Clumped isotope temperature calibration for calcite: Bridging theory and experimentation

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Abstract

Clumped isotopes (Δ_{47}) analysis in carbonates is becoming widespread across the geochemical community as a geothermometer that also allows for the reconstruction of the precipitating fluid $\delta^{18}\text{O}$ composition. While initial Δ_{47} –temperature relationship discrepancies between laboratories have been considerably reduced over the past 10 years, theoretical temperature calibration and laboratory experimental efforts have still not converged to common ground. Moreover, a lack of high temperature anchor points has weakened its application to high temperature calcite formation. Here we present a temperature calibration for carbonate clumped isotopes between 5 and 726 °C, using synthetically precipitated and heated calcites, to extend the calcite Δ_{47} –temperature calibration to higher temperatures. By showing a strong agreement between the empirical calibration proposed here, theoretical and all recently published T-calibrations made using a full carbonate referencing scheme, this study: (1) provides a calibration allowing more precise application in high temperature geological systems, (2) further supports the improvement of inter-laboratory comparison by using carbonate standards, (3) reconciles empirical temperature calibrations with theory.

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Introduction

Clumped isotope measurements on CO_2 extracted through acidification of carbonates has evolved over the past 15 years as a tool to probe directly the temperature (T) and the parent fluid oxygen isotope composition ($\delta^{18}\text{O}$) of precipitates (Schauble *et al.*, 2006). This is done by analysing the excess abundance of ^{13}C – ^{18}O bonds in the crystal lattice relative to a stochastic distribution (Δ_{47}). This measurement has a direct link to the formation temperature of the carbonate crystal (Schauble *et al.*, 2006) and, therefore, avoids needing to making potentially incorrect assumptions on the isotopic composition of the precipitating fluid as necessary when using the carbonate–water $\delta^{18}\text{O}$ geothermometer (Urey, 1947). The pioneering work of Ghosh *et al.* (2006) reported the first experimental calibration of the Δ_{47} –T relationship between 1 and 50 °C. The use of *ab initio* thermodynamic models (Schauble *et al.*, 2006; Guo *et al.*, 2009) allowed the calculation of the ^{13}C – ^{18}O bond ordering in the carbonate crystal lattice as a function of formation temperature, theoretically grounding this geothermometer.

Since its inception, this Δ_{47} –T calibration has been reproduced in different laboratories by measuring both natural (e.g., Kele *et al.*, 2015; Breitenbach *et al.*, 2018; Peral *et al.*, 2018;

Daëron *et al.*, 2019) and synthetic (e.g., Dennis and Schrag, 2010; Passey and Henkes, 2012; Defliese *et al.*, 2015; Kluge *et al.*, 2015) calcites. Improvements of the T-calibration have been based on refining the preparation and analytical techniques (e.g., sample preparation automatization, sample size reduction), establishing an absolute scale (carbon dioxide equilibrium scale at 25 °C acid digestion temperature; CDES25°C; Dennis *et al.*, 2011), increasing the number of replicates *per* anchor points, and abating the analytical artefacts inherent to clumped isotopic measurements. While these advances have considerably reduced the differences observed between the T-calibrations produced in independent laboratories, significant differences still remain. More recently, the clumped isotope community has put effort into understanding the causes of the remaining inter-laboratory differences. Practitioners have also promoted the principle of similar treatment for standards and unknown samples as a mean of improving inter-laboratory comparisons (Bernasconi *et al.*, 2018). However, a lack of temperature calibration points above 100 °C and large differences at higher temperatures persist, weakening the application of this thermometer to high temperature geological systems. More importantly, none of the published T-calibrations can reconcile theory and experimentation and the non-linearity of the theoretical Δ_{47} –T

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Figure 1 Δ_{47} - T linear relationships in the CDES25°C for the empirical and theoretical calibrations (see text for details). Lines represent the regression models based on all replicates, and shaded envelopes show their 95 % confidence intervals (CI). For more information on the reprocessing of these different datasets see [Supplementary Information S-6](#).

mathematical relationship (Guo *et al.*, 2009) also observed experimentally for dolomite (Müller *et al.*, 2019) has not been reproduced empirically at high temperatures for calcite (Fig. 1).

Apart from the challenges inherent to comparing T -calibrations directly based upon different standardisation strategies, the differences (*i.e.* slope p values $<1 \times 10^{-4}$ and intercept p values $<1 \times 10^{-4}$; [Supplementary Information S-1, Table S-1](#)) observed between the latest composite (Petersen *et al.*, 2019), the fully carbonate-based standardised (Kele *et al.*, 2015) recalculated by Bernasconi *et al.* (2018), and the theoretical T -calibrations (Guo *et al.*, 2009) could be due to the strong influence of the high temperature calcite calibration points (Passey and Henkes, 2012; Kluge *et al.*, 2015) used in the data compilation effort of Petersen *et al.* (2019) (Fig. 1). Some additional effects might have influenced the high temperature precipitates from Kluge *et al.* (2015) ([Supplementary Information S-2, Fig. S-1](#)) and the re-ordering experiments in Passey and Henkes (2012) (*e.g.*, incomplete solid state re-ordering), potentially influencing the slope of this composite Δ_{47} - T relationship (Petersen *et al.*, 2019).

This study attempts to bridge the gap between the fully stochastic isotope distribution reached at high temperature and the large number of low to medium temperature points produced since the onset of this new geochemical tool. We choose to work solely on calcites to avoid potential biases due to specific acid fractionation factors (AFF) when using different carbonates (*i.e.* aragonite, dolomite, siderite) as theoretically predicted (Guo *et al.*, 2009) and shown by recent experimental

work (Müller *et al.*, 2017a; van Dijk *et al.*, 2019) at the temperature of acid digestion used in this study (70 °C). We also took advantage of the growing number of laboratories that adopted a fully carbonate-based standardisation of Δ_{47} measurements – identical to the treatment used here – to evaluate further the improvement brought by this standardisation scheme to inter-laboratory comparison.

Methodology

Synthetic precipitates. Precipitation of synthetic calcites was performed using high pressure and temperature reaction cells (70–250 °C) and passive diffusion techniques (5–70 °C) ([Supplementary Information S-3, S-4, Table S-2, Fig. S-2](#)) (Dennis and Schrag, 2010; Defliese *et al.*, 2015). Briefly, solutions of NaHCO_3 and CaCl_2 were equilibrated separately at the target temperature for 24 to 144 hr prior to mixing. The solutions were then left to precipitate for at least 24 hr. We carried out near-equilibrium precipitation by keeping the calcite saturation index below 2.5 and verifying the $\delta^{18}\text{O}$ values of the precipitates relative to the $\delta^{18}\text{O}$ of the water used (−10.9 ‰; see [Fig. S-1, Table S-2, Supplementary Information S-2, S-3](#)). The production of the heated calcite (*i.e.* CM γ -5; 726 °C) is described in Schmid and Bernasconi (2010).

Measurements. Synthetic precipitates were analysed at the Delta-lab (Geological Survey of Canada) using a MAT 253 (Thermo Scientific, Bremen, Germany) equipped with six shielded faraday cups ($m/z = 44$ –49) and an additional half-mass

detector at $m/z = 47.5$ for live background monitoring. The preparation of carbonate was performed with a KIEL-IV carbonate device (Thermo Scientific, Bremen, Germany) modified according to Schmid and Bernasconi (2010). The sample is first acidified for 500 s with 3 drops of 104 % phosphoric acid prepared following the method of Burman *et al.* (2005). Evolved CO_2 and H_2O are trapped continuously at liquid N_2 (LN_2) temperature followed by a 60 s of non-condensable gas pumping. The CO_2 is then released at -100°C and cryopumped through a Porapak trap surrounded by Ag wool held at -14°C into a micro-volume at LN_2 temperature. The purified CO_2 is then released into the ion source of the mass spectrometer through an inert capillary. $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and δ_{47} data were acquired simultaneously using the long integration dual inlet (LIDI) method (Müller *et al.*, 2017b).

Each measurement comprises 70 cycles of 10 s integrations of the unknown gas followed by a similar integration strategy of the working gas ($\delta^{13}\text{C}_{\text{VPDB}} = -4.5\text{‰}$, $\delta^{18}\text{O}_{\text{VPDB}} = -14.05\text{‰}$). Each synthetic calcite measurement was replicated at least 20 times (80–100 μg aliquots) in order to achieve good precision for the evaluation of the Δ_{47} -T relationship. Error estimation is reported as 95 % confidence interval (CI) of all replicates.

Data processing. Raw beam intensities were imported into Easotope (John and Bowen, 2016) for calculation of the Δ_{47} . The IUPAC parameter set (Brand *et al.*, 2010) was used to correct for ^{17}O interferences (Daëron *et al.*, 2016; Schauer *et al.*, 2016). We adopted a fully carbonate-based calibration scheme by interspersing 50 % of carbonate standards developed at

ETH-Zurich (Meckler *et al.*, 2014) in every analytical session, and by keeping similar average sample and standard sizes. The recalculated values (IUPAC parameter) of the different standards (ETH1–4) were used (Bernasconi *et al.*, 2018) with an external long term standard deviation of 37 ppm. ETH-1 and ETH-2 were used to correct for non-linearity effects in the ion source, ETH-1, 2 and 3 aided with constructing the empirical transfer function (ETF) for translation of the measurements to the CDES, and ETH-4 was treated as an unknown for data acquisition and processing monitoring. The calibration was made on a running window of 56 standards before and after each unknown to correct for drift in ion source stability. Minor negative background correction was performed using the pressure baseline correction (Bernasconi *et al.*, 2013) after every 46 replicates using high voltage scans made from 5 to 25 V intensities ($m/z = 44$), in 5 V increments, to produce a correction function that can be applied to the decaying beam intensity inherent to the LIDI method of measurement. Discussion on the effect of linearities on the ETH carbonate standardisation scheme can be found in the Supplementary Information S-5.

Results and Discussion

Following the mentioned methodologies, we produced a linear T- Δ_{47} calibration over the temperature range of 5 to 250°C (Fig. 2).

To evaluate the efficiency of the ETH carbonate standardisation scheme in improving inter-laboratory comparisons, we compiled the T-calibrations from this study and recently

Figure 2 Δ_{47} -T linear relationship in the CDES70°C for the studies fully referenced to ETH carbonate standards; lines represent each study's linear models, with shaded envelopes representing their respective 95 % CI. For more information on the reprocessing of the different datasets, see Supplementary Information S-6.

published Δ_{47} -T relationships standardised with ETH carbonates (Bernasconi *et al.*, 2018; Breitenbach *et al.*, 2018; Peral *et al.*, 2018; Daëron *et al.*, 2019; Piasecki *et al.*, 2019; Meinicke *et al.*, 2020; Fig. 2) in the CDES70°C. This approach avoids the potential propagation of errors due to the use of somewhat loosely constrained AFF conversions. An analysis of covariance on the different slopes and y intercepts of the Δ_{47} -T relationships reveals strong similarities at the 95 % CI (*i.e.* slope and y intercept *p* values > 0.05; Table S-3). This exercise confirms that the proposition to use a fully carbonate-based calibration scheme (Bernasconi *et al.*, 2018) improves the comparison of data measured in different laboratories with various treatment, analytical methods and different types of calcite formation while avoiding the effects of the uncertainty in the AFF. Hence, this supports producing the following composite linear Δ_{47} -T relationship with T in K (Fig. 2).

$$\Delta_{47}(\text{CDES70}^\circ\text{C}) = 0.0435(\pm 0.0004) \times \frac{10^6}{T^2} + 0.118(\pm 0.0042)$$

We additionally plotted the composite calibration from Petersen *et al.* (2019) for qualitative comparison (Fig. 2). While partially overlapping within the 95 % CI error estimates of the low temperature calcite precipitates synthesised in this study, differences in Δ_{47} of up to 50 ppm are observed between the two calibrations at temperatures above 90 °C. These discrepancies at *ca.* 200 °C translate into temperature estimates differences of around 50 °C, which can influence the interpretation of high

temperature systems when using the clumped isotope geothermometer.

In an attempt to investigate the theoretical non-linear nature of the Δ_{47} -T relationship, we expanded the studied temperature range to the equivalent stochastic ^{13}C - ^{18}O bonds distribution by adding measurements of the heated calcite CM γ -5 (726 °C) (Schmid and Bernasconi, 2010) and the data for the three stochastic calcites (1000 °C) reported in Müller *et al.* (2017) (Fig. 3, Supplementary Information S-6).

The polynomial relationship from Guo *et al.* (2009) is projected into the CDES70°C frame by replacing the Δ_{47-63}^* (= 0.268 ‰ for a 25 °C acid digestion) with a 70 °C Δ_{47-63}^* (= 0.184 ‰) determined experimentally by Müller *et al.* (2017b) and updated to the IUPAC parameters (Supplementary Information S-6, S-7). While the theoretical Δ_{47} -T polynomial relationship (Guo *et al.*, 2009) fits relatively well with our empirical calibration curve at high temperature (*i.e.* within the 95 % CI), our curve lies above the theoretical line and outside the 95 % CI at low temperature. When we modify the theoretical curve by integrating the dependency of the Δ_{47-63}^* to the Δ_{63} of the reactant carbonates (Guo *et al.*, 2009), a significant fit between the two polynomial curves is observed (*i.e.* *p* value = 0.96; Supplementary Information S-1), reconciling the experimentation with theory at the 95 % CI over the full temperature spectrum (Fig. 3). This, in addition to the significant similarities of all Δ_{47} -T linear relationships (Fig. 2), further supports using the carbonate standardisation scheme for inter-laboratory

Figure 3 Δ_{47} -T third-order polynomial relationship (CDES70°C) for this study, the theoretical, thermodynamic based relationship in Guo *et al.* (2009) and a modified version of this equation taking into account the dependence of the Δ_{47-63}^* on the reactant Δ_{63} (35 ppm increase in Δ_{47-63}^* per 1 ‰ increase in Δ_{63}). ETH1 and 2 (*i.e.* 600 °C) are illustrated for visual comparison but are not included in the regression model.

comparisons (Bernasconi *et al.*, 2018; Peral *et al.*, 2018; Meinicke *et al.*, 2020). Moreover, this study provides an empirical T-calibration agreeing with theory over the broadest temperature range to date. This new T-calibration, which can be applied by any laboratory using a carbonate-based standardisation of their measurements on calcite, may also serve for investigating geological contexts of calcite formation at high temperature.

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Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article2021>.

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