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Clumped isotope thermometry of carbonate-bearing apatite: Revised sample pre-treatment, acid digestion, and temperature calibration

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ABSTRACT

It has recently been shown that the clumped isotopic composition (Δ_{47}) of carbonate-bearing hydroxyapatite (CHAP) from teeth and bones reveals important information about the body temperature of vertebrates (Eagle et al., 2010, 2011). In this study we reinvestigate the temperature dependence of Δ_{47} in CHAP, extending the temperature range from 2 to 59 °C. In addition, the effects of chemical pre-treatment of CHAP on its bulk and clumped isotopic composition are studied.

CHAP is best reacted with phosphoric acid at 90 to 110 °C minimizing the potential of evolved CO_2 or reaction intermediates to re-equilibrate with traces of water in the acid environment. Reaction at 110 °C ensures that digestions of CHAP samples are complete within 60 min. We determined a $\Delta_{47}{}^{*}{}_{90-110}$ value of 0.032 ± 0.008‰ that is - within errors - indistinguishable from a $\Delta_{47}{}^{*}{}_{90-110}$ value of 0.019 ± 0.007‰ received for aragonite.

For tooth enamel pre-treated with H_2O_2 lower Δ_{47} values, and higher $\delta^{18}O$ and $\delta^{13}C$ values were measured than for pre-treated tooth dentine. In addition, similar trends were observed for pre-treated dentine and bone material: higher Δ_{47} values, and lower $\delta^{18}O$ and $\delta^{13}C$ values were determined compared to untreated samples.

A new tentative clumped isotope temperature calibration based on a synthetic apatite, untreated tooth enamel of an African elephant and enameloid from teeth of a Greenland shark is presented using a reaction temperature of 110 °C. It follows the equation:

$\Delta_{47} = 0.0320\,(\pm 0.0022) \times 10^6/T^2 + 0.1977\,(\pm 0.0259)$ (Δ_{47} in‰ and T in K).

The slope of this regression line is identical to those previously obtained from 90 °C digestions of calcite and/or aragonite in several laboratories (e.g., Henkes et al., 2013; Wacker et al., 2014; Defliese and Lohmann, 2015). The Δ_{47} data of untreated enamel(oid) samples reacted at 90 °C closely match a Δ_{47}-$1/T^2$ relationship for calcite that was made at the same digestion temperature (Wacker et al., 2014). These preliminary results suggest that calcite calibrations made at a reaction temperature of 90 °C might be directly applicable to CHAP samples to determine their formation temperatures.

1. Introduction

Carbonate-bearing hydroxyapatite (CHAP) and its fluoride-bearing analogues are of fundamental and applied interest to the (bio)geochemical, paleontological, and medical scientific communities, since they form the major (bio)mineral phase of bones and teeth (Fleet, 2014, and references therein), as well as authigenic phosphate deposits (e.g., McKelvey, 1967; Notholt et al., 1989). The stable isotope composition of the phosphate and carbonate groups of biogenic and abiotic apatite has been determined in several studies to estimate the formation conditions of minerals, in particular the temperature (Longinelli and Nuti, 1973; Kolodny et al., 1983; Longinelli, 1984; Luz and Kolodny, 1985; Karhu and Epstein, 1986; Kolodny and Raab, 1988; Lécuyer et al., 2010, 2013; Picard et al., 1998; Joachimski et al., 2009; Pucéat et al., 2013). Recently, the clumped isotope composition of the structurally bound carbonate group of (bio)apatites came into the focus of interest (Eagle et al., 2010, 2011; Suarez and Passey, 2014; Bradbury et al., 2015; Stolper and Eiler, 2015, 2016). The knowledge of clumped isotope geothermometry of carbonates has increased steadily during the past decade and it is more and more applied to reconstruct paleoenvironmental conditions (e.g., Eiler, 2011 and references therein) and diagenetic settings (e.g., Huntington et al., 2011; Passey and Henkes, 2012; Loyed et al., 2012; Dale et al., 2014). The excess of

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