Clumped isotope thermometry of carbonate-bearing apatites: Digestion techniques and calibrations

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Δ_{47} data [1] indicate that ^{13}C-^{18}O clumping in carbonate groups of bioapatites ($Ca_5(PO_4,CO_3)_3(OH,F)$) may follow the Ghosh calibration [2] of the clumped isotope thermometer established for synthetic calcite. Eagle [3] used this T- Δ_{47} relationship to reconstruct body temperatures of extinct vertebrates such as dinosaurs.

Here we refine a previous calibration for bioapatite and extend the studied temperature range to 2 to 37 °C. The conventional acid digestion technique that is commonly used for clumped isotope analysis of carbonates was modified and the reaction temperature was raised to 110 °C. Beside of this, we investigated the influence of the pre-treatment of sample material on Δ_{47} data. Teeth of a greenland shark, ragged tooth sharks that lived under controlled conditions, crocodiles, an african elephant, and modern humans were analyzed for their clumped isotopic compositions. Distinct Δ_{47} values were determined for dentine and enamel. Finally, the calibration based on enamel seems to exhibit a similar temperature sensitivity like the T-Δ_{47} relationship of Wacker [4].

For calibration under well defined abiotic conditions, carbonate-bearing hydroxyapatite was synthesized at different temperatures (10-60 °C) following two different experimental approaches: (1) Mixing experiments of two different solutions modified after Lécuyer[5], and (2) Recrystallization of calcium carbonate powders in aqueous phosphate/bicarbonate bearing solutions containing different alkali salts. Tentative results indicate that the Δ_{47} values determined using material prepared after the (2) approach at 60°C support the calibration data obtained for the bioapatites, thereby extending the range of the calibration curve. We currently investigate whether A and B type substitution of the carbonate group has an influence on the Δ_{47} values.

[1]Eagle et al. (2010), *PNAS* **107** ; [2]Ghosh et al. (2006), *GCA* **70** ; [3]Eagle et al. (2011), *Science* **333**; [4]Wacker et al. (2014), *GCA* **141**; [5]Lécuyer et al. (2010), *GCA* **74**.