



A revised calibration of the clumped isotope thermometer



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ABSTRACT

A growing number of materials and environmental settings are studied using the carbonate clumped isotope (Δ_{47}) thermometer. The method has been applied in both biogenic and non-biogenic carbonate systems, in marine and terrestrial settings, over a wide range of geological timescales. The current Δ_{47} temperature calibration gives good temperature estimates for most biogenic materials, however, systematic biases are commonly observed at low temperatures.

In this study we report additional calibration data, that covers a wider temperature range, at more evenly distributed temperatures, and are measured at higher analytical precision than the original calibration. Combining these data with the original calibration yields a Δ_{47} - T relationship that is similar to the original calibration, though slightly less steep: $\Delta_{47} = (0.0526 \pm 0.0025) \times 10^6/T^2 + (0.0520 \pm 0.0284)$. This revised calibration is in better agreement with biogenic carbonates, including those grown at low temperatures. The difference between the original and revised calibrations is significant for carbonates forming below 16°C or above 49°C (Δ_{47} values of 0.68‰ and 0.56‰). Additionally, we include a comprehensive analysis of the sources of error associated with Δ_{47} measurements and estimated temperatures and recommend measurement strategies for obtaining the desired precision.

As an illustration, we apply the revised calibration and uncertainty analysis to 3 previously published studies. At low temperatures, the revised calibration results in significant differences from the original calibration and hence affects the interpretation of the environmental signal recorded. In light of our Δ_{47} errors analysis, in cases where the temperature signals are small, we find that replicate analyses are critical to identify a temperature signal.

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1. Introduction

Carbonate clumped isotope thermometry is a new proxy for estimating paleotemperatures. This technique is based on the natural abundance of ^{13}C - ^{18}O bonds in the carbonate lattice, relative to that expected for a random distribution of isotopes among all isotopologues, quantified by the parameter Δ_{47} (Affek, 2012; Eiler, 2007; Wang et al., 2004). As such, the thermometer is based on the thermodynamically controlled preference of two heavy isotopes to bind with each other, and it is independent of the absolute abundance of ^{13}C and ^{18}O in the carbonate mineral. Carbonate clumped isotope thermometry is therefore a powerful approach for determining the growth temperature of CaCO_3 minerals.

Ghosh et al. (2006a) were the first to present a calibration of the Δ_{47} - T CaCO_3 relationship. Their calibration is based on Δ_{47} measurements of 7 calcite samples that were formed by slow laboratory precipitation at controlled temperatures between 1°C and 50°C. This experimental approach followed the method used by Kim and O'Neil (1997) for defining the $\delta^{18}\text{O}$ - T relation-

ship in calcite. Biogenic carbonate materials, particularly of marine organisms, grown at known temperatures, generally agree with the Ghosh et al. (2006a) calibration (as reviewed by Eiler, 2007, 2011 and Tripati et al., 2010). Other studies, however, have shown disagreement with that calibration in both synthetic materials (Dennis and Schrag, 2010) and biogenic materials (Eagle et al., 2013; Henkes et al., 2013; Saenger et al., 2012). The source of these discrepancies is still unresolved.

The Ghosh et al. (2006a) calibration is based on analyses that were done in the early days of clumped isotope measurements. Since its publication, the importance of long acquisition times and replicate analysis had been recognized as essential for the precision required for the measurement of the low abundance $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ isotopologue (46 ppm of all CO_2 molecules; Eiler and Schauble, 2004).

In this study, we examine the sources of errors in clumped isotope measurements to improve the estimate of uncertainties for the derived temperatures. We then re-examine the clumped isotope thermometer calibration by independently repeating the carbonate precipitation experiments using the same method as Ghosh et al. (2006a). Our samples span a larger temperature range and are measured in triplicates; thus they have higher analytical

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precision. We further examine our findings to suggest an optimized protocol for lower sample uncertainties.

Our Δ_{47} - T relationship is similar to the original calibration but has a slightly lower slope and a better agreement with low temperature biogenic carbonates. The agreement of the biogenic carbonates with the revised calibration line strengthens and validates the applicability of the Δ_{47} thermometer. It further implies that this method of precipitation, even if not reflecting true equilibrium, is relevant for most biogenic carbonates that form between 0 °C and 40 °C.

2. Materials and methods

2.1. CaCO_3 precipitation experiments

We follow the precipitation method and setup described by Kim and O'Neil (1997) for $\delta^{18}\text{O}$ and that was used by Ghosh et al. (2006a) in the first carbonate clumped isotopes thermometer calibration. Saturated $\text{Ca}(\text{HCO}_3)_2$ solutions were prepared by bubbling 100% CO_2 for ~1 h through 1 L of deionized water. Reagent grade CaCO_3 (Mallinckrodt Chemical Works) was added to the solution while CO_2 bubbling continued for another hour, to increase carbonate solubility. The solution was then filtered (Whatman #40, 8 μm , filter paper) to remove non-dissolved calcium carbonate particles. Slow bubbling of humidified $\text{N}_{2(\text{g})}$ (roughly 20 bubbles per 30 seconds) deep in the solution was used to remove CO_2 and induce calcium carbonate precipitation. The humidity of the $\text{N}_{2(\text{g})}$ flow was adjusted to saturation at the experiment temperature in order to minimize water evaporation and enable reliable $\delta^{18}\text{O}$ measurements in addition to Δ_{47} . This precipitation method resulted in CaCO_3 formation deep within the solution. Samples were precipitated at 5, 8, 15, 25, 35, 50 and 65 °C, in a temperature controlled reactor (New Brunswick Scientific, Excella E24 incubator shaker series), which has an observed precision of $\sim\pm 0.5$ °C. The precipitation continued between 4 days and a few weeks, depending on the precipitation temperature, and was stopped when sufficient CaCO_3 accumulated for analysis. The precipitated CaCO_3 was collected using a rubber policeman, filtered through a glass microfiber filter (Whatman 934-AH, 0.3 μm), and dried under vacuum at room temperature. Mineralogy was determined by x-ray diffraction (in the XRD laboratory at Yale University).

2.2. Isotopic analysis

CaCO_3 (3–4 mg) was digested overnight in 105% H_3PO_4 ($\rho = 1.95 \text{ gr/cm}^3$) at 25 °C. CO_2 was extracted cryogenically on a vacuum line and cleaned by passing it through a GC column (Supelco Q-Plot, 30 m \times 0.53 mm) at -20 °C (following Affek and Eiler, 2006; Huntington et al., 2009; and Zaarur et al., 2011). Measurements were performed using a Thermo MAT253 gas source isotope ratio mass spectrometer (in the Earth Systems Center for Stable Isotopic Studies at Yale University), modified to simultaneously measure masses 44–49 in a dual inlet mode. Each measurement consisted of 90 cycles of sample-standard comparison, with a signal integration time of 20 s for each measurement. Samples were measured in triplicates, repeating the whole extraction procedure on separate aliquots of the powdered CaCO_3 .

Δ_{47} is defined as the excess of the mass 47 signal in CO_2 over what is expected based on random distribution of ^{13}C and ^{18}O among all CO_2 isotopologues (Eiler, 2007; Wang et al., 2004). Standardization is hence performed using a set of CO_2 gases that are heated at 1000 °C for ~2 h to obtain random distribution (Huntington et al., 2009; Wang et al., 2004). To compare our data to previous studies, we report our values standardized to the original reference frame (used by Ghosh et al., 2006a). Our system is normalized and traceable to that original reference frame by the

measurements of several carbonates with Δ_{47} values that were pre-determined in that original system; this normalization was later verified by inter-laboratory comparison as part of the development of the absolute reference frame (Dennis et al., 2011). To allow future inter-laboratory use of the calibration, we provide the data also in the absolute reference frame (Dennis et al., 2011, Section 4.2.5). Unless otherwise noted, values are reported in the original reference frame (Ghosh et al., 2006a). We refer the interested reader to Supplement SI1 for more details about the measurements and associated reference frames.

Both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, measured together with the Δ_{47} , are reported using the VPDB reference frame as defined by a pre-calibrated Oztech CO_2 tank used as a reference working gas with values of -15.80‰ and -3.64‰ for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, respectively. These values are verified using NBS-19 with measured $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of -2.17 ± 0.04 ‰ and $+2.11 \pm 0.13$ ‰ (1 SD, $n = 12$), respectively (Kluge and Affek, 2012), which are comparable to the IAEA nominal values of -2.2‰ and +1.95‰. Oxygen isotopic fractionation factors associated with the acid digestion reaction at 25 °C are $^{18}\alpha_{\text{acid}} = 1.01030$ and 1.01063 for calcite and aragonite, respectively (Kim et al., 2007a, 2007b). The temperature dependence of calcite-water oxygen isotopic fractionation ($^{18}\alpha_{\text{calcite-water}}$) is compared to the temperature dependence relationships derived by Friedman and O'Neil (1977) and by Kim and O'Neil (1997), modified to account for the above acid digestion fractionation (Eqs. (1), (2), respectively). The aragonite-water oxygen isotope fractionation is compared to Kim et al. (2007b) (Eq. (3)):

$$1000 \ln \alpha_{(\text{calcite-water})} = 2.78(10^6 T^{-2}) - 2.89 \quad (1)$$

$$1000 \ln \alpha_{(\text{calcite-water})} = 18.03(10^3 T^{-1}) - 32.17 \quad (2)$$

$$1000 \ln \alpha_{(\text{aragonite-water})} = 17.88(10^3 T^{-1}) - 31.14 \quad (3)$$

3. Results

3.1. Synthetic carbonate precipitation

Δ_{47} values range between 0.741‰ and 0.513‰ for precipitation temperatures of 5 °C to 65 °C, respectively (Table 1). Depending on precipitation temperatures, first particles were observed within 1 to 5 days for high and low temperatures, respectively. As was observed in other precipitation experiments (e.g. Wray and Daniels, 1957; Zhou and Zheng, 2001), our precipitated carbonates are mixed polymorphs. Most samples are predominantly calcite with traces of aragonite and vaterite, but one sample (carb #37, precipitated at $T = 50$ °C) is a mixture of calcite and aragonite and another (carb #43, precipitated at $T = 65$ °C) is primarily aragonite. Note that although Ghosh et al. (2006a) reports the original calibration samples to be calcite, renewed inspection of the XRD spectra of these samples reveals traces of aragonite as well.

A positive correlation is observed between Δ_{47} and $\delta^{18}\text{O}$ values. This correlation is likely due to the temperature dependence of both isotopic systems and not to a kinetic affect. It strengthens the assumption of precipitation close to isotopic equilibrium in both systems. The fractionation derived from carbonate and water $\delta^{18}\text{O}$ values approximately agrees with the temperature dependence defined by Kim and O'Neil (1997) and Friedman and O'Neil (1977) for calcite and by Kim et al. (2007b) for aragonite (Fig. 1).

3.2. Long and short term standard measurements

Δ_{47} measurements are influenced by two independent sources of error, Poisson-distributed shot noise and additional non-Poisson errors (see Eq. (21) in SI2). Internal precision is the combination

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