



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 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 $\Delta_{47}^{*90-110}$ value of $0.032 \pm 0.008\%$ that is - within errors - indistinguishable from a $\Delta_{47}^{*90-110}$ value of $0.019 \pm 0.007\%$ received for aragonite.

For tooth enamel pre-treated with H₂O₂ lower Δ_{47} values, and higher $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ 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 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ 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:

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

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 $\Delta_{47}-1/T^2$ 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.

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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 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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multiple substituted carbonate isotopologues (CO_3^{2-} groups containing more than one heavy isotope, e.g., $^{13}\text{C}^{16}\text{O}_2^{18}\text{O}$) relative to their stochastically predicted abundance is controlled by temperature (Schauble et al., 2006). Its measure is the Δ_{47} value (Eiler and Schauble, 2004) that is determined on the CO_2 gas liberated from carbonates via phosphoric acid digestion (Ghosh et al., 2006). Ideally, the Δ_{47} value preserves information about crystal growth temperature and is, therefore, an important tool for paleothermometric investigations (e.g., Ghosh et al., 2006; Schauble et al., 2006; Guo et al., 2009; Dennis and Schrag, 2010; Wacker et al., 2014; Defliese and Lohmann, 2015). In addition, the combination of the new temperature proxy with the classical $\delta^{18}\text{O}$ paleothermometer allows for an estimate of the oxygen isotope composition of the aqueous mineral-forming solution (e.g., Eiler, 2011 and references therein).

In most studies clumped isotope analysis has been applied to carbonate minerals in which the CO_3^{2-} group is the main anion such as calcite, aragonite and dolomite (see Eiler, 2007, 2011 and references therein). However, in their pioneering study Eagle et al. (2010) showed that reproducible Δ_{47} values can also be obtained from structurally bound carbonate in bioapatites, even though their carbonate content is typically substantially lower than 10 wt.% (Fleet, 2014). Stable carbon and oxygen isotope compositions of carbonate in fossil teeth and bones are widely used for studying paleodiets and (thermo-)physiologies of mammals and for paleoenvironmental reconstructions (e.g., Kohn and Cerling, 2002 and references therein). Clumped isotope thermometry of CHAP provides further insight into the thermophysiology of extinct animals such as dinosaurs (Eagle et al., 2011), into the chemical preservation of fossil samples (Eagle et al., 2011; Suarez and Passey, 2014), and into the formation of CHAP during diagenesis. Authigenic apatites permit the investigation of growth conditions of phosphatic hardgrounds (Bradbury et al., 2015) and allow detailed reconstructions of the thermal histories of rocks (Stolper and Eiler, 2015, 2016).

Eagle et al. (2010) found that bioapatite Δ_{47} data of teeth from modern mammals, reptiles and fish shared a relationship with temperature indistinguishable from that obtained in the first study on synthetic calcites (Ghosh et al., 2006). Published clumped isotope temperatures of carbonate-bearing apatites were, therefore, mostly based on the calibration of Ghosh et al. (2006) (Eagle et al., 2010, 2011; Suarez and Passey, 2014). Exceptions to this are the estimated temperatures reported by Bradbury et al. (2015) who applied a relationship between Δ_{47} values and $1/T^2$ published by Passey and Henkes (2012) to their results.

In the present study, we re-investigated the acid digestion technique of carbonate-bearing apatites for clumped isotope analysis. We have modified the commonly applied extraction of CO_2 from phosphoric acid. Furthermore, we propose to digest apatites at 110 °C instead of 90 and 25 °C. This reduces the reaction time of the apatite powder to <60 min at 110 °C using a reaction vessel of 9 cm diameter. In addition, effects on the bulk and clumped isotope compositions of tooth enamel and dentine of an elephant, as well as bone material of an ostrich were investigated after subjecting them to a chemical cleaning recommended by Eagle et al. (2010). While the cleaning procedure did not affect the clumped and bulk oxygen and carbon isotope composition of enamel, higher Δ_{47} values, and lower $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values were determined for pre-treated dentine and bone material. For un-/pre-treated enamel and untreated dentine similar Δ_{47} values were received. We combined the low and intermediate temperature results from untreated tooth enamel(oid) of a Greenland shark and of an elephant, respectively, with Δ_{47} data of synthetic apatite prepared at 59 °C to derive a tentative revised and extended calibration for the apatite clumped isotope thermometer in the range between 2 and 59 °C.

2. Materials

We sampled an upper, left molar of an African elephant (*Loxodonta africana*, body temperature 37 ± 1 °C, Table 1). The enamel of this tooth is composed of tightly arranged hydroxyapatite crystals with a

low organic and water content (<1 wt.% and <3 wt.%, respectively; Kohn and Cerling, 2002; Boskey, 2007). In contrast to enamel, porous dentine is characterized by plate-like nanometer-sized crystals which are finer and characterized by a higher content of organic matter and water than those of enamel (20–30 wt.% and 10 wt.%, respectively; Pasteris et al., 2008). Mechanical separation of enamel and dentine was carried out with a drill, a hammer and a chisel. Afterwards fragments of the two phases were pulverized and homogenized in an agate vibratory disc mill and dried at 50 °C for 2 days. The enamel powder used in our study is an aliquot of the standard AG-LOX (Gehler et al., 2012).

Additionally, tooth enameloid of a Greenland shark (*Somniosus microcephalus*) was sampled (Table 1). These cold-water sharks live in the North Atlantic Ocean and near the coasts of Canada, Greenland and Iceland at depths of 0 to 2200 m (Herdendorf and Berra, 1995). Little is known about migration paths and further physiological and behavioural features of these sharks. Stokesbury et al. (2005) assume that they choose their swimming depth according to the ambient water temperature. Logger data implies that specimen larger than 2.5 m live in depth ranging from 30 to 300 m at which the water temperatures are -1.2 and 3.4 °C (Watanabe et al., 2012). Sharks are ectothermic with their mouth being permanently exposed to water, growth temperatures of the teeth are considered to represent ambient water temperatures (Watanabe et al., 2012). We have estimated the ambient water temperature of the *S. microcephalus* analyzed in this study from $\delta^{18}\text{O}_{\text{PO}_4}$ of its dental tissues. Enameloid of 100 teeth from four tooth rows of the jaw was pooled in two bulk samples. The enameloid was converted to Ag_3PO_4 using the rapid precipitation protocol (Tütken et al., 2006). Triplicate $\delta^{18}\text{O}_{\text{PO}_4}$ measurements of the Ag_3PO_4 were made using a Finnigan TC-EA at the Johannes Gutenberg-University (Mainz) with a precision of 0.3‰. Raw $\delta^{18}\text{O}_{\text{PO}_4}$ values were normalized to an Ag_3PO_4 standard produced by Elemental Microanalysis (silver phosphate P/N IVA33802207, batch nr. 180,097) with a certified value of 21.7‰ relative to the V-SMOW reference scale. To calculate water temperatures from the $\delta^{18}\text{O}_{\text{PO}_4}$ we used the phosphate-water oxygen isotope fractionation equation of Longinelli and Nuti (1973) assuming a $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of -0.25 ‰ (VSMOW, Schmidt et al., 1999) for the deeper waters between Greenland and Iceland. This yields a biomineralization temperature for the enameloid of -0.4 ± 1.3 °C ($\delta^{18}\text{O}_{\text{PO}_4} = 25.74 \pm 0.32$ ‰ (VSMOW); $n = 3$), which is indistinguishable from the temperature for a mixture of enameloid and dentine 1.5 ± 1.2 °C ($\delta^{18}\text{O}_{\text{PO}_4} = 25.32 \pm 0.29$ ‰ (VSMOW); $n = 3$). Similar, ~ 1 °C warmer water temperatures of 0.4 and 2.4 °C are calculated using the equation from Lécuyer et al. (2013). However, the phosphate-water fractionation equation of Pucéat et al. (2013), accounting for the normalization of our data to NIST SRM 120c value of 21.7‰, yields about ~ 5.5 °C higher water temperatures of 5.2 and 7.0 °C, respectively. A discussion of the reasons for this discrepancy between the different phosphate-water oxygen isotope temperature calibrations is beyond the scope of this study (see Longinelli, 2013; Pucéat et al., 2013; Lécuyer et al., 2013 for details). It is clear that the latter temperatures are not realistic for the water masses in which the Greenland shark lived. In contrast, both temperatures calculated with either the equations of Longinelli and Nuti (1973) or Lécuyer et al. (2013) match the temperature range reported by Watanabe et al. (2012). We, therefore, assume a mean growth temperature of 1 ± 2 °C for the Greenland shark (Table 1).

Although the enameloid of sharks consists mainly of fluorapatite, it also contains small amounts of hydroxyapatite and carbonate ions in solid-solution (Vennemann et al., 2001; Enax et al., 2012). Shark teeth are formed continuously throughout the entire lifespan of the animal. The Greenland shark has several rows of teeth with different shapes in the upper and lower jaw. The replacement of rows of single teeth takes place within days to weeks (Berkovitz, 2000; Botella et al., 2009). The teeth used in this study were taken from the jaw of a specimen (size >4 m) that was caught in 2012 in the Arctic waters surrounding Iceland. Teeth were removed from the tissue of the upper and lower

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