

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

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Introduction

This Supplement contains all supplementary text and figures for the manuscript. All data files, scripts and large tables are deposited in the accompanying Zenodo repository (<https://doi.org/10.5281/zenodo.6524705>, see Open Research chapter).

Text S1: Supplementary Methodology

1. Culture experiments

Living specimens of juvenile *Arctica islandica* (bivalvia) were collected from the Süderfart site in the Kieler Bucht to the north-east of Kiel, Germany (54°34'11"N, 10°51'59"E; see Schaefer et al., 1985). All animals were placed in sand-filled containers in a basin with aerated seawater which

was refreshed two days a week with water from the Marsdiep tidal inlet directly outside the Royal Netherlands Institute for Sea Research (NIOZ, Texel, the Netherlands; 53°00'04"N, 4°47'23"E). Specimens used for this study were grown under four different, constant, and monitored temperature regimes: $1.1 \pm 0.2^{\circ}\text{C}$, $3.2 \pm 0.3^{\circ}\text{C}$, $15 \pm 0.4^{\circ}\text{C}$ and $18 \pm 0.3^{\circ}\text{C}$ and fed *ad libitum* with a suspension of *Isochrysis galbana* and *Dunaliella marina* algae. Specimens were left to acclimatize to the culturing conditions for four weeks. During the experiments, shell growth, temperature, phytoplankton cell counts, chlorophyll concentration, particulate organic carbon content and siphon activity were monitored. The experiment lasted for 95 days, after which the specimens were euthanized, and soft tissue was removed from the shells. Clean shells were rinsed with fresh water, dried at room temperature ($\sim 20^{\circ}\text{C}$), and stored under cool and dry conditions after the growth experiment. Additional details on the growing conditions of the specimens and the setup of the experiments can be found in Witbaard et al. (1998).

2. Sampling strategy

Aragonite from cleaned and dried shells from these lab-grown *Arctica islandica* specimens was sampled using a hand-held Dremel 3000 rotary drill at low speed equipped with a tungsten-carbide drill bit. Minimal pressure was applied to carefully flake off parts of the shell and prevent heating of the samples due to friction, which may alter the Δ_{47} value of the aragonite (Staudigel and Swart, 2016). Care was taken to only sample the part of the shells that grew during the experiment. Pre-experimental shell material was easily avoided due to a clear growth line and color change that separated natural from lab-grown shell material (see **Fig. S1**).

3. Clumped isotope analyses

Aragonite aliquots were reacted with nominally anhydrous (103%) phosphoric acid at 70°C . The produced CO_2 gas was led through two liquid nitrogen-cooled (-196°C) cryogenic traps and a

PoraPak™ Q trap (Merck KGaA, Darmstadt, Germany) kept at -40°C or (after October 2020) -50°C through a custom-built external cooling unit (Dennis and Schrag, 2010). The purified CO_2 gas was analyzed in micro-volume mode using the LIDI workflow with 400 s integration time against a clean CO_2 working gas ($\delta^{13}\text{C} = -2.82\text{‰}$; $\delta^{18}\text{O} = -4.67\text{‰}$) and corrected for pressure baseline effects (Bernasconi et al., 2013; Meckler et al., 2014; Müller et al., 2017). Clumped isotope values were corrected to the Intercarb-Carbon Dioxide Equilibrium Scale (I-CDES) by creating an empirical transfer function (ETF) using measurements of ETH standards (ETH-1, -2 and -3) and their accepted Intercarb values (Bernasconi et al., 2021). We applied the ETF in a moving window of 200 analyses before and after the sample, considering standards measured within a time window of 2–3 weeks surrounding the sample for its correction. This typically resulted in 13 ETH-1, 13 ETH-2 and 70 ETH-3 measurements to constrain the ETF for each sample aliquot. Higher amounts of ETH-3 standards were analyzed to better constrain uncertainties around the expected Δ_{47} values of samples (Kocken et al., 2019). Measurements of the ETH-3 standard were also included every 3–5 samples to check for measurement drift at shorter timescales than the moving window of the ETF.

4. Data compilation

All included datasets except for Kluge et al. (2015) reported measured values for the ETH-1, -2 and -3 standards, yielding three anchor points for the reference scale calibration. The Kluge et al. (2015) data was calibrated to I-CDES using the ETH-3 and Carrara marble standard using the simplified linear correction in Appendix A of Bernasconi et al. (2021). To obtain an I-CDES Δ_{47} value for the Carrara marble standard (which is not reported in Bernasconi et al., 2021), we averaged the 19 replicates of Carrara marble reported in Bernasconi et al. (2018) after correcting their values to the I-CDES scale through the ETH standards, resulting in a value of $0.325 \pm 0.008\text{‰}$ (95% confidence level).

Where possible, we used means and standard deviations of the calcification temperature of the samples as reported in the literature. Measurement uncertainty was often reported at the level of standard errors on the mean of multiple aliquots of the same sample. The standard deviation of Δ_{47} values on individual aliquots was estimated from repeated measurements of reference materials not involved in the calibration (e.g. ETH-4 or Carrara marble) or, if these were not reported, by back-calculating the standard deviation from the standard error through multiplication by the square root of the sample size. In absence of uncertainties on the calcification temperature, the standard deviation of the temperatures was assumed to be 1°C for samples in the low-temperature domain (<100°C) and 10°C for high-temperature samples (the 850°C heated aragonites from Müller et al., 2017).

The Guo et al. (2009) temperature dependencies were brought into the I-CDES reference frame by updating the Δ_{47} - Δ_{63} fractionation factor to 0.268‰ (following Dennis et al., 2011), applying the Δ_{47} -dependent scaling of the Δ_{47} - Δ_{63} fractionation factor of 35 ppm/‰ (cited in Guo et al., 2009 and implemented in Jautzy et al., 2020) and calibrating to the I-CDES scale using a linear calibration through the Δ_{47} values of ETH-1 and ETH-3. For this calibration, the “new” I-CDES values for ETH-1 and ETH-3 were retrieved from Bernasconi et al. (2021) and the “old” CDES25 (CDES with reference to a reaction temperature of 25°C) values were obtained by solving the polynomial functions for the formation temperatures of the ETH standards (assumed to be 20°C for ETH-3 and 600°C for ETH-1, following Meckler et al., 2014).

5. Statistical evaluation

Differences between temperatures and between specimens within the same temperature treatment were tested using a one-way ANOVA and post-hoc Tukey multiple pairwise comparisons (see **S5**). Uncertainties on Δ_{47} values and calcification temperatures on the aliquot level are propagated through all statistical procedures, and uncertainty-weighted means and 95% confidence levels of samples are used for plotting throughout the manuscript (see section 6 below). The difference in

reproducibility between aliquots measured on our MAT253 (σ of reproducibility of IAEA-C2 of 0.046‰) and our MAT253 plus (σ of reproducibility of IAEA-C2 of 0.026‰) was considered in our error propagation by initially grouping aliquots by instrument and summarizing statistics (means and σ). The weighted mean and uncertainty of all aliquots from the same specimen or treatment group, but measured on different instruments, was then calculated by combining the statistics of groups of aliquots from the two machines and weighting the contribution of the two instrument groups by the factor $\frac{N}{\sigma^2}$, in which N is the number of aliquots in the instrument group and σ is the standard deviation representing the reproducibility within the group. For the value of σ , either the external standard deviation based on IAEA-C2 measurements on that instrument was used or the standard deviation between the Δ_{47} values of the aliquots within the group, whichever yielded the largest (and therefore most conservative) estimate of the uncertainty. This approach was based on work by Tatebe (2005) and Kirchner (2006) and the calculations are worked out in detail below (derivation) and **S5** (R script). To incorporate uncertainty on both Δ_{47} values and calcification temperatures at the aliquot level into our regressions, we apply a York regression (York, 1966) that takes into account errors on the independent variable as implemented in the “bfsI” R package by Patrick Sturm (Sturm, 2018). This linear York regression is repeated for the full dataset and for the dataset excluding high temperature (>30°C) datapoints to test the effect of these measurements on the regression. Throughout these statistical evaluations, it is assumed that uncertainties on Δ_{47} values and calcification temperatures are normally distributed.

6. Calculating weighted means and standard deviations

Suppose we have a dataset of measurements that measure the same quantity with different uncertainty. This difference in uncertainty can be taken into account when determining the mean and standard deviation of the dataset. In this document we derive equations for the weighted mean and standard deviation for a dataset of raw measurements, and for a dataset consisting pre-binned data in two or more bins.

6.1 Dataset of individual measurements

Suppose we have a dataset consisting of several raw measurements, all with their own uncertainty. The mean and standard deviation of the dataset can be calculated by weighting the measurements, and the optimal choice of weights is based on the inverse of the measurement variance (Kirchner, 2006).

To put this in mathematical terms: we have a dataset of n measurements x_1, \dots, x_n each with known variance $\sigma_1^2, \dots, \sigma_n^2$ (note that we express the variance as the square of the standard deviation σ). In order to calculate the weighted mean μ and standard deviation σ , we define weights $w_i = 1/\sigma_i^2 = \sigma_i^{-2}$ for $i = 1, \dots, n$. Following equations (1) and (2) of Kirchner, (2006), we find:

$$\mu = \frac{\sum_{i=1}^n w_i \cdot x_i}{\sum_{i=1}^n w_i} \quad (1)$$

$$\sigma = \sqrt{\frac{n}{n-1} \cdot \frac{\sum_{i=1}^n w_i \cdot (x_i - \mu)^2}{\sum_{i=1}^n w_i}} \quad (2)$$

Note that in case of equal weights for all measurements (i.e. $w_i = 1$ for $i = 1, \dots, n$), Equations (1) and (2) coincide with the well-known formulas for unweighted mean and standard deviation:

$$\mu = \frac{\sum_{i=1}^n 1 \cdot x_i}{\sum_{i=1}^n 1} = \frac{\sum_{i=1}^n x_i}{n}$$
$$\sigma = \sqrt{\frac{n}{n-1} \cdot \frac{\sum_{i=1}^n 1 \cdot (x_i - \mu)^2}{\sum_{i=1}^n 1}} = \sqrt{\frac{n}{n-1} \cdot \frac{\sum_{i=1}^n (x_i - \mu)^2}{n}} = \sqrt{\frac{\sum_{i=1}^n (x_i - \mu)^2}{n-1}}$$

6.2 Binned datasets

Consider now the situation where the raw measurements have been binned in two or more bins. We know the mean, standard deviation, and bin size of the bins. From this information, we can estimate the weighted mean and standard deviation of the combination of bins. In this case, we weight the measurements using the inverse of the bin variance.

6.3 Dataset of two bins

First suppose we have two bins. Let's put this in mathematical terms again. We have two bins: B_1 with mean μ_1 , standard deviation σ_1 , and size n_1 , and B_2 with mean μ_2 , standard deviation σ_2 , and size n_2 . Bin B_1 consists of (unknown) measurements y_1, \dots, y_{n_1} , and B_2 consists of (unknown) measurements z_1, \dots, z_{n_2} . The combination of the bins has size $n = n_1 + n_2$ and consists of (unknown) measurements $x_1, \dots, x_n = y_1, \dots, y_{n_1}, z_1, \dots, z_{n_2}$. We want to estimate the weighted mean and standard deviation using weights $w_1 = 1/\sigma_1^2$ for the measurements of B_1 , and $w_2 = 1/\sigma_2^2$ for the measurements of B_2 . The derivations in this section were inspired by the analysis of Tatebe (2005).

For the weighted mean, we apply Equation (1) to find:

$$\begin{aligned} \mu &= \frac{\sum_{i=1}^n w_i \cdot x_i}{\sum_{i=1}^n w_i} && \text{Apply Equation (1)} \\ &= \frac{\sum_{i=1}^{n_1} w_1 \cdot y_i + \sum_{i=1}^{n_2} w_2 \cdot z_i}{\sum_{i=1}^{n_1} w_1 + \sum_{i=1}^{n_2} w_2} && \text{Split sums into the two bins} \\ &= \frac{w_1 \cdot \sum_{i=1}^{n_1} y_i + w_2 \cdot \sum_{i=1}^{n_2} z_i}{n_1 \cdot w_1 + n_2 \cdot w_2} && \begin{array}{l} \text{The weights in the sums are constants, so the} \\ \text{sums can be simplified} \end{array} \\ &= \frac{w_1 \cdot n_1 \cdot \mu_1 + w_2 \cdot n_2 \cdot \mu_2}{n_1 \cdot w_1 + n_2 \cdot w_2} && \begin{array}{l} \text{For } B_1 \text{ we have } \sum_{i=1}^{n_1} y_i = n_1 \cdot \mu_1, \\ \text{(3)} \end{array} \end{aligned}$$

and a similar relation holds for B_2 .

Note that in case of equal weighting (i.e., $w_1 = w_2 = 1$), Equation (3) comes down to a weighted mean that only takes the difference in bin size into account.

The derivation for the weighted standard deviation is more elaborate. First, we apply Equation (2).

Using the same line of reasoning as for the mean, we find:

$$\begin{aligned}
 \sigma &= \sqrt{\frac{n}{n-1} \cdot \frac{\sum_{i=1}^n w_i \cdot (x_i - \mu)^2}{\sum_{i=1}^n w_i}} \\
 &= \sqrt{\frac{n}{n-1} \cdot \frac{\sum_{i=1}^{n_1} w_1 \cdot (y_i - \mu)^2 + \sum_{i=1}^{n_2} w_2 \cdot (z_i - \mu)^2}{\sum_{i=1}^{n_1} w_1 + \sum_{i=1}^{n_2} w_2}} \\
 &= \sqrt{\frac{n}{n-1} \cdot \frac{w_1 \cdot \sum_{i=1}^{n_1} (y_i - \mu)^2 + w_2 \cdot \sum_{i=1}^{n_2} (z_i - \mu)^2}{n_1 \cdot w_1 + n_2 \cdot w_2}} \tag{4}
 \end{aligned}$$

We can rewrite the terms $\sum_{i=1}^{n_1} (y_i - \mu)^2$ and $\sum_{i=1}^{n_2} (z_i - \mu)^2$ to eliminate the unknown measurements y_i and z_i from the equation. We consider the first term and note that the same line of reasoning holds for the second term. The keys to rewriting the terms are first adding $(\mu_1 - \mu) = 0$ to the sum, and then writing out the product of sums in separate sums:

$$\begin{aligned}
 \sum_{i=1}^{n_1} (y_i - \mu)^2 &= \sum_{i=1}^{n_1} ((y_i - \mu_1) + (\mu_1 - \mu))^2 \\
 &= \sum_{i=1}^{n_1} (y_i - \mu_1)^2 + 2 (y_i - \mu_1) \cdot (\mu_1 - \mu) + (\mu_1 - \mu)^2 \\
 &= \sum_{i=1}^{n_1} (y_i - \mu_1)^2 + \sum_{i=1}^{n_1} 2 (y_i - \mu_1) \cdot (\mu_1 - \mu) + \sum_{i=1}^{n_1} (\mu_1 - \mu)^2 \tag{5}
 \end{aligned}$$

We rewrite each of the three sums in Equation (5) separately. For the first sum, we use the formula of the (unweighted) standard deviation applied to bin B_1 :

$$\sum_{i=1}^{n_1} (y_i - \mu_1)^2 = (n_1 - 1) \cdot \sigma_1^2 \quad (6)$$

For the second sum, we note that $(\mu_1 - \mu)$ is a constant, so we can take it out of the summation:

$$\begin{aligned} \sum_{i=1}^{n_1} 2 (y_i - \mu_1) \cdot (\mu_1 - \mu) &= 2 \cdot (\mu_1 - \mu) \cdot \sum_{i=1}^{n_1} (y_i - \mu_1) \\ &= 2 \cdot (\mu_1 - \mu) \cdot (\sum_{i=1}^{n_1} y_i - \sum_{i=1}^{n_1} \mu_1) \\ &= 2 \cdot (\mu_1 - \mu) \cdot (n_1 \cdot \mu_1 - \sum_{i=1}^{n_1} \mu_1) \\ &= 2 \cdot (\mu_1 - \mu) \cdot (n_1 \cdot \mu_1 - n_1 \cdot \mu_1) \\ &= 0 \end{aligned} \quad (7)$$

For the third sum, we again use that $(\mu_1 - \mu)$ is a constant:

$$\sum_{i=1}^{n_1} (\mu_1 - \mu)^2 = n_1 \cdot (\mu_1 - \mu)^2 \quad (8)$$

Plugging Equations (6), (7) and (8) in Equation (5), we find:

$$\begin{aligned} \sum_{i=1}^{n_1} (y_i - \mu)^2 &= \sum_{i=1}^{n_1} (y_i - \mu_1)^2 + \sum_{i=1}^{n_1} 2 (y_i - \mu_1) \cdot (\mu_1 - \mu) + \sum_{i=1}^{n_1} (\mu_1 - \mu)^2 \\ &= (n_1 - 1) \cdot \sigma_1^2 + n_1 \cdot (\mu_1 - \mu)^2 \end{aligned} \quad (9)$$

The same derivation yields:

$$\sum_{i=1}^{n_2} (z_i - \mu)^2 = (n_2 - 1) \cdot \sigma_2^2 + n_2 \cdot (\mu_2 - \mu)^2 \quad (10)$$

Plugging Equations (9) and (10) in Equation (4), the formula for the weighted standard deviation becomes:

$$\sigma = \sqrt{\frac{n}{n-1} \cdot \frac{w_1 \cdot (n_1-1) \cdot \sigma_1^2 + w_1 \cdot n_1 \cdot (\mu_1 - \mu)^2 + w_2 \cdot (n_2-1) \cdot \sigma_2^2 + w_2 \cdot n_2 \cdot (\mu_2 - \mu)^2}{n_1 \cdot w_1 + n_2 \cdot w_2}} \quad (11)$$

This equation consists of all known values, making use of Equation (3) for the mean μ . Note that in case of equal weighting (i.e., $w_1 = w_2 = 1$), Equation (11) comes down to an unweighted

standard deviation of all measurements in the two bins in relation to the mean of Equation (3).

Equation (11) can also be written in terms of only the characteristics of the two bins, by plugging

Equation (3) in Equation (11) and rewriting the outcome. Consider the term $(\mu_1 - \mu)^2$. We can write:

$$\begin{aligned}
 (\mu_1 - \mu)^2 &= \left(\mu_1 - \frac{w_1 \cdot n_1 \cdot \mu_1 + w_2 \cdot n_2 \cdot \mu_2}{n_1 \cdot w_1 + n_2 \cdot w_2} \right)^2 \\
 &= \left(\frac{n_1 \cdot w_1 + n_2 \cdot w_2}{n_1 \cdot w_1 + n_2 \cdot w_2} \cdot \mu_1 - \frac{n_1 \cdot w_1}{n_1 \cdot w_1 + n_2 \cdot w_2} \cdot \mu_1 - \frac{n_2 \cdot w_2}{n_1 \cdot w_1 + n_2 \cdot w_2} \cdot \mu_2 \right)^2 \\
 &= \left(\frac{n_2 \cdot w_2}{n_1 \cdot w_1 + n_2 \cdot w_2} \cdot \mu_1 - \frac{n_2 \cdot w_2}{n_1 \cdot w_1 + n_2 \cdot w_2} \cdot \mu_2 \right)^2 \\
 &= \left(\frac{n_2 \cdot w_2}{n_1 \cdot w_1 + n_2 \cdot w_2} \cdot (\mu_1 - \mu_2) \right)^2 \\
 &= \frac{n_2^2 \cdot w_2^2}{(n_1 \cdot w_1 + n_2 \cdot w_2)^2} (\mu_1 - \mu_2)^2
 \end{aligned}$$

In the same way we can rewrite:

$$(\mu_2 - \mu)^2 = \frac{n_1^2 \cdot w_1^2}{(n_1 \cdot w_1 + n_2 \cdot w_2)^2} (\mu_2 - \mu_1)^2$$

Now, we can use the fact that $(\mu_2 - \mu_1)^2 = (\mu_1 - \mu_2)^2$ to simplify part of Equation (11):

$$\begin{aligned}
 &w_1 \cdot n_1 \cdot (\mu_1 - \mu)^2 + w_2 \cdot n_2 \cdot (\mu_2 - \mu)^2 \\
 &= w_1 \cdot n_1 \cdot \frac{n_2^2 \cdot w_2^2}{(n_1 \cdot w_1 + n_2 \cdot w_2)^2} (\mu_1 - \mu_2)^2 + w_2 \cdot n_2 \cdot \frac{n_1^2 \cdot w_1^2}{(n_1 \cdot w_1 + n_2 \cdot w_2)^2} (\mu_2 - \mu_1)^2 \\
 &= \frac{w_1 \cdot n_1 \cdot n_2^2 \cdot w_2^2 + w_2 \cdot n_2 \cdot n_1^2 \cdot w_1^2}{(n_1 \cdot w_1 + n_2 \cdot w_2)^2} (\mu_1 - \mu_2)^2 \\
 &= \frac{w_1 \cdot n_1 \cdot w_2 \cdot n_2 \cdot (n_1 \cdot w_1 + n_2 \cdot w_2)}{(n_1 \cdot w_1 + n_2 \cdot w_2)^2} (\mu_1 - \mu_2)^2 \\
 &= \frac{w_1 \cdot n_1 \cdot w_2 \cdot n_2}{n_1 \cdot w_1 + n_2 \cdot w_2} (\mu_1 - \mu_2)^2
 \end{aligned} \tag{12}$$

Plugging Equation (12) into Equation (11), we find:

$$\begin{aligned}
\sigma &= \sqrt{\frac{n}{n-1} \cdot \frac{w_1 \cdot (n_1-1) \cdot \sigma_1^2 + w_1 \cdot n_1 \cdot (\mu_1 - \mu)^2 + w_2 \cdot (n_2-1) \cdot \sigma_2^2 + w_2 \cdot n_2 \cdot (\mu_2 - \mu)^2}{n_1 \cdot w_1 + n_2 \cdot w_2}} \\
&= \sqrt{\frac{n_1 + n_2}{(n_1 + n_2 - 1) \cdot (n_1 \cdot w_1 + n_2 \cdot w_2)} \cdot \left(w_1 \cdot (n_1 - 1) \cdot \sigma_1^2 + w_2 \cdot (n_2 - 1) \cdot \sigma_2^2 + \frac{w_1 \cdot n_1 \cdot w_2 \cdot n_2}{n_1 \cdot w_1 + n_2 \cdot w_2} (\mu_1 - \mu_2)^2 \right)} \quad (13)
\end{aligned}$$

Equation (3) and (13) give the weighted mean and standard deviation in terms of the characteristics of the two bins. Filling in the weights $w_i = \sigma_i^{-2}$, we arrive at

$$\mu = \frac{\sigma_1^{-2} \cdot n_1 \cdot \mu_1 + \sigma_2^{-2} \cdot n_2 \cdot \mu_2}{\sigma_1^{-2} \cdot n_1 + \sigma_2^{-2} \cdot n_2} \quad (14)$$

$$\begin{aligned}
\sigma &= \sqrt{\frac{n_1 + n_2}{(n_1 + n_2 - 1) \cdot (n_1 \cdot \sigma_1^{-2} + n_2 \cdot \sigma_2^{-2})} \cdot \left(\sigma_1^{-2} \cdot (n_1 - 1) \cdot \sigma_1^2 + \sigma_2^{-2} \cdot (n_2 - 1) \cdot \sigma_2^2 + \frac{\sigma_1^{-2} \cdot n_1 \cdot \sigma_2^{-2} \cdot n_2}{n_1 \cdot \sigma_1^{-2} + n_2 \cdot \sigma_2^{-2}} (\mu_1 - \mu_2)^2 \right)} \\
&= \sqrt{\frac{n_1 + n_2}{(n_1 + n_2 - 1) \cdot (n_1 \cdot \sigma_1^{-2} + n_2 \cdot \sigma_2^{-2})} \cdot \left(n_1 + n_2 - 2 + \frac{\sigma_1^{-2} \cdot n_1 \cdot \sigma_2^{-2} \cdot n_2}{n_1 \cdot \sigma_1^{-2} + n_2 \cdot \sigma_2^{-2}} (\mu_1 - \mu_2)^2 \right)} \quad (15)
\end{aligned}$$

6.4 Dataset of more than two bins

Equation (3) gives the formula for a weighted mean of two bins. It can straightforwardly be generalized to hold for any number of bins B_j with means μ_j , standard deviations σ_j , sizes n_j , and weights $w_j = 1/\sigma_j^2$:

$$\mu = \frac{\sum w_j \cdot n_j \cdot \mu_j}{\sum w_j \cdot n_j} = \frac{\sum \sigma_j^{-2} \cdot n_j \cdot \mu_j}{\sum \sigma_j^{-2} \cdot n_j} \quad (16)$$

In the same way, Equation (11) can be generalized to hold for any number of bins B_j , using Equation (16) for the mean μ :

$$\begin{aligned}
\sigma &= \sqrt{\frac{\sum n_j}{(\sum n_j) - 1} \cdot \frac{\sum w_j \cdot (n_j - 1) \cdot \sigma_j^2 + \sum w_j \cdot n_j \cdot (\mu_j - \mu)^2}{\sum w_j \cdot n_j}} \\
&= \sqrt{\frac{\sum n_j}{(\sum n_j) - 1} \cdot \frac{\sum \sigma_j^{-2} \cdot (n_j - 1) \cdot \sigma_j^2 + \sum \sigma_j^{-2} \cdot n_j \cdot (\mu_j - \mu)^2}{\sum \sigma_j^{-2} \cdot n_j}}
\end{aligned}$$

$$= \sqrt{\frac{\sum n_j}{(\sum n_j) - 1} \cdot \frac{\sum (n_j - 1) + \sigma_j^{-2} \cdot n_j \cdot (\mu_j - \mu)^2}{\sum \sigma_j^{-2} \cdot n_j}} \quad (17)$$

Note that Equations (13) and (15) for the standard deviation cannot readily be generalized to hold for any number of bins. In case of more than two bins, the weighted mean is first calculated using Equation (16), and then the standard deviation can be calculated using this mean and Equation (17).

References

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Tatebe, K. (2005). *Combining Multiple Averaged Data Points And Their Errors*. <https://docplayer.net/33088897-Combining-multiple-averaged-data-points-and-their-errors.html>

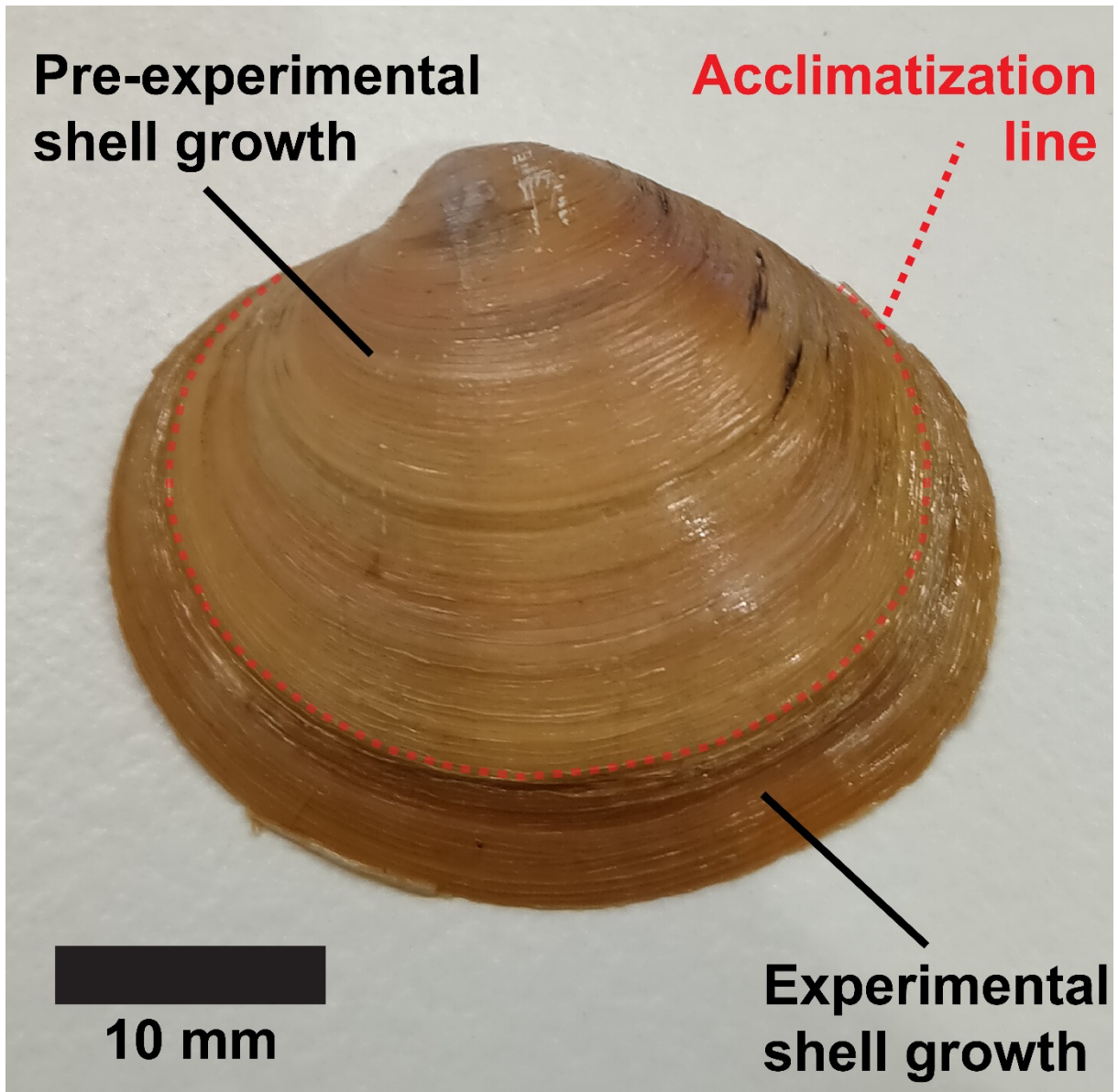


Figure S1. Showing a shell of cultured *Arctica islandica* with a clearly visible growth mark highlighting transplantation into the culturing conditions.

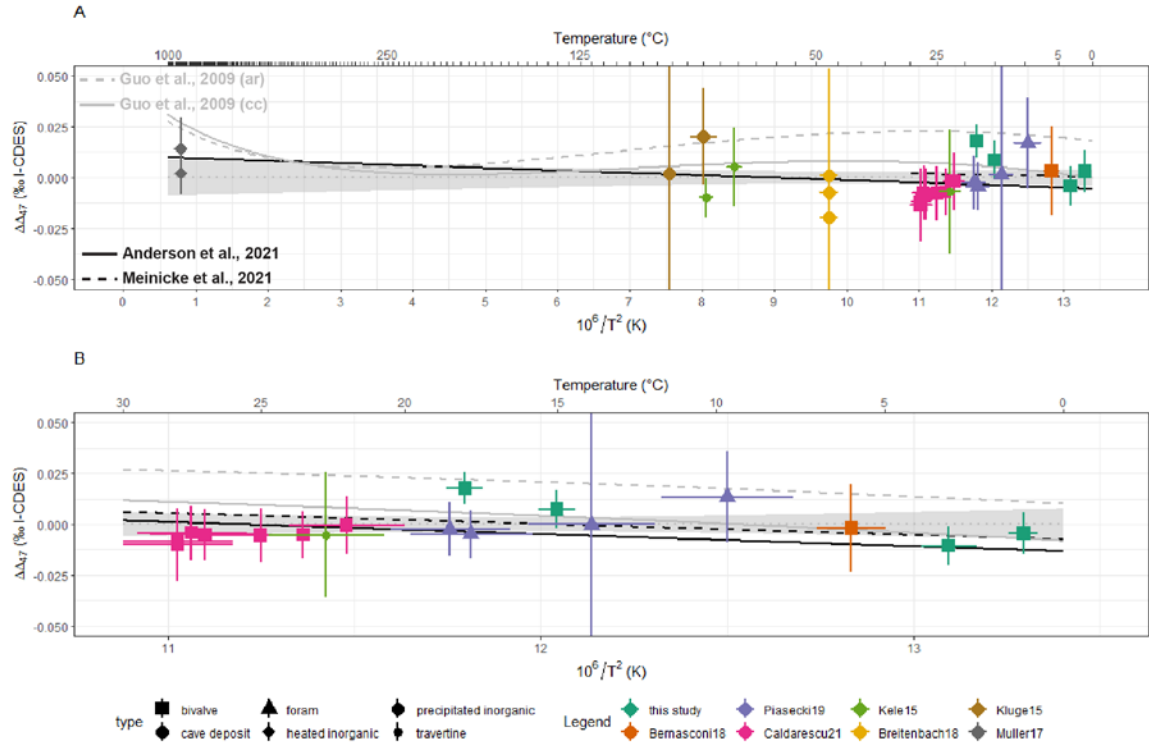


Figure S2. Residuals of aragonite $\Delta 47$ -temperature relationships. Showing the difference in clumped isotope value ($\Delta \Delta 47$) between aragonite $\Delta 47$ data and the two $\Delta 47$ -temperature regressions through the aragonite data compilation (see Fig. 2): A) Residuals relative to the York regression through the full dataset. B) Residuals relative to the York regression through only the low-temperature data (<30°C). Results are colored based on the study from which they originated and symbols code for the type of aragonite that was measured (see legend in A, following Fig. 2). Vertical and horizontal bars on symbols indicate uncertainty on $\Delta 47$ and formation temperature at the 95% confidence level. Note that some vertical error bars are cropped by the restricted extent of the vertical axis. The solid black line shows the unified clumped isotope calibration by Anderson et al. (2021) while the dashed black line represents the temperature relationship by Meinicke et al. (2020; 2021; only plotted for temperatures below 100°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 in the main text).

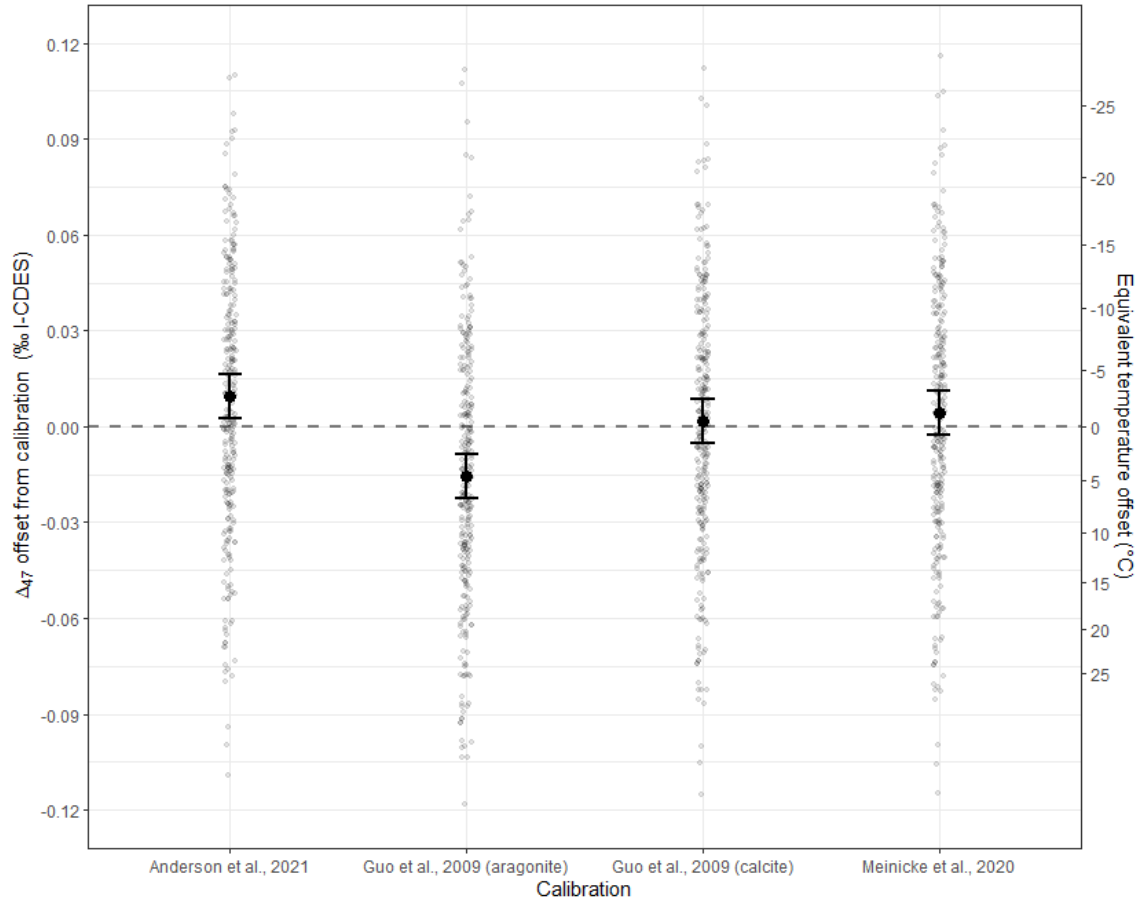


Figure S3. Zoomed out version of Figure 3 in the main text showing residuals of all *A. islandica* aliquots used in this study relative to the four previous clumped isotope temperature calibrations.

Overview of datasets included in aragonite compilation

Sample type	Temperature range $\pm 1\sigma$	Number of Δ_{47} aliquots	Reference
Precipitated aragonite	$80 \pm 2^\circ\text{C} - 91 \pm 0.5^\circ\text{C}$	11	Kluge et al., 2015
Heated aragonite	$850 \pm 10^\circ\text{C}$	35	Müller et al., 2017
Cave deposit	$47 \pm 1^\circ\text{C}$	16	Breitenbach et al., 2018
Travertine	$22.7 \pm 1^\circ\text{C} - 79.2 \pm 1^\circ\text{C}$	78	Kele et al., 2015
Foraminifera	$9.7 \pm 1^\circ\text{C} - 18.5 \pm 1^\circ\text{C}$	63	Piasecki et al., 2019
Mollusk	$6 \pm 0.5^\circ\text{C}$	12	Bernasconi et al., 2018
Mollusk	$22 \pm 1^\circ\text{C} - 28 \pm 1^\circ\text{C}$	165	Caldarescu et al., 2021
Mollusk	$1.1 \pm 0.2^\circ\text{C} - 18 \pm 0.3^\circ\text{C}$	278	This study
TOTAL		8	

Table S1. Overview of aragonite data from previous studies used for the compilation in this study.