Temperature dependence of clumped isotopes (Δ_{47}) in aragonite

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Key points

- Precise control on carbonate formation temperatures enables more accurate clumped isotope-temperature calibrations
- Isotopic ordering and acid fractionation in aragonite have a similar temperature dependence as in calcite, enabling combined calibrations
- The Δ_{47}-$\frac{1}{T^2}$ relation in carbonates is non-linear, including hot calibration data offsets the calibration in the cold temperature range

Abstract

Clumped isotope thermometry can independently constrain the formation temperatures of carbonates, but a lack of precisely temperature-controlled calibration samples limits its application on aragonites. To address this issue, we present clumped isotope compositions of aragonitic bivalve shells grown under highly controlled temperatures (1–18°C), which we combine with clumped isotope data from natural and synthetic aragonites from a wide range of temperatures (1–850°C). We observe no discernible offset in clumped isotope values between aragonitic foraminifera, mollusks, and abiogenic aragonites or between aragonites and calcites, eliminating the need for a mineral-specific calibration or acid fractionation factor. However, due to non-linear behavior of the clumped isotope thermometer, including high-temperature (>100°C) datapoints in linear clumped isotope calibrations causes them to underestimate temperatures of cold (1–18°C) carbonates by 2.7 ± 2.0°C (95% confidence level). Therefore, clumped isotope-based paleoclimate reconstructions should be calibrated using samples with well constrained formation temperatures close to those of the samples.

Plain language summary

Clumped isotope analysis is a highly accurate method for reconstructing temperatures in Earth’s past climate from calcium carbonate fossils of calcifying organisms. Unfortunately, calibration studies so far were predominantly based on samples of calcite, a common calcium carbonate mineral. It is therefore unknown whether these clumped isotope calibrations yield accurate temperature reconstructions when applied to aragonite, another carbonate mineral which corals and many shells consist of. Therefore, we grew mollusks that build their shell out of aragonite in a lab at constant water temperatures to test the clumped isotope method on aragonitic shells. We find no significant difference in the temperature sensitivity of the method between our aragonites and the previous calibrations and show that the temperature calibration can be improved by combining data from different minerals. However, we find subtle differences in the temperature dependence of clumped isotopes between hot (>100°C) carbonates and cold (<30°C) carbonates, which cause previous calibrations to underestimate temperatures of colder carbonates. We conclude that using carbonate samples grown at temperatures close to the temperatures of the samples used in climate reconstructions can eliminate a bias of 2.7°C, resulting in more accurate reconstructions of past temperatures.

Keywords

Clumped isotopes, aragonite, paleoclimate, mollusk, temperature

1. Introduction

Since its first applications (e.g. Schauble et al., 2003; Wang et al., 2004; Ghosh et al., 2006), carbonate clumped isotope analysis has developed into a valuable tool for paleothermometry in the geosciences. Clumped isotope analysis is based on the thermodynamic principle that molecules with multiple heavy isotopes (so-called “multiply-substituted isotopologues”) have lower vibrational energies than molecules containing lighter isotopes (Urey, 1947). Consequently, the increase in system entropy at higher temperatures causes a decrease in the occurrence of multiply-substituted isotopologues, and “clumping” of heavy isotopes within the same molecule is favored in low-energy systems (Eiler, 2007). In carbonates, this principle causes heavy carbonate ions (e.g. $^{13}C^{18}O^{16}O_2$; mass 63 or $^{12}C^{18}O_2{}^{16}O$; mass 64) to become more abundant with decreasing calcification temperatures (Ghosh et al., 2006). The distribution of these isotopologues is proportional in the CO_2 gas after reaction of carbonates with acid (e.g. $^{13}C^{18}O^{16}O$; mass 47 and $^{12}C^{18}O_2$, mass 48 respectively) and is measured with reference to the distribution of isotopologues in a fully scrambled heated CO_2 gas with the same isotopic composition:

$$\Delta_{47}[‰] = \left(\frac{R^{47}}{R^{47}*} - 1\right) \quad (1)$$

In which R^{47} is the ratio of CO_2 molecules with mass 47 (predominantly $^{13}C^{18}O^{16}O$) relative to CO_2 with the most common mass 44 ($^{12}C^{16}O_2$) in the sample, and $R^{47}*$ is the same ratio in stochastic equilibrium (Daëron et al., 2016). This Δ_{47} value is a measure for the degree of “clumping” in the sample which depends on its calcification temperature.

The main advantage of carbonate clumped isotope analysis over previous paleothermometers is its basis on thermodynamic principles and its independence from the chemistry of the precipitation fluid (Eiler, 2007). The latter represents an improvement over the often-used oxygen isotope paleothermometer ($\delta^{18}O$), which requires knowledge of the oxygen isotope composition of the precipitation fluid ($\delta^{18}O_w$; e.g. Epstein et al., 1953; Kim & O’Neil, 1997). The clumped isotope method has many applications, notably to reconstruct absolute temperature variability throughout Earth’s history (Rodríguez-Sanz et al., 2017; Henkes et al., 2018; Vickers et al., 2020a; de Winter et al., 2021a; Meckler et al., 2022; Agterhuis et al., 2022).

Inter-lab standardization of carbonate Δ_{47} measurements has reconciled former offsets between laboratories using different CO_2 preparation methods and reconciled the clumped isotope temperature calibration of calcites with the results of thermodynamic *ab initio* models (Bernasconi et al., 2018; 2021; Petersen et al., 2019; Jautzy et al., 2020). A unified linear calibration was established through re-standardized Δ_{47} values of carbonates precipitated at a wide range of known temperatures (0.5-1100°C; Anderson et al., 2021). This eliminates concerns over the confounding effects of differences in the origin of carbonates (e.g. biogenic vs. inorganic; Henkes et al., 2013), varying mineralization rates (Daëron et al., 2019), different acid digestion temperatures and different carbonate mineralogies (e.g. dolomite vs. calcite; Müller et al., 2019) on the clumped isotope thermometer. However, it remains unclear whether biological process (i.e. “vital effects”) influence isotopic ordering in some biogenic carbonates.

The unified calibration dataset includes only one aragonitic carbonate, insufficient to test for different clumped isotope temperature dependencies between aragonites and calcites (Anderson et al., 2021). Results of *ab initio* models suggest that such a difference between the two polymorphs may exist (Schauble et al., 2006; Guo et al., 2009) and experimental studies disagree on a difference in acid fractionation factor (AFF) between calcite and aragonite (Guo et al., 2009; Müller et al., 2019; Petersen et al., 2019). These uncertainties are confounded by the fact that most carbonates used in current calibrations are precipitated under natural circumstances with indirectly estimated or else poorly controlled temperature regimes (e.g. Kele et al., 2015; Peral et al., 2018). The potential Δ_{47} offset between aragonite and calcite might introduce an unknown bias when using the unified temperature calibration on aragonite data (e.g. Caldarescu et al., 2021); a severe limitation given the common occurrence of aragonite in biogenic calcifiers (e.g. bivalves; Kennedy et al., 1969, gastropods; Taylor and Reid, 1990, and foraminifera; Hansen, 1979) as well as inorganic natural carbonates (e.g. speleothems; Frisia et al., 2000, and travertines; Kele et al., 2015).

This study presents new clumped isotope results from precisely temperature controlled, lab-grown aragonitic *Arctica islandica* bivalve shells. The bivalve *Arctica islandica* is a highly utilized climate archive, and a promising substrate for clumped isotope-based paleothermometry (e.g. Witbaard et al., 1997; Burchardt and Simonarson, 2003; Schöne et al., 2005; Schöne and Fiebig, 2009; Butler et al., 2013). Combined with preexisting aragonite clumped isotope data (Kluge et al., 2015; Kele et al., 2015; Müller et al., 2017; Breitenbach et al., 2018; Bernasconi et al., 2018; Piasecki et al., 2019; Caldarescu et al., 2021) standardized to the new Intercarb-Carbon Dioxide Equilibrium Scale (I-CDES) reference frame (Bernasconi et al., 2021), our dataset resolves potential vital effects on clumped isotopes in aragonitic mollusks by comparing species and specimens grown under the same controlled conditions. This study aims to offer a detailed investigation of the clumped isotope temperature dependence in aragonites.

2. Materials and Methods

2.1 Lab grown Arctica islandica

Arctica islandica bivalves were cultured inside the lab of the Royal Netherlands Institute for Sea Research (NIOZ, Texel, the Netherlands). Specimens used for this study were grown under four different, constant, and monitored temperature regimes: 1.1 ± 0.2°C, 3.2 ± 0.3°C, 15 ± 0.4°C and 18 ± 0.3°C (see **Table 1**; **S9**). Details on the culturing setup are provided in **S1** and Witbaard et al. (1998). Aragonite from cleaned and dried *Arctica islandica* shells was sampled using a hand-held Dremel 3000 rotary drill at low speed equipped with a tungsten-carbide drill bit (see **S1**). Gathering enough aragonite for reliable Δ_{47} analyses for each temperature treatment (>2 mg; Müller et al., 2017; Fernandez et al., 2017) typically required combining material from multiple (3–5) specimens grown under the same temperature conditions. To test potential inter-specimen differences, results were tracked per individual specimen for the 1.1 ± 0.2°C and 18 ± 0.3°C treatments (see **Table 1**).

2.2 Clumped isotope analysis

The clumped isotope composition of 278 aliquots of shell aragonite were analyzed over two 6-month periods (March – August 2020; May – November 2021) on two Thermo isotope ratio mass spectrometers (one MAT253 and one MAT253 plus) coupled to Kiel IV carbonate preparation devices (see **S1**). After correcting for variability in the pressure baseline (He et al.,2012), clumped isotope results were processed relative to the I-CDES through an empirical transfer function (ETF) based on measurements of ETH standards (ETH-1, -2 and -3) and their accepted I-CDES values (Bernasconi et al., 2021). Isotopic values were calculated using the latest IUPAC values (Brand et al., 2010; Daëron et al., 2016). No AFF was applied after I-CDES standardization because the carbonate standards used for the ETF undergo the same acid reaction as the samples (Bernasconi et al., 2021). Long-term accuracy and reproducibility of Δ_{47} results were assessed based on repeated measurements of the IAEA-C2 monitoring standard (Δ_{47_IAEA} on MAT253 plus: 0.6382 ± 0.026‰; Δ_{47_IAEA} on MAT253: 0.6445 ± 0.046‰; 1σ). Results were indistinguishable from the accepted value for IAEA-C2 (0.6409 ± 0.003‰; 95% CL; Bernasconi et al., 2021). Full results of all sample aliquots and standards used to standardize the results are provided in **S2**.

2.3 Data compilation

The *Arctica islandica* dataset was augmented with literature Δ_{47} values of aragonites with known calcification temperatures (see **S3**). The dataset includes samples from mollusks (Bernasconi et al., 2018; aragonitic *Megapitaria aurantiaca* samples in Caldarescu et al., 2021; this study), foraminifera (Piasecki et al., 2019), travertines (Kele et al., 2015; Bernasconi et al., 2018), cave deposits (Breitenbach et al., 2018), lab-grown aragonites (Kluge et al., 2015) and heated aragonites (Müller et al., 2017). Data from several older studies (e.g. Ghosh et al., 2006; 2007; Tripati et al., 2010; Wacker et al., 2013; 2014; Zhang et al., 2018; Zhai et al., 2019; Dong et al., 2021) were not included because they were not corrected for the pressure baseline (He et al., 2012; Bernasconi et al., 2013), could not be transferred into the standard reference frame (Dennis et al., 2011), lacked the standardization required to bring Δ_{47} values into the I-CDES scale (Bernasconi et al., 2021) or because the aragonite was precipitated out of equilibrium (e.g. Kimball et al., 2015; Chen et al., 2019; **S1**; **S3**). Clumped isotope data from the literature was brought to the I-CDES reference frame using the multi-linear correction proposed in Appendix A of Bernasconi et al. (2021) using values of carbonate standards reported in the studies (see **S1**). Uncertainties on the formation temperatures of the non-temperature controlled datapoints from previous studies were generally in the order of 1°C (1σ; see **S1**). The full dataset including Δ_{47} values and temperatures with their uncertainties used in this study is provided in **S4**. Unless stated otherwise, uncertainties are cited at the 95% confidence level.

All data processing for this study is done in R (R Core Team, 2022) and scripts are provided in **S5** and published on Github (https://github.com/nielsjdewinter/Aragonite_clumped). Details on data processing are provided in **S1**. We compare our data with calibrations by Anderson et al. (2021) and Meinicke et al. (2020) as well as with temperature dependencies of aragonite and calcite clumped isotope compositions from *ab initio* modelling in Guo et al. (2009) brought into the I-CDES reference frame (see **S1**).

3. Results

3.1 Clumped isotope values in Arctica islandica

Clumped isotope results from *A. islandica* are summarized in **Table 1** and **Figure 1**. There is no significant clumped isotope difference between specimens in the same temperature treatment (F(4,77) = 1.937, *p* = 0.11 for the 1°C specimens and F(3,63) = 0.377, *p* = 0.77 for the 18°C specimens; see **S6**). The number of measurements per specimen was large enough to exclude per-specimen Δ_{47} differences outside the reproducibility standard deviation of the clumped isotope analyses (0.046‰; see **Table 1** and **S6**). Differences between all temperature treatments are statistically significant (P(3,274) = 15.68, $p < 0.01$), except for differences between the 15°C and 18°C temperature bin and the difference between 1°C and 3°C (95%CL; **S6**).

We investigated the Δ_{47}-$\frac{1}{T^2}$ relationship and how it varies along the temperature domain by performing linear regressions on increasingly large parts of our compilation. Note that the uncertainty on clumped isotope data compared to the range of temperatures of the lab-grown *A. islandica* leaves relatively high uncertainty on a clumped isotope-temperature regression through these results alone compared to the unified clumped isotope calibration (Anderson et al. 2021). We therefore do not advice using this and other regression equations in this section for calibrating clumped isotope results (see **Discussion**). Firstly, a statistically significant temperature relationship (Δ_{47}-$\frac{1}{T^2}$ slope >0; 95% CL) is found for Δ_{47} exclusively from *Arctica islandica* samples:

$$\Delta_{47}(I-CDES) = 0.0280 \pm 0.0042 * \frac{10^6}{T^2} + 0.304 \pm 0.0524 \ (\text{T in K}, \pm 1\sigma; \sigma_{res} = 0.047\text{‰}) \qquad (1)$$

Secondly, including other aragonitic mollusk data (Caldarescu et al., 2021) yields a regression indistinguishable from the Anderson et al. (2021) unified clumped isotope calibration:

$$\Delta_{47}(I-CDES) = 0.0443 \pm 0.0024 * \frac{10^6}{T^2} + 0.097 \pm 0.0291 \ (\text{T in K}, \pm 1\sigma; \sigma_{res} = 0.043\text{‰}) \qquad (2)$$

3.2 Aragonite clumped isotope temperature dependence

When including clumped isotope values of other low-temperature (<30°C) aragonites in the compilation, the regression remains indistinguishable from the calibration of Anderson et al. (2021) and similar to Meinicke et al. (2020; 2021) and the Guo et al. (2009) theoretical temperature relationships (**Fig. 2B**):

$$\Delta_{47}(I-CDES) = 0.0451 \pm 0.0024 * \frac{10^6}{T^2} + 0.0871 \pm 0.0287 \text{ (T in K, } \pm 1\sigma; \sigma_{res} = 0.042\text{‰)} \tag{3}$$

Finally, we included higher temperature (>30°C) datapoints, such as the cave deposits of Breitenbach et al. (2018), travertine samples from Kele et al. (2015), precipitated aragonites from Kluge et al. (2015) and heated aragonites from Müller et al. (2017) in the linear regression. This decreases the slope and increases the intercept (see **Fig. 2**):

$$\Delta_{47}(I-CDES) = 0.0403 \pm 0.0005 * \frac{10^6}{T^2} + 0.1435 \pm 0.0485 \text{ (T in K, } \pm 1\sigma; \sigma_{res} = 0.040\text{‰)} \tag{4}$$

The formation temperatures of our *A. islandica* data on the very cold end of the calibration domain are significantly underestimated by Anderson et al. (2021; $\Delta\Delta_{47}$ = +0.009 ± 0.007‰; −2.71 ± 2.03°C; **Fig. 3**; $\Delta\Delta_{47}$ = offset between data and calibration). The theoretical aragonite clumped isotope-temperature relationship (Guo et al., 2009) severely overestimates *A. islandica* temperatures (−0.016 ± 0.007‰; +4.35 ± 1.88°C; **Fig. 3**). Contrarily, the Meinicke et al. (2020; 2021) calibration ($\Delta\Delta_{47}$ = +0.004 ± 0.007‰; −1.17 ± 2.00°C; **Fig. 3**) and the theoretical calcite temperature relationship (Guo et al., 2009; $\Delta\Delta_{47}$ = +0.002 ± 0.007‰; −0.47 ± 1.98°C; **Fig. 4**) do not significantly over- or underestimate the formation temperature of our *A. islandica* shells.

4. Discussion

4.1 Isotope ordering in aragonitic mollusks

Clumped isotope values of our temperature-controlled *A. islandica* samples consistently plot on a Δ_{47}-$\frac{1}{T^2}$ linear relationship with other low-temperature aragonite datapoints (**Fig. 1 and 2**; see **section 4.2**). The absence of a consistent offset between *A. islandica* datapoints and other aragonites (mean Δ_{47} difference of +0.003 ± 0.004‰, see **Fig. 2** and **S8**) and agreement between the linear Δ_{47}-$\frac{1}{T^2}$ dependence of the aragonitic mollusk data in this study and the regression through the complete low-temperature aragonite dataset (**Fig. 1** and **section 3.1**) strongly supports a common temperature dependence for all aragonites in this study, biogenic or inorganic, and argues against disequilibrium fractionation in aragonite precipitated inorganically or vital effect in bivalves or foraminifera (see **section 3.1**; **Fig. 1 and 2**). Our highly temperature-controlled growth experiments uniquely allow us to exclude variability in the growth environment between specimens from the same growth treatment as a driver of shell composition. Strong similarity of Δ_{47} values between individual *A. islandica* specimens grown at the same temperature thus rules out specimen-specific vital effects on the clumped isotope composition aragonitic bivalve shells outside the uncertainty of our measurements (see **section 3.1**; **Fig. 1**, **Table 1** and **S6**). These findings corroborate measurements in calcitic mollusks showing that clumped isotope values in mollusk carbonates adhere to the same temperature relationship as other carbonates precipitated in equilibrium (except for juvenile oyster shells; Huyghe et al., 2022). Clumped isotope analyses in (fossil) mollusk shells thus provide an independent temperature proxy, allowing paleoclimatologists to disentangle the effects of variability in temperature and the hydrological cycle (as measured in $\delta^{18}O_w$) throughout geological history down to the seasonal timescale (e.g. Caldarescu et al., 2021; de Winter et al., 2021; Letulle et al., 2022).

4.2 Mineral-specific acid fractionation factor

Residuals of aragonite clumped isotope data around the low-temperature (<30°C) York regression (0.042‰; 1σ; see **section 3.**1 and **Fig. 2**) are predominantly explained by analytical uncertainty on Δ_{47} measurements (external precision of 0.026‰ and 0.046‰ on the 253Plus and the MAT253 mass spectrometers; 1σ; see **section 2.2**). Uncertainty on formation temperatures in the low-temperature dataset (±0.8°C; 1σ; see **S4**) would add an additional uncertainty of 0.0024‰ (1σ) if applied to the weighted average formation temperature of all low-temperature (<30°C) data points (22.0°C; see **S4**). Outside these uncertainties in the compilation data, there is little uncertainty on the temperature relationship in the low-temperature domain (<30°C; see **section 3.2**; **Fig. 2**). If clumped isotope fractionation during acid digestion was indeed different between aragonite and calcite (as suggested in Müller et al., 2017; Petersen et al., 2019) the difference in AFF would be indicated by the difference between our aragonite dataset and the previous calcite-based calibrations (Meinicke et al., 2020; 2021). The close similarity between our *A. islandica* data and the calcite calibration ($\Delta\Delta_{47} = 0.004 \pm 0.007$‰; **Fig. 3**; **S7**) leaves little room for the 0.007‰ and 0.025‰ difference in AFF reported in Petersen et al. (2019) and Müller et al. (2017), respectively. We therefore conclude that the calcite AFF in Petersen et al. (2019), which are included in the I-CDES reference scale (Bernasconi et al., 2021) can be used for aragonite samples.

4.3 Non-linear temperature dependence of clumped isotopes in aragonites

Current clumped isotope calibrations (Meinicke et al., 2020; 2021; Anderson et al., 2021) show subtle differences in the low-temperature end of the calibration (<30°C) that would result in ~1.5°C colder temperatures when applying Anderson et al. (2021) compared to Meinicke et al. (2020). In addition, the cold-water (<30°C) carbonate based Meinicke et al. (2020) calibration more closely resembles the modelled temperature relationship for calcites in Guo et al. (2009). Including high-temperature (>30°C) data in our linear regression leads to overestimation of the temperature of warmer (>18°C) datapoints ($\Delta\Delta_{47}$ of -0.005 ± 0.006‰, or $+1.8^{+2.1}_{-2.0}$°C for data precipitated at 30°C), while underestimating colder datapoints ($\Delta\Delta_{47}$ of +0.009 ± 0.008‰, or $-2.0^{+2.0}_{-2.0}$°C for data precipitated at 0°C; **Fig. 2**; **S7**). Point-by-point offsets of all data from the calibration lines are provided in **S8**.

This difference between Δ_{47}-$\frac{1}{T^2}$ regressions through the low-temperature (<30°C) and the full dataset (see **section 3.2**; **Fig 2**) likely highlights non-linear behavior of the Δ_{47}-$\frac{1}{T^2}$ relationship in aragonites. In fact, previous studies based on both clumped isotope analyses and *ab initio* modelling have suggested a non-linear Δ_{47}-$\frac{1}{T^2}$ relationship to be a better fit for both calcites (Guo et al., 2009; Jautzy et al., 2020) and dolomites (Guo et al., 2009; Müller et al., 2019) precipitated on a large range of known temperatures. Non-linear behavior is also observed in the Anderson et al. (2021) dataset, where Δ_{47} values of calcites precipitated between 100°C and 1000°C are underestimated by the linear relationship, while the hottest datapoints (calcites heated to 1100°C) fall on the linear regression, mimicking the reduced Δ_{47}-$\frac{1}{T^2}$ slope at the high temperature end of the polynomial regressions through calcite and dolomite data (Guo et al., 2009; Jautzy et al., 2020; Müller et al., 2019). A linear Δ_{47}-$\frac{1}{T^2}$ relationship through a calibration dataset with a large temperature range will thus overestimate temperatures for samples with Δ_{47} values between 0.2‰ and 0.4‰ (temperatures of 100°C–1000°C; see residuals in Anderson et al., 2021) and underestimate temperatures of cold (<30°C) samples, as confirmed by regressions through our low-temperature datapoints (see **Fig. 2-3** and **section 4.4**). Therefore, more high-temperature aragonite datapoints are needed to constrain the clumped isotope-temperature relationship for temperatures >100°C.

4.4 Calibrating the clumped isotope-temperature relationship in cold (<30°C) carbonates

Our lab-grown *A. islandica* shells offer more control on formation temperature than naturally grown carbonates precipitated under variable temperatures. Ideally, the temperature of these natural samples is monitored so an average temperature can be calculated for the targeted growth period (e.g. Kele et al., 2015; de Winter et al., 2020; 2021b; Huyghe et al., 2021). However, formation temperatures are often indirectly estimated through other proxies (e.g. $\delta^{18}O_c$) and/or estimates of the living environment (e.g. water depth) of the carbonate producer, accumulating uncertainty (e.g. Peral et al., 2018; Piasecki et al., 2018; Meinicke et al., 2020). These caveats obscure the full uncertainty of the formation temperatures of natural carbonates as well as the effect of this unknown uncertainty on the calibrations. Considering the methods by which the “known” temperatures of natural carbonates are estimated in previous studies, part of the ~1.5°C temperature offset between Anderson et al. (2021) and Meinicke et al. (2020; 2021; see **Fig. 3**) and the 2.7 ± 2.0°C offset between Anderson et al. (2021) and our *A. islandica* data might be caused by uncertainty on the formation temperatures of the calibration dataset. However, our highly temperature-controlled *A. islandica* datapoints reveal that, despite uncertainty on formation temperature, the Meinicke et al. (2021) calibration locally approximates the non-linear Δ_{47}-$\frac{1}{T^2}$ relationship in the cold temperature domain with higher accuracy than the Anderson et al. (2021) calibration (**Fig. 1**, **Fig. 3**; **S8**). The non-linear theoretical calcite temperature dependence by Guo et al. (2009) also fits well with the data. Precisely temperature-controlled carbonates thus better constrain the slope of the Δ_{47}-$\frac{1}{T^2}$ relationship for cold carbonates (improving calibration accuracy) while reducing the uncertainty on the calibration (improving calibration precision).

The ~1.5°C difference in reconstructed temperature between the calibrations in the low temperature range (<30°C) may seem trivial and requires the complete *A. islandica* dataset (N = 278; see **Fig. 4**) to resolve. However, in paleoclimate reconstructions (e.g. Petersen et al., 2016; de Winter et al., 2017; 2021a; Vickers et al., 2020b; Agterhuis et al., 2021; Meckler et al., 2022), this temperature offset may have significant consequences. A ~1.5°C cold bias in temperature reconstructions may lead to a significant underestimation of climate sensitivity to CO_2 forcing, biasing the physical science basis for informing policymakers about future climate change (e.g. Dennis et al., 2013; Modestou et al., 2020; Westerhold et al., 2020; Tierney et al., 2020; IPCC, 2021). Accurate clumped isotope-based temperature reconstructions therefore require calibration datasets with precisely constrained formation temperatures tailored to the temperature range of the samples.

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Open Research

Supplementary materials are deposited on the open-source repository Zenodo and can be accessed through the following link: https://doi.org/10.5281/zenodo.6524706. R scripts are uploaded on GitHub (https://github.com/nielsjdewinter/Aragonite_clumped) and archived in Zenodo (https://doi.org/10.5281/zenodo.6560188).

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Table 1 *Arctica islandica* clumped isotope results compared to previous calibrations

“mixed” = combined samples from multiple specimens, number codes (e.g. “29” or “6A”) = material from one individual. “Ais” = *Arctica islandica*. Significant Δ_{47} and temperature offsets are labeled in bold. cc = calcite, ar = aragonite

Sample	**Culturing temperature**	**Δ_{47} (I-CDES; ± 95%CL)**		**N**	**Offset from Anderson**	**Offset from Meinicke**	**Offset from Guo (cc)**	**Offset from Guo (ar)**
Ais1	1.1 ± 0.2°C	mixed	0.695 ± 0.019‰	34				
		3	0.661 ± 0.023‰	13				
		29	0.688 ± 0.025‰	15				
		6A	0.684 ± 0.028‰	11				
		6B	0.649 ± 0.026‰	9				
		TOTAL	0.682 ± 0.010‰	82	+0.008‰ -2.12°C	+0.002‰ -0.61°C	+0.003‰ -0.75°C	**−0.016‰** **+4.48°C**
Ais3	3.2 ± 0.3°C	mixed	0.667 ± 0.010‰	72	+0.001‰ -0.27°C	−0.005‰ +1.24°C	−0.006‰ +1.57°C	**−0.023‰** **+6.80°C**
Ais15	15 ± 0.4°C	mixed	0.637 ± 0.009‰	57	**+0.013‰** **-3.63°C**	+0.008‰ -2.10°C	+0.004‰ -0.99°C	**−0.013‰** **+4.25°C**
Ais18	18 ± 0.3°C	mixed	0.635 ± 0.010‰	39				
		67	0.647 ± 0.024‰	9				
		89	0.640 ± 0.028‰	8				
		111	0.630 ± 0.022‰	11				
		TOTAL	0.637 ± 0.005‰	67	**+0.021‰** **-6.63°C**	**+0.016‰** **-5.10°C**	**+0.012‰** **-3.99°C**	−0.004‰ +1.25°C

Figure 1: *Arctica islandica* Δ_{47} results. Clumped isotope results are aggregated by specimen or multi-specimen sample (round symbols; see **Table 1**). Vertical lines represent 95% CL and number indicate sample size. Data is color-coded per temperature treatment (1°C, 3°C, 15°C and 18°C), with bold error bars indicating 95% CL, pairs of letter labels (a and b) indicate statistically indistinguishable Δ_{47} values ($p < 0.05$). The grey error bar at 6°C highlights *A. islandica* data from Bernasconi et al. (2018; recalculated to I-CDES). Solid and dashed black lines show calibrations by Anderson et al. (2021) and Meinicke et al. (2020; projected on I-CDES scale; Meinicke et al., 2021), respectively. Grey solid and dashed lines represent, respectively, the theoretical calcite ("cc") and aragonite ("ar") temperature dependencies from Guo et al. (2009; projected on the I-CDES scale, see **S1**). The horizontal axis is scaled to $\frac{10^6}{T^2}$, with T in K, to show the assumed linear relationship with the clumped isotope value.

Figure 2: Aragonite Δ_{47} temperature dependence. Clumped isotope data of aragonite samples plotted against formation temperature. **A**. All data plotted over the full temperature range (1°C–850°C). Individual datapoints, averages and uncertainty on temperature and Δ_{47} values (95% CL) are color-coded by study. Symbols highlight different types of aragonite. The solid and dashed black lines show calibrations by Anderson et al. (2021) and Meinicke et al. (2020; 2021; plotted for temperatures <30°C). Grey solid and dashed lines represent, respectively, the theoretical calcite ("cc") and aragonite ("ar") temperature dependencies from Guo et al. (2009; projected on the I-CDES scale, see **section 2.5**). Colored dashed lines and shaded envelopes show York regressions through aragonite data and their 95% confidence envelopes, respectively. **B**. Shows a zoom-in of the plot in **A**. for the low-temperature domain (1–30°C). Note that the horizontal axis is scaled to $\frac{10^6}{T^2}$, with T in K, to show the assumed linear relationship with the clumped isotope value.

Figure 3: **Offset of *A. islandica* data from temperature regressions**. Shaded grey points show residual Δ_{47} values relative to four clumped isotope temperature relationships (see horizontal axis). Black symbols with error bars (95% CL) show mean offsets of all *A. islandica* datapoints (grown at 1°C, 3°C, 6°C, 15°C and 18°C) from the calibrations. The vertical axis on the right shows the temperature offset relative to the weighted mean calcification temperature of the full *A. islandica* dataset (8.6°C; see **S4**) based on Anderson et al. (2021).