Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 197 (2017) 104–131

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

# Toward a universal carbonate clumped isotope calibration: Diverse synthesis and preparatory methods suggest a single temperature relationship

Julia R. Kelson [a,*], Katharine W. Huntington [a,*], Andrew J. Schauer [a], Casey Saenger [a,b], Alex R. Lechler [c]

[a] *Department of Earth and Space Sciences, University of Washington, 4000 15th Ave NE, Seattle, WA 98195, USA*
[b] *Joint Institute for the Study of the Atmosphere and Ocean, University of Washington, 3737 Brooklyn Ave NE, Seattle, WA 98105, USA*
[c] *Department of Geosciences, Pacific Lutheran University, Rieke Room 158, Tacoma, WA 98447, USA*

Received 22 April 2016; accepted in revised form 16 October 2016; Available online 21 October 2016

## Abstract

Carbonate clumped isotope ($\Delta_{47}$) thermometry has been applied to a wide range of problems in earth, ocean and biological sciences over the last decade, but is still plagued by discrepancies among empirical calibrations that show a range of $\Delta_{47}$-temperature sensitivities. The most commonly suggested causes of these discrepancies are the method of mineral precipitation and analytical differences, including the temperature of phosphoric acid used to digest carbonates. However, these mechanisms have yet to be tested in a consistent analytical setting, which makes it difficult to isolate the cause(s) of discrepancies and to evaluate which synthetic calibration is most appropriate for natural samples. Here, we systematically explore the impact of synthetic carbonate precipitation by replicating precipitation experiments of previous workers under a constant analytical setting. We (1) precipitate 56 synthetic carbonates at temperatures of 4–85 °C using different procedures to degas $CO_2$, with and without the use of the enzyme carbonic anhydrase (CA) to promote rapid dissolved inorganic carbon (DIC) equilibration; (2) digest samples in phosphoric acid at both 90 °C and 25 °C; and (3) hold constant all analytical methods including acid preparation, $CO_2$ purification, and mass spectrometry; and (4) reduce our data with $^{17}O$ corrections that are appropriate for our samples. We find that the $CO_2$ degassing method does not influence $\Delta_{47}$ values of these synthetic carbonates, and therefore probably only influences natural samples with very rapid degassing rates, like speleothems that precipitate out of drip solution with high $pCO_2$. CA in solution does not influence $\Delta_{47}$ values in this work, suggesting that disequilibrium in the DIC pool is negligible. We also find the $\Delta_{47}$ values of samples reacted in 25 and 90 °C acid are within error of each other (once corrected with a constant acid fractionation factor). Taken together, our results show that the $\Delta_{47}$-temperature relationship does not measurably change with either the precipitation methods used in this study or acid digestion temperature. This leaves phosphoric acid preparation, $CO_2$ gas purification, and/or data reduction methods as the possible sources of the discrepancy among published calibrations. In particular, the use of appropriate $^{17}O$ corrections has the potential to reduce disagreement among calibrations. Our study nearly doubles the available synthetic carbonate calibration data for $\Delta_{47}$ thermometry (adding 56 samples to the 74 previously published samples). This large population size creates a robust calibration that enables us to examine the potential for calibration slope aliasing due to small sample size. The similarity of $\Delta_{47}$ values among carbonates precipitated under such diverse conditions suggests that many natural samples grown at 4–85 °C in moderate pH conditions (6–10) may also be described by our $\Delta_{47}$-temperature relationship.

---

* Corresponding authors.
*E-mail addresses:* jrkelson@uw.edu (J.R. Kelson), kate1@uw.edu (K.W. Huntington).

http://dx.doi.org/10.1016/j.gca.2016.10.010
0016-7037/

*Keywords:* Clumped isotopes; Oxygen isotopes; Paleothermometer calibration; Carbonate precipitation

## 1. INTRODUCTION

Carbonate clumped isotope ($\Delta_{47}$) thermometry is applied to an increasing range of natural systems, contributing to discoveries in areas such as paleoclimate, paleoaltimetry, and basinal fluid migration (e.g., see reviews of Eiler, 2007, 2011; Affek, 2012; Eiler et al., 2013, 2014; Huntington and Lechler, 2015). $\Delta_{47}$ thermometry estimates mineral growth temperature using the thermodynamic tendency for $^{13}C$ and $^{18}O$ to bond in carbonate molecules at lower temperatures (e.g., Schauble et al., 2006). The $\Delta_{47}$ value of $CO_2$, derived from phosphoric acid digestion of carbonate minerals, measures the abundance of $^{13}C$ and $^{18}O$ in the same molecule in excess of what would occur by random chance (Ghosh et al., 2006; Schauble et al., 2006). The temperature dependence of $^{13}C$–$^{18}O$ clumping in carbonates has been studied from a theoretical perspective (Schauble et al., 2006; Guo et al., 2009; Passey and Henkes, 2012; Hill et al., 2014; Tripati et al., 2015). However, given the as of yet imperfect knowledge of carbonate precipitation processes, acid fractionation effects, and analytical artifacts, accurate empirical $\Delta_{47}$-temperature calibrations are necessary to apply the thermometer with confidence. Many empirical calibrations have been published based on analyses of carbonates with known growth temperatures, including synthetic carbonates (Ghosh et al., 2006; Dennis and Schrag, 2010; Daëron et al., 2011; Passey and Henkes, 2012; Zaarur et al., 2013; Fernandez et al., 2014; Tang et al., 2014; Defliese et al., 2015; Kluge et al., 2015; Tripati et al., 2015) and natural biogenic and abiogenic carbonates (Ghosh et al., 2007; Eagle et al., 2010, 2013, 2015; Tripati et al., 2010, 2015; Thiagarajan et al., 2011; Saenger et al., 2012; Henkes et al., 2013; Grauel et al., 2013; Came et al., 2014; Wacker et al., 2014; Petrizzo et al., 2014; Kele et al., 2015).

Despite the extensive body of research on calibrating the $\Delta_{47}$ thermometer, unresolved discrepancies of up to 10–15 °C exist among published empirical calibrations (Table 2). The first two published synthetic calcite calibrations differ in their temperature sensitivity: Ghosh et al. (2006) report a steep $\Delta_{47}$-temperature slope ($m = 0.0636 \times 10^6/T^2$), while Dennis and Schrag (2010) report a relatively shallower slope ($m = 0.0362 \times 10^6/T^2$) (both slopes as reported in the absolute reference frame in Dennis et al. (2011)). More recent calibrations have slopes that fall between these two end-members, such that a spectrum of temperature sensitivities has been published (Table 2). These discrepancies in slope and resulting temperature estimates are large enough to significantly change interpretations of $\Delta_{47}$ measured in natural samples. Yet it is unclear if these calibrations disagree because of true differences in the $\Delta_{47}$ values of carbonates synthesized or because of differences in laboratory analysis methods.

Previous workers have suggested that calibrations diverge because different carbonate precipitation methods cause calibration samples to have $\Delta_{47}$ values that reflect variables other than growth temperature (e.g. Dennis and Schrag, 2010; Dennis et al., 2011; Henkes et al., 2013; Zaarur et al., 2013; Fernandez et al., 2014; Tang et al., 2014). Most notably, opposing views have been expressed about which method of $CO_2$ degassing during synthetic calcite growth (passive degassing or active degassing with $N_2$, sensu Kim and O'Neil (1997) and Dennis and Schrag (2010)) favors clumped isotope disequilibrium (Affek and Zaarur, 2014; cf. Fernandez et al., 2014). Recent publications have shown that $\Delta_{47}$ values can also be influenced by growth rate, pH, and DIC disequilibrium (Hill et al., 2014; Tang et al., 2014; Watkins and Hunt, 2015; Tripati et al., 2015).

However, the influence of carbonate precipitation methods used by previous workers to create empirical $\Delta_{47}$-temperature calibrations remains to be systematically evaluated in a single analytical setting, making it difficult to determine if calibration discrepancies arise due to differences in carbonate precipitation techniques or analysis techniques. Differences in analysis methods that could cause calibrations to diverge could occur at multiple steps in the sample preparation and measurement process including: digestion of the carbonate sample to produce $CO_2$ gas for analysis (e.g., Wacker et al., 2013, 2014; Fernandez et al., 2014; Came et al., 2014; Petrizzo et al., 2014; Defliese et al., 2015), sample gas purification, data processing and absolute reference frame construction (Dennis et al., 2011; Daëron et al., 2016; Olack and Colman, 2016; Schauer et al., 2016), or background measurements (He et al., 2012; Bernasconi et al., 2013; Fiebig et al., 2015).

Here, we systematically explore the influence of carbonate precipitation methods on $\Delta_{47}$ values. We precipitate carbonate at known temperatures using various methods, including the methods used in previously published synthetic carbonate clumped isotope calibrations over the temperature range 4–85 °C. We then digest samples in phosphoric acid at both 90 °C and 25 °C, but control for other preparatory and analytical variables by purifying and measuring the resulting $CO_2$ using identical procedures. Our results support previous findings that rule out acid digestion temperature as the cause of the calibration discrepancies (Defliese et al., 2015). Most importantly, our large dataset (56 samples; 200 individual sample analyses bracketed by extensive equilibrated $CO_2$ and carbonate standard measurements) shows that synthetic carbonate precipitation methods are unlikely to be responsible for previous calibration discrepancies. Furthermore, we define a robust $\Delta_{47}$-temperature calibration that is appropriate for estimating temperature from natural, abiogenic carbonates precipitated via a variety of pathways. Our findings point toward specific analytical and data correction methods that contribute to discrepancies among previous calibrations, including $^{17}O$ corrections (Daëron et al., 2016; Olack and Colman, 2016; Schauer et al., 2016). Normalizing these methods across laboratories will be required to decrease dispersion among calibration data and correctly interpret