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 (Δε) 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 Δε 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 CO2 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 Δε of 5 ± 0.008% that is - within errors - indistinguishable from a Δε of 5 ± 0.007% received for aragonite.

For tooth enamel pre-treated with H2O2, lower Δε values, and higher δ18O and δ13C values were measured than for pre-treated tooth dentine. In addition, similar trends were observed for pre-treated dentine and bone material: higher Δε values, and lower δ18O and δ13C 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 enameland from teeth of a Greenland shark is presented using a reaction temperature of 110 °C. It follows the equation:

Δε = 0.0320 ± 0.0022 × 10^6/T^2 + 0.1977 ± 0.00259 (Δε in % and T in K).

This 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; Deflise and Lohmann, 2015). The Δε data of untreated enamel (ch) samples reacted at 90 °C closely match a Δε-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.

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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 isotopic 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; Koldony et al., 1983; Longinelli, 1984; Luz and Koldony, 1985; Karkus and Epstein, 1986; Kolodny and Raab, 1988; Lécuyer et al., 2010, 2013; Picard et al., 1998; Joachimski et al., 2009; Pučkat 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; Passsey and Henkes, 2012; Loyed et al., 2012; Dale et al., 2014). The excess of