ADVANCING EARTH AND SPACE SCIENCE

Geophysical Research Letters

RESEARCH LETTER
10.1029/2022GL099479

Temperature Dependence of Clumped Isotopes (Δ_{47}) in Aragonite

Niels J. de Winter[1,2,3], Rob Witbaard[4], Ilja J. Kocken[3], Inigo A. Müller[5], Jingjing Guo[3], Barbara Goudsmit[3,4], and Martin Ziegler[3]

[1]Department of Earth Sciences, Faculty of Science, Vrije Universiteit Amsterdam, Amsterdam, The Netherlands, [2]Analytical, Environmental and Geochemistry Group, Vrije Universiteit Brussel, Brussel, Belgium, [3]Department of Earth Sciences, Utrecht University, Utrecht, The Netherlands, [4]Department of Estuarine and Delta Systems, Royal Netherlands Institute for Sea Research, 't Horntje, Texel, The Netherlands, [5]Department of Earth Science, University of Geneva, Geneva, Switzerland

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 $\Delta_{47} - \frac{1}{T^2}$ relation in carbonate is non-linear, therefore adding hot calibration data offsets calibrations in the cold temperature range

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

N. J. de Winter,
niels_de_winter@live.nl

Citation:

de Winter, N. J., Witbaard, R., Kocken, I. J., Müller, I. A., Guo, J., Goudsmit, B., & Ziegler, M. (2022). Temperature dependence of clumped isotopes (Δ_{47}) in aragonite. *Geophysical Research Letters*, *49*, e2022GL099479. https://doi.org/10.1029/2022GL099479

Received 18 MAY 2022
Accepted 1 OCT 2022

Author Contributions:

Conceptualization: Niels J. de Winter, Martin Ziegler
Data curation: Niels J. de Winter, Ilja J. Kocken, Jingjing Guo, Barbara Goudsmit, Martin Ziegler
Formal analysis: Niels J. de Winter, Ilja J. Kocken, Inigo A. Müller, Martin Ziegler
Funding acquisition: Niels J. de Winter, Rob Witbaard, Martin Ziegler
Investigation: Niels J. de Winter, Inigo A. Müller, Jingjing Guo, Barbara Goudsmit, Martin Ziegler

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.

1. Introduction

Since its first applications (e.g., Ghosh et al., 2006; Schauble et al., 2003; Wang et al., 2004), 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:

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

Methodology: Niels J. de Winter, Rob Witbaard, Ilja J. Kocken, Inigo A. Müller, Martin Ziegler
Project Administration: Niels J. de Winter, Martin Ziegler
Resources: Niels J. de Winter, Rob Witbaard, Martin Ziegler
Software: Niels J. de Winter, Ilja J. Kocken
Supervision: Rob Witbaard, Inigo A. Müller, Martin Ziegler
Validation: Niels J. de Winter, Inigo A. Müller, Jingjing Guo, Barbara Goudsmit, Martin Ziegler
Visualization: Niels J. de Winter, Ilja J. Kocken, Inigo A. Müller, Jingjing Guo, Barbara Goudsmit, Martin Ziegler
Writing – original draft: Niels J. de Winter, Martin Ziegler
Writing – review & editing: Niels J. de Winter, Rob Witbaard, Ilja J. Kocken, Inigo A. Müller, Jingjing Guo, Barbara Goudsmit, Martin Ziegler

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 (e.g., Agterhuis et al., 2022; de Winter, Müller et al., 2021; Meckler et al., 2022; Henkes et al., 2018; Rodríguez-Sanz et al., 2017; Vickers, Lengger, et al., 2020).

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; Jautzy et al., 2020; Petersen et al., 2019). A unified linear $\Delta_{47} - \frac{1}{T^2}$ calibration was established through re-standardized Δ_{47} values of carbonates precipitated at a wide range of known temperatures (0.5–1,100°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 data set 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 (Guo et al., 2009; Schauble et al., 2006) 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 & 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., Buchardt & Símonarson, 2003; Butler et al., 2013; Schöne & Fiebig, 2009; Schöne et al., 2005; Witbaard et al., 1997). Combined with preexisting aragonite clumped isotope data (Bernasconi et al., 2018; Breitenbach et al., 2018; Caldarescu et al., 2021; Kele et al., 2015; Kluge et al., 2015; Müller et al., 2017; Piasecki et al., 2019) standardized to the new Intercarb-Carbon Dioxide Equilibrium Scale (I-CDES) reference frame (Bernasconi et al., 2021), our data set resolves potential vital effects on clumped isotopes in aragonitic mollusks by comparing species as well as 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; Supporting Information S9, https://doi.org/10.5281/zenodo.6524705). Details on the culturing setup are provided in Supporting Information S1 and Witbaard et al. (1998). Aragonite from cleaned and dried *Arctica islandica* shells was sampled using

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

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‰	+0.002‰	+0.003‰	**−0.016‰**
					−2.12°C	−0.61°C	−0.75°C	**+4.48°C**
Ais3	3.2 ± 0.3°C	Mixed	0.667 ± 0.010‰	72	+0.001‰	−0.005‰	−0.006‰+1.57°C	**−0.023‰**
					−0.27°C	+1.24°C		**+6.80°C**
Ais15	15 ± 0.4°C	Mixed	0.637 ± 0.009‰	57	**+0.013‰**	+0.008‰	+0.004‰	**−0.013‰**
					−3.63°C	−2.10°C	−0.99°C	**+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‰**	**+0.016‰**	**+0.012‰**	−0.004‰
					−6.63°C	**−5.10°C**	**−3.99°C**	+1.25°C

Note. "Ais" = Arctica islandica. Significant Δ47 and temperature offsets are labeled in bold. cc = calcite, ar = aragonite.

a hand-held Dremel 3,000 rotary drill at low speed equipped with a tungsten-carbide drill bit (see Supporting Information 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 Supporting Information 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 International Union of Pure and Applied Chemistry 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 Supporting Information S2, https://doi.org/10.5281/zenodo.6524705.

2.3. Data Compilation

The *Arctica islandica* data set was augmented with literature Δ_{47} values of aragonites with known calcification temperatures (see Supporting Information S3, https://doi.org/10.5281/zenodo.6524705). The data set 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 (Bernasconi et al., 2018; Kele et al., 2015), 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., Dong et al., 2021; Ghosh et al., 2006, 2007; Tripati et al., 2010; Wacker et al., 2013, 2014; Zhai et al., 2019; Zhang et al., 2018) were not included because they were not corrected for the pressure baseline (Bernasconi et al., 2013; He et al., 2012), 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., 2016; Chen et al., 2019; Supporting Information S1 and Supporting Information S3, https://doi.org/10.5281/zenodo.6524705). 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 Supporting Information 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 Supporting Information S1). The full data set including Δ_{47} values and temperatures with their uncertainties used in this study is provided in Supporting Information S4, https://doi.org/10.5281/zenodo.6524705. Unless stated otherwise, uncertainties are cited at the 95% confidence level.

All data processing for this study was done in *R* (R Core Team, 2022) and scripts are provided in Supporting Information S5, https://doi.org/10.5281/zenodo.6524705 and published on Github (https://github.com/nielsjdewinter/Aragonite_clumped). Details on data processing are provided in Supporting Information S1. We compare our data with calibrations by Anderson et al. (2021) and a compilation of foraminifera calibration data from Peral et al. (2018) and Meinicke et al. (2020) as well as with temperature dependencies of aragonite and calcite clumped isotope compositions from ab initio modeling in Guo et al. (2009) brought into the I-CDES reference frame (see Supporting Information 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 Supporting Information S6, https://doi.org/10.5281/zenodo.6524705). 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 Supporting Information S6, https://doi.org/10.5281/zenodo.6524705). 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; Supporting Information S6, https://doi.org/10.5281/zenodo.6524705).

We investigated the $\Delta_{47} - \frac{1}{T^2}$ 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 with the small range of temperatures of the lab-grown *A. islandica* leaves relatively high uncertainty on a clumped isotope-temperature regression through these results alone compared with calibrations covering a larger temperature range such as the unified clumped isotope calibration (Anderson et al., 2021). We therefore do not advice using this and other regression equations in Section 3 for calibrating clumped isotope results (see Discussion).

Firstly, a statistically significant temperature relationship ($\Delta_{47} - \frac{1}{T^2}$ slope >0; 95% CL) is found for Δ_{47} exclusively from *Arctica islandica* samples:

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

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

$$\Delta_{47}(I-\mathrm{CDES}) = 0.0443 \pm 0.0024 * \frac{10^6}{T^2} + 0.097 \pm 0.0291 \ (\mathrm{T\ in\ K},\ \pm 1\sigma;\ \sigma_{\mathrm{res}} = 0.043‰) \quad (3)$$

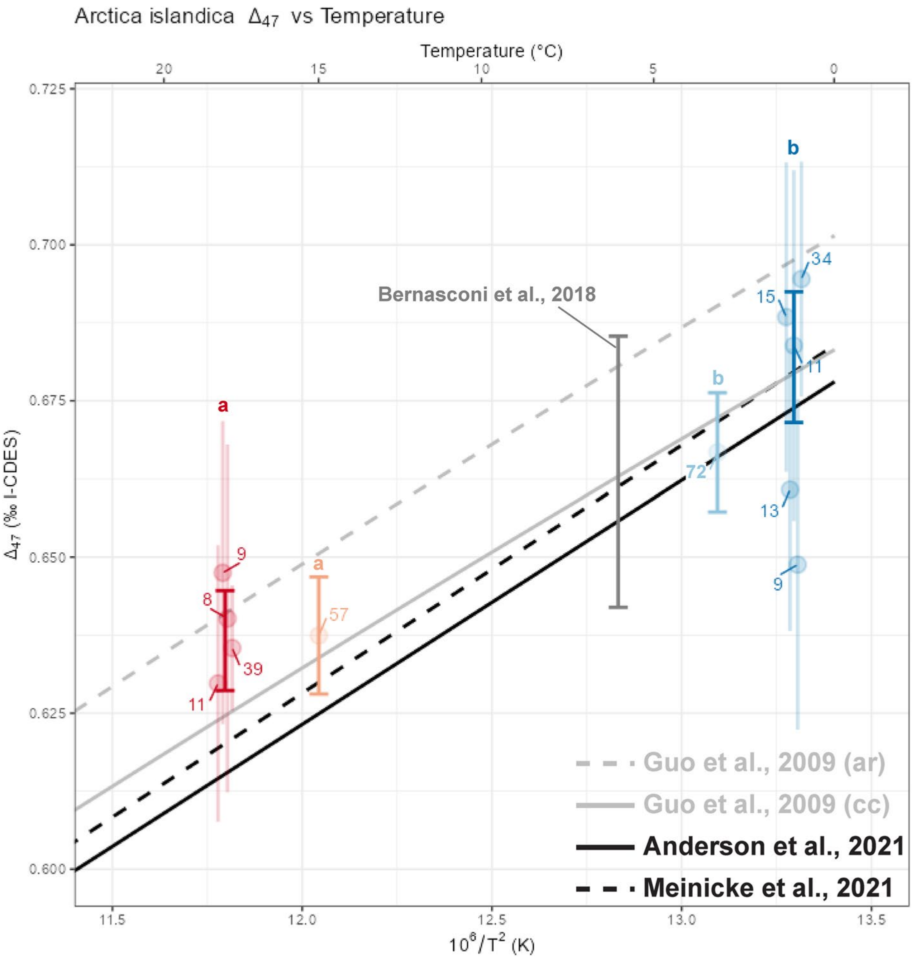

Figure 1. *Arctica islandica* Δ_{47} results. Clumped isotope results are aggregated by specimen or multi-specimen sample (round symbols; see Table 1). Vertical lines represent 95% CL and number indicate sample size. Data is color-coded per temperature treatment (1°C, 3°C, 15°C and 18°C), with bold error bars indicating 95% CL, pairs of letter labels (a and b) indicate statistically indistinguishable Δ_{47} values ($p < 0.05$). The gray error bar at 6°C highlights (a) *islandica* data from Bernasconi et al. (2018; recalculated to Intercarb-Carbon Dioxide Equilibrium Scale (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. Gray 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 Supporting Information 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.

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 the foraminifera-based calibration by Peral et al. (2018) and Meinicke et al. (2020) combined with reference to I-CDES in Meinicke et al. (2021) and the Guo et al. (2009) theoretical temperature relationships (Figure 2b):

$$\Delta_{47}(I-\mathrm{CDES}) = 0.0451 \pm 0.0024 * \frac{10^6}{T^2} + 0.0871 \pm 0.0287 \;(\mathrm{T\ in\ K},\ \pm 1\sigma;\ \sigma_{\mathrm{res}} = 0.042‰) \tag{4}$$

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 Figure 2):

$$\Delta_{47}(I-\mathrm{CDES}) = 0.0403 \pm 0.0005 * \frac{10^6}{T^2} + 0.1435 \pm 0.0485 \;(\mathrm{T\ in\ K},\ \pm 1\sigma;\ \sigma_{\mathrm{res}} = 0.040‰) \tag{5}$$

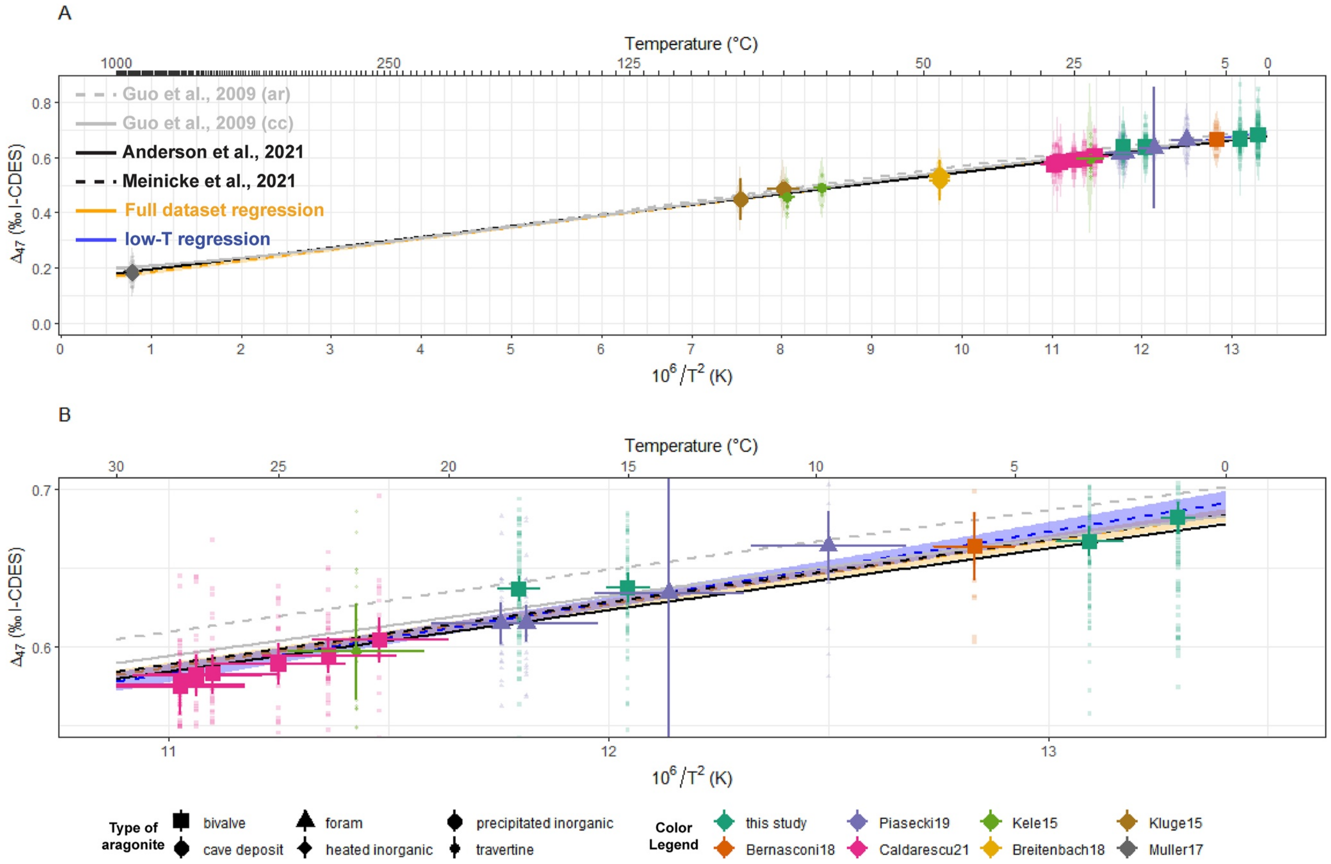

Figure 2. Aragonite Δ_{47} temperature dependence. Clumped isotope data of aragonite samples plotted against formation temperature. (a) All data plotted over the full temperature range (1°C–850°C). Individual datapoints, averages and uncertainty on temperature and Δ_{47} values (95% CL) are color-coded 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). Gray solid and dashed lines represent, respectively, the theoretical calcite ("cc") and aragonite ("ar") temperature dependencies from Guo et al. (2009; projected on the Intercarb-Carbon Dioxide Equilibrium Scale (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.

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; $\Delta\Delta_{47} = +0.009 \pm 0.007$‰; -2.71 ± 2.03°C; Figure 3; $\Delta\Delta_{47}$ = offset between data and calibration). The theoretical aragonite clumped isotope-temperature relationship (Guo et al., 2009) severely overestimates our *A. islandica* temperatures (-0.016 ± 0.007‰; $+4.35 \pm 1.88$°C; Figure 3). Contrarily, the Meinicke et al. (2020, 2021) calibration ($\Delta\Delta_{47} = +0.004 \pm 0.007$‰; -1.17 ± 2.00°C; Figure 3) and the theoretical calcite temperature relationship (Guo et al., 2009; $\Delta\Delta_{47} = +0.002 \pm 0.007$‰; -0.47 ± 1.98°C; Figure 3) 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 $\Delta_{47} - \frac{1}{T^2}$ linear relationship with other low-temperature aragonite datapoints (Figures 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 $+0.003 \pm 0.004$‰, see Figure 2 and Supporting Information S8, https://doi.org/10.5281/zenodo.6524705) and agreement between the linear $\Delta_{47} - \frac{1}{T^2}$ dependence of the aragonitic mollusk data in this study and the regression through the complete low-temperature aragonite data set (Figure 1 and Section 3.1) strongly supports a common

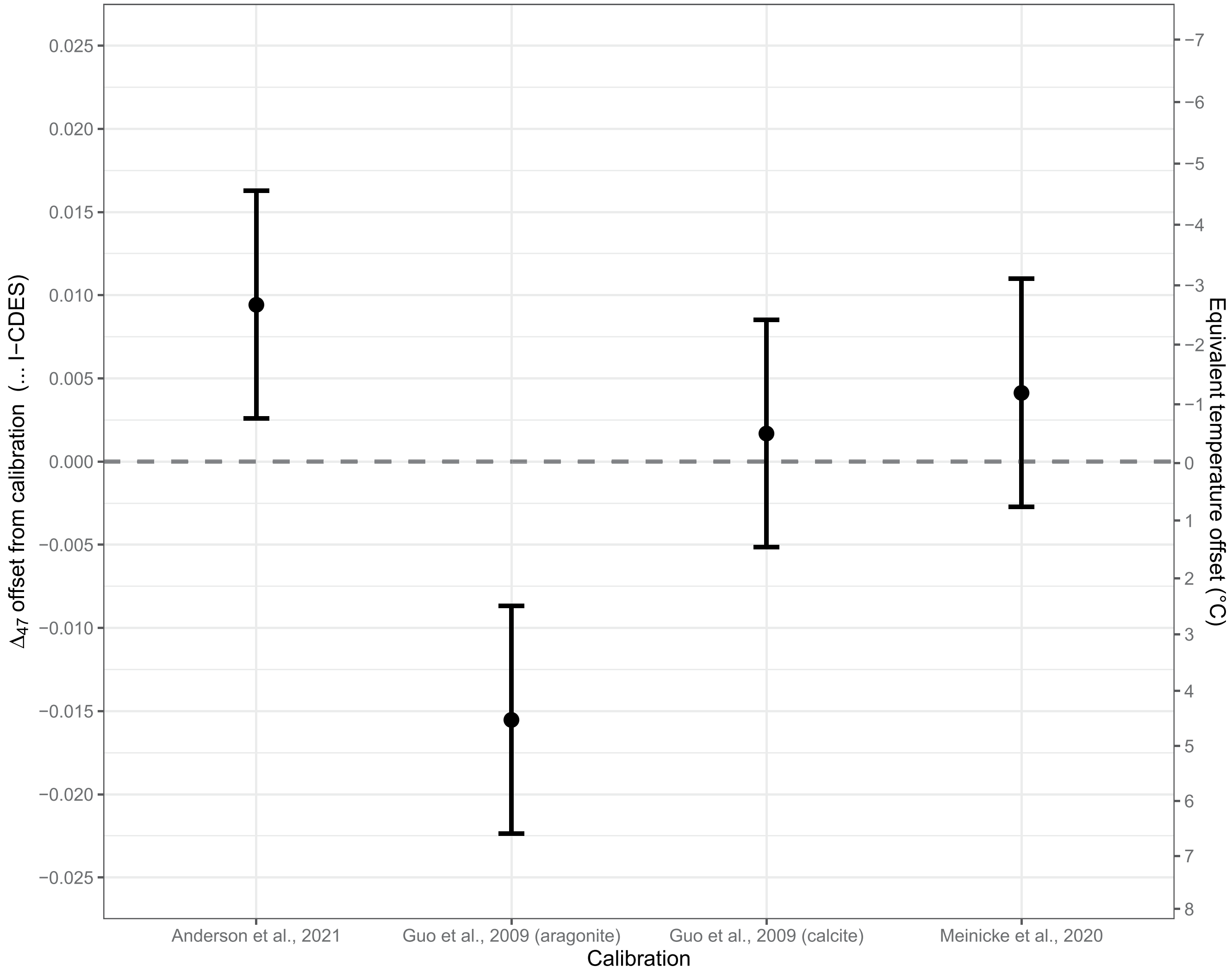

Figure 3. Offset of *A. islandica* data from temperature regressions. Shaded gray points show residual Δ_{47} values relative to four clumped isotope temperature relationships (see horizontal axis). Black symbols with error bars (95% CL) show mean offsets of all *A. islandica* datapoints (grown at 1°C, 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* data set (8.6°C; see Supporting Information S4, https://doi.org/10.5281/zenodo.6524705) based on Anderson et al. (2021).

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; Figures 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; Figure 1, Table 1 and Supporting Information S6, https://doi.org/10.5281/zenodo.6524705). 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 3.2, Equation 4 and Figure 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 data set (±0.8°C; 1σ; see Supporting Information S4, https://doi.org/10.5281/zenodo.6524705) 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 Supporting Information S4, https://doi.org/10.5281/zenodo.6524705). 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; Figure 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) this would result in an offset between our aragonite data set and the previous calcite-based calibrations (e.g., Meinicke et al., 2020, 2021). The close similarity between our *A. islandica* data and the calcite calibration ($\Delta\Delta_{47} = 0.004 \pm 0.007$‰; Figure 3; Supporting Information S7, https://doi.org/10.5281/zenodo.6524705) 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 (Anderson et al., 2021; Meinicke et al., 2020, 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 modeled 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 samples precipitated at 30°C), while underestimating colder datapoints ($\Delta\Delta_{47}$ of $+0.009 \pm 0.008$‰, or $-2.0^{+2.0}_{-2.0}$ °C for samples precipitated at 0°C; Figure 2; Supporting Information S7, https://doi.org/10.5281/zenodo.6524705). Point-by-point offsets of all data from the calibration lines are provided in Supporting Information S8, https://doi.org/10.5281/zenodo.6524705.

This difference between $\Delta_{47} - \frac{1}{T^2}$ regressions through the low-temperature (<30°C) and the full data set (see Section 3.2; Figure 2) likely highlights non-linear behavior of the $\Delta_{47} - \frac{1}{T^2}$ relationship in aragonites. In fact, previous studies based on both clumped isotope analyses and ab initio modeling have suggested a non-linear $\Delta_{47} - \frac{1}{T^2}$ 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) data set, where Δ_{47} values of calcites precipitated between 100°C and 1,000°C are underestimated by the linear relationship, while the hottest datapoints (calcites heated to 1,100°C) fall on the linear regression, mimicking the reduced $\Delta_{47} - \frac{1}{T^2}$ 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 $\Delta_{47} - \frac{1}{T^2}$ relationship through a calibration data set 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 Figures 2 and 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., de Winter et al., 2020, de Winter, Dämmer et al., 2021; Huyghe et al., 2022; Kele et al., 2015). 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., Meinicke et al., 2020; Peral et al., 2018; Piasecki et al., 2019). 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 Figure 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 data set. 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 $\Delta_{47} - \frac{1}{T^2}$ relationship in the cold temperature domain with higher accuracy than the Anderson et al. (2021) calibration (Figures 1 and 3; Supporting Information S8, https://doi.org/10.5281/zenodo.6524705). 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 $\Delta_{47} - \frac{1}{T^2}$ 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* data set ($N = 278$; see Figure 3) to resolve. However, in paleoclimate reconstructions (e.g., Agterhuis et al., 2022; de Winter, Müller et al., 2021; de Winter et al., 2017; Meckler et al., 2022; Petersen et al., 2016; Vickers, Fernandez, et al., 2020), 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; IPCC, 2021; Modestou et al., 2020; Tierney et al., 2020; Westerhold et al., 2020). Accurate clumped isotope-based temperature reconstructions therefore require calibration data sets with precisely constrained formation temperatures tailored to the temperature range of the samples.

Data Availability Statement

Supplementary materials are deposited on the open-source repository Zenodo and can be accessed through the following link: https://doi.org/10.5281/zenodo.6524705. *R* scripts are uploaded on GitHub (https://github.com/nielsjdewinter/Aragonite_clumped) and archived in Zenodo (https://doi.org/10.5281/zenodo.6560188). In addition, all clumped isotope data produced for this study were deposited in the EarthChem Library and are freely accessible through the following DOI: https://doi.org/10.26022/IEDA/112316.

Acknowledgments
The authors would like to thank Nele Meckler and Stefano Bernasconi for their thoughtful review of the manuscript, and editor Angelicque White for moderating the review process. Thanks to Arnold van Dijk and Desmond Eefting for their technical assistance in the UU clumped isotope lab. This work is part of the UNBIAS project jointly funded by a Flemish Research Foundation (FWO; 12ZB220N) post-doctoral fellowship (NJW) and a MSCA Individual Fellowship (H2020-MSCA-IF-2018; 843011—UNBIAS; awarded to NJW). BG is supported by an UU-NIOZ collaboration grant.

References

Agterhuis, T., Ziegler, M., de Winter, N. J., & Lourens, L. J. (2022). Warm deep-sea temperatures across Eocene Thermal Maximum 2 from clumped isotope thermometry. *Communications Earth & Environment*, *3*, 1–9. https://doi.org/10.1038/s43247-022-00350-8

Anderson, N. T., Kelson, J. R., Kele, S., Daëron, M., Bonifacie, M., Horita, J., et al. (2021). A unified clumped isotope thermometer calibration (0.5–1, 100°C) using carbonate-based standardization. *Geophysical Research Letters*, *48*(7), e2020GL092069. https://doi.org/10.1029/2020GL092069

Bernasconi, S. M., Daëron, M., Bergmann, K. D., Bonifacie, M., Meckler, A. N., Affek, H. P., et al. (2021). InterCarb: A community effort to improve interlaboratory standardization of the carbonate clumped isotope thermometer using carbonate standards. *Geochemistry, Geophysics, Geosystems*, *22*(5), e2020GC009588. https://doi.org/10.1029/2020GC009588

Bernasconi, S. M., Hu, B., Wacker, U., Fiebig, J., Breitenbach, S. F., & Rutz, T. (2013). Background effects on Faraday collectors in gas-source mass spectrometry and implications for clumped isotope measurements. *Rapid Communications in Mass Spectrometry*, *27*(5), 603–612. https://doi.org/10.1002/rcm.6490

Bernasconi, S. M., Müller, I. A., Bergmann, K. D., Breitenbach, S. F., Fernandez, A., Hodell, D. A., et al. (2018). Reducing uncertainties in carbonate clumped isotope analysis through consistent carbonate-based standardization. *Geochemistry, Geophysics, Geosystems*, *19*(9), 2895–2914. https://doi.org/10.1029/2017gc007385

Brand, W. A., Assonov, S. S., & Coplen, T. B. (2010). Correction for the 17O interference in δ(13C) measurements when analyzing CO_2 with stable isotope mass spectrometry (IUPAC Technical Report). *Pure and Applied Chemistry*, *82*(8), 1719–1733. https://doi.org/10.1351/pac-rep-09-01-05

Breitenbach, S. F. M., Mleneck-Vautravers, M. J., Grauel, A.-L., Lo, L., Bernasconi, S. M., Müller, I. A., et al. (2018). Coupled Mg/Ca and clumped isotope analyses of foraminifera provide consistent water temperatures. *Geochimica et Cosmochimica Acta*, *236*, 283–296. https://doi.org/10.1016/j.gca.2018.03.010

Buchardt, B., & Símonarson, L. A. (2003). Isotope palaeotemperatures from the Tjörnes beds in Iceland: Evidence of pliocene cooling. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *189*(1–2), 71–95. https://doi.org/10.1016/S0031-0182(02)00594-1

Butler, P. G., Wanamaker, A. D., Scourse, J. D., Richardson, C. A., & Reynolds, D. J. (2013). Variability of marine climate on the North Icelandic Shelf in a 1357-year proxy archive based on growth increments in the bivalve Arctica Islandica. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *373*, 141–151. https://doi.org/10.1016/j.palaeo.2012.01.016

Caldarescu, D. E., Sadatzki, H., Andersson, C., Schäfer, P., Fortunato, H., & Meckler, A. N. (2021). Clumped isotope thermometry in bivalve shells: A tool for reconstructing seasonal upwelling. *Geochimica et Cosmochimica Acta*, *294*, 174–191. https://doi.org/10.1016/j.gca.2020.11.019

Chen, S., Ryb, U., Piasecki, A. M., Lloyd, M. K., Baker, M. B., & Eiler, J. M. (2019). Mechanism of solid-state clumped isotope reordering in carbonate minerals from aragonite heating experiments. *Geochimica et Cosmochimica Acta*, *258*, 156–173. https://doi.org/10.1016/j.gca.2019.05.018

Daëron, M., Blamart, D., Peral, M., & Affek, H. P. (2016). Absolute isotopic abundance ratios and the accuracy of Δ47 measurements. *Chemical Geology*, *442*, 83–96. https://doi.org/10.1016/j.chemgeo.2016.08.014

Daëron, M., Drysdale, R. N., Peral, M., Huyghe, D., Blamart, D., Coplen, T. B., et al. (2019). Most Earth-surface calcites precipitate out of isotopic equilibrium. *Nature Communications*, *10*(1), 429. https://doi.org/10.1038/s41467-019-08336-5

Dennis, K. J., Affek, H. P., Passey, B. H., Schrag, D. P., & Eiler, J. M. (2011). Defining an absolute reference frame for 'clumped' isotope studies of CO_2. *Geochimica et Cosmochimica Acta*, *75*(22), 7117–7131. https://doi.org/10.1016/j.gca.2011.09.025

Dennis, K. J., Cochran, J. K., Landman, N. H., & Schrag, D. P. (2013). The climate of the Late Cretaceous: New insights from the application of the carbonate clumped isotope thermometer to Western Interior Seaway macrofossil. *Earth and Planetary Science Letters*, *362*, 51–65. https://doi.org/10.1016/j.epsl.2012.11.036

De Winter, N., Vellekoop, J., Vorsselmans, R., Golreihan, A., Soete, J., Petersen, S., et al. (2017). An assessment of latest Cretaceous pycnodonte vesicularis (Lamarck, 1806) shells as records for palaeoseasonality: A multi-proxy investigation. *Climate of the Past Discussions*, *14*(6), 725–749. https://doi.org/10.5194/cp-14-725-2018

de Winter, N. J., Dämmer, L. K., Falkenroth, M., Reichart, G.-J., Moretti, S., Martínez-García, A., et al. (2021). Multi-isotopic and trace element evidence against different formation pathways for oyster microstructures. *Geochimica et Cosmochimica Acta*, *308*, 326–352. https://doi.org/10.1016/j.gca.2021.06.012

de Winter, N. J., Muller, I. A., Kocken, I. J., Thibault, N., Ullmann, C. V., Farnsworth, A., et al. (2021). Absolute seasonal temperature estimates from clumped isotopes in bivalve shells suggest warm and variable greenhouse climate. *Communications Earth & Environment*, *2*, 1–8. https://doi.org/10.1038/s43247-021-00193-9

de Winter, N. J., Vellekoop, J., Clark, A. J., Stassen, P., Speijer, R. P., & Claeys, P. (2020). The giant marine gastropod Campanile giganteum (Lamarck, 1804) as a high-resolution archive of seasonality in the Eocene greenhouse world. *Geochemistry, Geophysics, Geosystems*, *21*(4), e2019GC008794. https://doi.org/10.1029/2019GC008794

Dong, J., Eiler, J., An, Z., Li, X., Liu, W., & Hu, J. (2021). Clumped isotopic compositions of cultured and natural land-snail shells and their implications. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *577*, 110530. https://doi.org/10.1016/j.palaeo.2021.110530

Eiler, J. M. (2007). "Clumped-isotope" geochemistry—The study of naturally-occurring, multiply-substituted isotopologues. *Earth and Planetary Science Letters*, *262*(3–4), 309–327. https://doi.org/10.1016/j.epsl.2007.08.020

Epstein, S., Buchsbaum, R., Lowenstam, H. A., & Urey, H. C. (1953). Revised carbonate-water isotopic temperature scale. *Geological Society of America Bulletin*, *64*(11), 1315–1326. https://doi.org/10.1130/0016-7606(1953)64[1315:RCITS]2.0.CO;2

Fernandez, A., Müller, I. A., Rodríguez-Sanz, L., van Dijk, J., Looser, N., & Bernasconi, S. M. (2017). A reassessment of the precision of carbonate clumped isotope measurements: Implications for calibrations and paleoclimate reconstructions. *Geochemistry, Geophysics, Geosystems*, *18*(12), 4375–4386. https://doi.org/10.1002/2017gc007106

Frisia, S., Borsato, A., Fairchild, I. J., & McDermott, F. (2000). Calcite fabrics, growth mechanisms, and environments of formation in speleothems from the Italian Alps and Southwestern Ireland. *Journal of Sedimentary Research*, *70*(5), 1183–1196. https://doi.org/10.1306/022900701183

Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W., Schauble, E. A., et al. (2006). 13C–18O bonds in carbonate minerals: A new kind of paleothermometer. *Geochimica et Cosmochimica Acta*, *70*(6), 1439–1456. https://doi.org/10.1016/j.gca.2005.11.014

Ghosh, P., Eiler, J., Campana, S. E., & Feeney, R. F. (2007). Calibration of the carbonate 'clumped isotope' paleothermometer for otoliths. *Geochimica et Cosmochimica Acta*, *71*(11), 2736–2744. https://doi.org/10.1016/j.gca.2007.03.015

Guo, W., Mosenfelder, J. L., Goddard, W. A., & Eiler, J. M. (2009). Isotopic fractionations associated with phosphoric acid digestion of carbonate minerals: Insights from first-principles theoretical modeling and clumped isotope measurements. *Geochimica et Cosmochimica Acta*, *73*(24), 7203–7225. https://doi.org/10.1016/j.gca.2009.05.071

Hansen, H. J. (1979). Test structure and evolution in the Foraminifera. *Lethaia*, *12*(2), 173–182. https://doi.org/10.1111/let.1979.12.2.173

He, B., Olack, G. A., & Colman, A. S. (2012). Pressure baseline correction and high-precision CO2 clumped-isotope (Δ 47) measurements in bellows and micro-volume modes. *Rapid Communications in Mass Spectrometry*, *26*(24), 2837–2853. https://doi.org/10.1002/rcm.6436

Henkes, G. A., Passey, B. H., Grossman, E. L., Shenton, B. J., Yancey, T. E., & Pérez-Huerta, A. (2018). Temperature evolution and the oxygen isotope composition of Phanerozoic oceans from carbonate clumped isotope thermometry. *Earth and Planetary Science Letters*, *490*, 40–50. https://doi.org/10.1016/j.epsl.2018.02.001

Henkes, G. A., Passey, B. H., Wanamaker, A. D., Grossman, E. L., Ambrose, W. G., & Carroll, M. L. (2013). Carbonate clumped isotope compositions of modern marine mollusk and brachiopod shells. *Geochimica et Cosmochimica Acta*, *106*, 307–325. https://doi.org/10.1016/j.gca.2012.12.020

Huyghe, D., Daëron, M., de Rafelis, M., Blamart, D., Sébilo, M., Paulet, Y.-M., & Lartaud, F. (2022). Clumped isotopes in modern marine bivalves. *Geochimica et Cosmochimica Acta*, *316*, 41–58. https://doi.org/10.1016/j.gca.2021.09.019

IPCC. (2021). Climate change 2021: The physical science basis. In *Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press.

Jautzy, J. J., Savard, M. M., Dhillon, R. S., Bernasconi, S. M., & Smirnoff, A. (2020). Clumped isotope temperature calibration for calcite: Bridging theory and experimentation. *Geochemical Perspectives Letters*, *14*, 36–41. https://doi.org/10.7185/geochemlet.2021

Kele, S., Breitenbach, S. F., Capezzuoli, E., Meckler, A. N., Ziegler, M., Millan, I. M., et al. (2015). Temperature dependence of oxygen-and clumped isotope fractionation in carbonates: A study of travertines and tufas in the 6–95 C temperature range. *Geochimica et Cosmochimica Acta*, *168*, 172–192. https://doi.org/10.1016/j.gca.2015.06.032

Kennedy, W. J., Taylor, J. D., & Hall, A. (1969). Environmental and biological controls on bivalve shell mineralogy. *Biological Reviews*, *44*(4), 499–530. https://doi.org/10.1111/j.1469-185X.1969.tb00610.x

Kim, S.-T., & O'Neil, J. R. (1997). Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochimica et Cosmochimica Acta*, *61*(16), 3461–3475. https://doi.org/10.1016/S0016-7037(97)00169-5

Kimball, J., Eagle, R., & Dunbar, R. (2016). Carbonate "clumped" isotope signatures in aragonitic scleractinian and calcitic gorgonian deep-sea corals. *Biogeosciences*, *13*(23), 6487–6505. https://doi.org/10.5194/bg-13-6487-2016

Kluge, T., John, C. M., Jourdan, A.-L., Davis, S., & Crawshaw, J. (2015). Laboratory calibration of the calcium carbonate clumped isotope thermometer in the 25–250°C temperature range. *Geochimica et Cosmochimica Acta*, *157*, 213–227. https://doi.org/10.1016/j.gca.2015.02.028

Letulle, T., Suan, G., Daëron, M., Rogov, M., Lécuyer, C., Vinçon-Laugier, A., et al. (2022). Clumped isotope evidence for Early Jurassic extreme polar warmth and high climate sensitivity. *Climate of the Past*, *18*(3), 435–448. https://doi.org/10.5194/cp-18-435-2022

Meckler, A. N., Sexton, P. F., Piasecki, A. M., Leutert, T. J., Marquardt, J., Ziegler, M., et al. (2022). Cenozoic evolution of deep ocean temperature from clumped isotope thermometry. *Science*, *377*, 86–90. https://doi.org/10.1126/science.abk0604

Meinicke, N., Ho, S. L., Hannisdal, B., Nürnberg, D., Tripati, A., Schiebel, R., & Meckler, A. N. (2020). A robust calibration of the clumped isotopes to temperature relationship for foraminifers. *Geochimica et Cosmochimica Acta*, *270*, 160–183. https://doi.org/10.1016/j.gca.2019.11.022

Meinicke, N., Reimi, M. A., Ravelo, A. C., & Meckler, A. N. (2021). Coupled Mg/Ca and clumped isotope measurements indicate lack of substantial mixed layer cooling in the Western Pacific warm pool during the last ~5 million years. *Paleoceanography and Paleoclimatology*, *36*(8), e2020PA004115. https://doi.org/10.1029/2020PA004115

Modestou, S. E., Leutert, T. J., Fernandez, A., Lear, C. H., & Meckler, A. N. (2020). Warm middle miocene Indian Ocean bottom water temperatures: Comparison of clumped isotope and Mg/Ca-based estimates. *Paleoceanography and Paleoclimatology*, *35*(11), e2020PA003927. https://doi.org/10.1029/2020PA003927

Müller, I. A., Rodriguez-Blanco, J. D., Storck, J.-C., do Nascimento, G. S., Bontognali, T. R. R., Vasconcelos, C., et al. (2019). Calibration of the oxygen and clumped isotope thermometers for (proto-)dolomite based on synthetic and natural carbonates. *Chemical Geology*, *525*, 1–17. https://doi.org/10.1016/j.chemgeo.2019.07.014

Müller, I. A., Violay, M. E. S., Storck, J.-C., Fernandez, A., van Dijk, J., Madonna, C., & Bernasconi, S. M. (2017). Clumped isotope fractionation during phosphoric acid digestion of carbonates at 70°C. *Chemical Geology*, *449*, 1–14. https://doi.org/10.1016/j.chemgeo.2016.11.030

Peral, M., Daëron, M., Blamart, D., Bassinot, F., Dewilde, F., Smialkowski, N., et al. (2018). Updated calibration of the clumped isotope thermometer in planktonic and benthic foraminifera. *Geochimica et Cosmochimica Acta*, *239*, 1–16. https://doi.org/10.1016/j.gca.2018.07.016

Petersen, S. V., Defliese, W. F., Saenger, C., Daëron, M., Huntington, K. W., John, C. M., et al. (2019). Effects of improved ^{17}O correction on interlaboratory agreement in clumped isotope calibrations, estimates of mineral-specific offsets and temperature dependence of acid digestion fractionation. *Geochemistry, Geophysics, Geosystems*, *20*(7), 3495–3519. https://doi.org/10.1029/2018GC008127

Petersen, S. V., Tabor, C. R., Lohmann, K. C., Poulsen, C. J., Meyer, K. W., Carpenter, S. J., et al. (2016). Temperature and salinity of the Late Cretaceous western interior seaway. *Geology*, *44*(11), 903–906. https://doi.org/10.1130/g38311.1

Piasecki, A., Bernasconi, S. M., Grauel, A., Hannisdal, B., Ho, S. L., Leutert, T. J., et al. (2019). Application of clumped isotope thermometry to benthic foraminifera. *Geochemistry, Geophysics, Geosystems*, *20*(4), 2082–2090. https://doi.org/10.1029/2018gc007961

R Core Team. (2022). *R: A language and environment for statistical computing*. R Foundation for Statistical Computing.

Rodríguez-Sanz, L., Bernasconi, S. M., Marino, G., Heslop, D., Müller, I. A., Fernandez, A., et al. (2017). Penultimate deglacial warming across the Mediterranean Sea revealed by clumped isotopes in foraminifera. *Scientific Reports*, *7*(1), 16572. https://doi.org/10.1038/s41598-017-16528-6

Schauble, E. A., Eiler, J. M., & Kitchen, N. (2003). Measurement and significance of ^(13)C^(18)O^(16)O in thermodynamically equilibrated and environmental CO_2. *Geochimica et Cosmochimica Acta*, *67*, A419.

Schauble, E. A., Ghosh, P., & Eiler, J. M. (2006). Preferential formation of 13C–18O bonds in carbonate minerals, estimated using first-principles lattice dynamics. *Geochimica et Cosmochimica Acta*, *70*(10), 2510–2529. https://doi.org/10.1016/j.gca.2006.02.011

Schöne, B. R., & Fiebig, J. (2009). Seasonality in the North sea during the Allerød and late medieval climate optimum using bivalve sclerochronology. *International Journal of Earth Sciences*, *98*(1), 83–98. https://doi.org/10.1007/s00531-008-0363-7

Schöne, B. R., Fiebig, J., Pfeiffer, M., Gleβ, R., Hickson, J., Johnson, A. L., et al. (2005). Climate records from a bivalved Methuselah (Arctica islandica, Mollusca; Iceland). *Palaeogeography, Palaeoclimatology, Palaeoecology*, *228*(1–2), 130–148. https://doi.org/10.1016/j.palaeo.2005.03.049

Taylor, J. D., & Reid, D. G. (1990). Shell microstructure and mineralogy of the littorinidae: Ecological and evolutionary significance. In *Progress in littorinid and muricid biology* (pp. 199–215). https://doi.org/10.1007/978-94-009-0563-4_16

Tierney, J. E., Poulsen, C. J., Montañez, I. P., Bhattacharya, T., Feng, R., Ford, H. L., et al. (2020). Past climates inform our future. *Science*, *370*(6517), eaay3701. https://doi.org/10.1126/science.aay3701

Tripati, A. K., Eagle, R. A., Thiagarajan, N., Gagnon, A. C., Bauch, H., Halloran, P. R., & Eiler, J. M. (2010). 13C–18O isotope signatures and 'clumped isotope' thermometry in foraminifera and coccoliths. *Geochimica et Cosmochimica Acta*, *74*(20), 5697–5717. https://doi.org/10.1016/j.gca.2010.07.006

Urey, H. C. (1947). The thermodynamic properties of isotopic substances - Google Scholar. *Journal of the Chemical Society*, 562–581.

Vickers, M. L., Fernandez, A., Hesselbo, S. P., Price, G. D., Bernasconi, S. M., Lode, S., et al. (2020b). Unravelling Middle to Late Jurassic palaeoceanographic and palaeoclimatic signals in the Hebrides Basin using belemnite clumped isotope thermometry. *Earth and Planetary Science Letters*, *546*, 116401. https://doi.org/10.1016/j.epsl.2020.116401

Vickers, M. L., Lengger, S. K., Bernasconi, S. M., Thibault, N., Schultz, B. P., Fernandez, A., et al. (2020). Cold spells in the Nordic Seas during the early eocene greenhouse. *Nature Communications*, *11*(1), 4713. https://doi.org/10.1038/s41467-020-18558-7

Wacker, U., Fiebig, J., & Schoene, B. R. (2013). Clumped isotope analysis of carbonates: Comparison of two different acid digestion techniques. *Rapid Communications in Mass Spectrometry*, *27*(14), 1631–1642. https://doi.org/10.1002/rcm.6609

Wacker, U., Fiebig, J., Tödter, J., Schöne, B. R., Bahr, A., Friedrich, O., et al. (2014). Empirical calibration of the clumped isotope paleothermometer using calcites of various origins. *Geochimica et Cosmochimica Acta*, *141*, 127–144. https://doi.org/10.1016/j.gca.2014.06.004

Wang, Z., Schauble, E. A., & Eiler, J. M. (2004). Equilibrium thermodynamics of multiply substituted isotopologues of molecular gases. *Geochimica et Cosmochimica Acta*, *68*(23), 4779–4797. https://doi.org/10.1016/j.gca.2004.05.039

Westerhold, T., Marwan, N., Drury, A. J., Liebrand, D., Agnini, C., Anagnostou, E., et al. (2020). An astronomically dated record of Earth's climate and its predictability over the last 66 million years. *Science*, *369*(6509), 1383–1387. https://doi.org/10.1126/science.aba6853

Witbaard, R., Duineveld, G. C. A., & De Wilde, P. (1997). A long-term growth record derived from Arctica islandica (Mollusca, Bivalvia) from the Fladen Ground (northern North Sea). *Journal of the Marine Biological Association of the United Kingdom*, *77*(3), 801–816. https://doi.org/10.1017/s0025315400036201

Witbaard, R., Franken, R., & Visser, B. (1998). Growth of juvenileArctica islandica under experimental conditions. *Helgolaender Meeresuntersuchungen*, *51*(4), 417–431. https://doi.org/10.1007/BF02908724

Zhai, J., Wang, X., Qin, B., Cui, L., Zhang, S., & Ding, Z. (2019). Clumped isotopes in land snail shells over China: Towards establishing a biogenic carbonate paleothermometer. *Geochimica et Cosmochimica Acta*, *257*, 68–79. https://doi.org/10.1016/j.gca.2019.04.028

Zhang, N., Yamada, K., Kano, A., Matsumoto, R., & Yoshida, N. (2018). Equilibrated clumped isotope signatures of land-snail shells observed from laboratory culturing experiments and its environmental implications. *Chemical Geology*, *488*, 189–199. https://doi.org/10.1016/j.chemgeo.2018.05.001

References From the Supporting Information

Schaefer, R., Trutschler, K., & Rumohr, H. (1985). Biometric studies on the bivalvesAstarte elliptica, A. borealis and*A*. montagui in Kiel Bay (Western Baltic Sea). *Helgolaender Meeresuntersuchungen*, *39*(3), 245–253. https://doi.org/10.1007/BF01992772

Staudigel, P. T., & Swart, P. K. (2016). Isotopic behavior during the aragonite-calcite transition: Implications for sample preparation and proxy interpretation. *Chemical Geology*, *442*, 130–138. https://doi.org/10.1016/j.chemgeo.2016.09.013

Sturm, P. (2018). bfsl: Best-Fit straight line.