures of extinct vertebrates. The oxygen isotopic composition of the body fluid of the corresponding extinct vertebrates is, however, rarely known, severely limiting the use of the oxygen isotope thermometer.

Recently, a new paleothermometer was introduced that is based on the abundance of ^{13}C-^{18}O bondings within carbonates and its relative deviation from the corresponding stochastic distribution. It, therefore, enables temperature estimations independent of the $\delta^{18}O$ of the parental fluid. Unfortunately, the abundance of ^{13}C-^{18}O bondings cannot be measured directly within the carbonate, but Ghosh et al. (2006) demonstrated that the CO_2 evolving from phosphoric acid digestion of the carbonates still contains information about the originial ^{13}C-^{18}O-clumping (expressed as Δ_{47} value) inside the mineral. Eagle et al. (2010), analyzing modern endo- and ectothermics with body temperatures ranging from 23°C to 37°C, observed that the relationship between $\Delta_{47}$and temperature in bioapatite is indistinguishable from that determined for inorganic calcite by Ghosh et al. (2006). However, it remains to be proven if these calibrations were successfully projected to the absolute reference frame proposed by Dennis et al. (2011), allowing comparison of Δ_{47}values among different laboratories.

Our work focuses on the refinement of the temperature dependency of absolute Δ_{47}valuesfor bioapatite (0-39°C). For this purpose, we analyze the clumped isotopic composition (Δ_{47}) of bioapatites from modern vertebrates with well-known body temperatures, reporting Δ_{47} on the absolute scale of Dennis et al. (2011). Amongst these samples are a tooth from an elephant (37°C), teeth from a crocodile (26-29°C), bones from ostriches (39°C), as well as teeth from a Great White Shark (13-15°C) and from Greenland Sharks (0-2°C). Different bioapatites from these five taxa will be investigated, such as tooth enamel, enameloid and dentin as well as bone tissue. Besides, the effects of different pre-treatment and purification techniques on Δ_{47} values will be investigated.

Preliminary measurements yield consistent Δ_{47} values of around (0.66±0.01)‰ for both enamel and dentin from the same elephant tooth. This value agrees with that predicted for 37°C using the Ghosh-calibration transferred to the absolute reference frame of Dennis et al. (2011). Sample pre-treatment with 3% H_2O_2 for removal of organic matter does not seem to affect Δ_{47} measurements.

References:

Ghosh et al. (2006), GCA 70, 1439-1456

Eagle et al. (2010), PNAS 107, 10377-10382

Dennis et al. (2011), GCA 75, 7117-7131