Appendix

A.1 Further details on the analysis of clumped isotopes

The mass 47 anomaly is temperature-dependent and forms the basis of the clumped isotope thermometer (Wang et al., 2004; Eiler, 2007). It is reported as:

$$\Delta_{47}\ (‰) = [(R^{47} / R^{47*} - 1) - (R^{46} / R^{46*} - 1) - (R^{45} / R^{45*} - 1)] \times 1000 \quad (A.1)$$

where R^i are the measured ratios of the rare isotopologues with masses 45-47 to the most abundant isotopologue with mass 44. R^{i*} represents the corresponding ratios under stochastic (or random) distribution of the isotopes among all possible isotopologues and is calculated from the measured abundances of ^{13}C and ^{18}O. The measured enrichment of the mass 47 isotopologue is defined as:

$$\delta^{47}\ (‰) = (R^{47}_{Sample} / R^{47}_{Reference} - 1) \times 1000 \quad (A.2)$$

Sample measurements were done in a randomized manner spanning an extended period of time (November 2016 to February 2018). Mass 44-49 ion beams of sample and reference CO_2 gas were collected in six Faraday cups. We used reference gas from two commercial compressed gas tanks: (1) $\delta^{18}O_{VPDB}$ = -5.38 ‰ and $\delta^{13}C_{VPDB}$ = -4.45 ‰ from October 2016 to October 2017, (2) $\delta^{18}O_{VPDB}$ = -5.61 ‰ and $\delta^{13}C_{VPDB}$ = -3.54 ‰ from October 2017 to March 2018. Samples were reacted with phosphoric acid at 70°C. During a measurement run, the Porapak trap (Schmid et al., 2012) was cooled to -20°C in order to trap contaminants (e.g., Halocarbons, Hydrocarbons), and baked out (120°C) for at least 1 h after each run. The signals of m/z 48 and 49 were monitored to detect possible contamination (e.g., Bernasconi et al., 2013).

For the measuring interval from October 2016 to October 2017, we used the carbonate standards ETH 1, 3 and 4 for correction and the carbonate standard ETH 2 for monitoring. From November 2017 to March 2018, ETH 1, 2 and 3 were utilized for correction and ETH 4 for monitoring. Using the software "Easotope" (John and Bowen, 2016), the measured $\delta^{18}O$ values were corrected for drift using "stretching" based on the three correction standards and a correction interval of 30-40 standard replicates before and after each sample analysis. $\delta^{13}C$ values were also corrected for drift with the same standards, but without stretching. Δ_{47} was corrected for composition (δ^{47})-dependent (negative baseline) and composition-independent (scale compression) mass spectrometer effects using the same three standards. In order to characterize the pressure-sensitive baseline (PBL) on all Faraday cups and determine the dependence of the PBL on the m/z 44 intensity for the other masses, we performed high-voltage peak scans at 5 different m/z 44 signal intensities on a daily basis. The dependence of the PBL on the m/z 44 intensity was then used to do a PBL correction on the raw beam signals accounting for negative baseline/non-linearity effects caused by the formation of secondary electrons (He et al., 2012; Bernasconi et al., 2013; Meckler et al., 2014). The PBL corrected signals were used to calculate $\delta^{18}O_{VPDB}$, $\delta^{13}C_{VPDB}$ and raw Δ_{47} values with the "Brand" isotopic parameters (Brand et al., 2010; Daëron et al., 2016). The empirical transfer function based on the three correction standards corrects for scale compression caused by fragmentation/recombination reactions in the electron ionization impact source and standardizes Δ_{47} data for inter-laboratory comparison (Dennis et al., 2011). Application of the empirical transfer function obtained from the correlation of raw and accepted Δ_{47} values of the three standards converted our Δ_{47} to the absolute

reference frame. For that, we used standard replicate measurements from a correction interval of ±30-40 standards and the accepted standard Δ_{47} values from Bernasconi et al. (2018). Finally, we added an acid fractionation correction of +0.062 ‰ (Defliese et al., 2015) to the Δ_{47} value in the absolute reference frame, in order to transfer our data into a more common acid fractionation framework (from 70°C to 25°C digestion). To account for ^{18}O fractionation during calcite digestion at 70°C, an acid fractionation factor of 1.00871 was applied (Kim et al., 2007).

For the period from October 2016 to October 2017, mean Δ_{47} and external reproducibility (1σ standard deviation) of ETH 2 after correction were 0.2516±0.0334 ‰ (n=901) (Tables S3 and S4). The external reproducibilities of ETH 1, 3 and 4 were ±0.0351 ‰ (n=907), ±0.0325 ‰ (n=911) and ±0.0308 ‰ (n=918), respectively. From November 2017 to March 2018, mean Δ_{47} and external reproducibility of ETH 4 after correction were 0.5145±0.0385 ‰ (n=456), whereas the external reproducibilities of ETH 1, 2 and 3 were ±0.0365 ‰ (n=458), ±0.0340 ‰ (n=402) and ±0.0356 ‰ (n=460), respectively. All standard measurement data are listed in Table S3.

A.2 Δ_{47} end-member calculations

Δ_{47} end-member calculations to derive glassy foraminiferal Δ_{47} were carried out in R. Following the procedure described in Defliese and Lohmann (2015), we calculated δ^{45}, δ^{46} and δ^{47} from Δ_{47}, $\delta^{13}C$ and $\delta^{18}O$ for both frosty foraminiferal calcite (δ^i_{frost}) and inorganic calcite (δ^i_{diag}, as derived from benthic foraminiferal calcite). For that, we utilized the ^{18}O acid fractionation correction of Kim et al. (2007), the Δ_{47} acid fractionation correction of Defliese et al. (2015), the parameters recommended by Daëron et al. (2016) and the following reference gas: $\delta^{18}O_{VPDB}$ = -5.38 ‰ and

$\delta^{13}C_{VPDB}$ = -4.45 ‰ (all clumped isotope measurements included in the non-linear mixing calculations were measured with the same reference gas).

In a CO_2 mixture, end-members of different isotopic composition have been shown to mix linearly with respect to δ^{45}, δ^{46} and δ^{47} (e.g., Affek and Eiler, 2006; Defliese and Lohmann, 2015). Therefore, we used a simple linear mixing equation to derive glassy foraminiferal δ^i values (δ^i_{glassy}):

$$\delta^i_{glassy} = (\delta^i_{frosty} - F_{diag} \times \delta^i_{diag}) / (1 - F_{diag}) \quad (A.3)$$

Glassy foraminiferal Δ_{47} was then calculated from glassy foraminiferal δ^{45}, δ^{46} and δ^{47}. This necessitates the estimation of a hypothetical ETF slope and intercept for glassy calcite. For each calculation, we assumed that the ETF slope from the clumped isotope measurement on frosty material represents the mean (weighted with the fraction of diagenetic calcite) of the hypothetical glassy calcite ETF slope and the ETF slope of the benthic clumped isotope measurement that was used to approximate diagenetic inorganic calcite. Accordingly, a mean glassy calcite ETF slope was calculated from the mean ETF slopes of the measurements on frosty and benthic foraminifera. The same approach was applied to the ETF intercept. Code in R format is provided upon request.

References

Affek, H. and Eiler, J. (2006) Abundance of mass 47 CO_2 in urban air, car exhaust, and human breath. *Geochimica et Cosmochimica Acta* **70,** 1-12.

Bernasconi, S.M., Hu, B., Wacker, U., Fiebig, J., Breitenbach, S.F.M. and 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,** 603-612.

Bernasconi, S.M., Müller, I.A., Bergmann, K.D., Breitenbach, S.F.M., Fernandez, A., Hodell, D.A., Jaggi, M., Meckler, A.N., Millan, I. and Ziegler, M. (2018) Reducing uncertainties in carbonate clumped isotope analysis through consistent carbonate-based standardization. *Geochemistry, Geophysics, Geosystems* **19,** 2895-2914.

Brand, W.A., Assonov, S.S. and Coplen, T.B. (2010) Correction for the ^{17}O interference in $\delta^{13}C$ measurements when analyzing CO_2 with stable isotope mass spectrometry (IUPAC Technical Report). *Pure and Applied Chemistry* **82,** 1719-1733.

Daëron, M., Blamart, D., Peral, M. and Affek, H.P. (2016) Absolute isotopic abundance ratios and the accuracy of Δ_{47} measurements. *Chemical Geology* **442,** 83-96.

Defliese, W.F., Hren, M.T. and Lohmann, K.C. (2015) Compositional and temperature effects of phosphoric acid fractionation on Δ_{47} analysis and implications for discrepant calibrations. *Chemical Geology* **396,** 51-60.

Defliese, W.F. and Lohmann, K.C. (2015) Non-linear mixing effects on mass-47 CO_2 clumped isotope thermometry: Patterns and implications. *Rapid Communications in Mass Spectrometry* **29,** 901-909.

Dennis, K.J., Affek, H.P., Passey, B.H., Schrag, D.P. and Eiler, J.M. (2011) Defining an absolute reference frame for 'clumped' isotope studies of CO_2. *Geochimica et Cosmochimica Acta* **75,** 7117-7131.

Eiler, J.M. (2007) "Clumped-isotope" geochemistry—The study of naturally-occurring, multiply-substituted isotopologues. *Earth and Planetary Science Letters* **262,** 309-327.

He, B., Olack, G.A. and Colman, A.S. (2012) Pressure baseline correction and high-precision CO_2 clumped-isotope (Δ_{47}) measurements in bellows and micro-volume modes. *Rapid Communications in Mass Spectrometry* **26,** 2837-2853.

John, C.M. and Bowen, D. (2016) Community software for challenging isotope analysis: First applications of 'Easotope' to clumped isotopes. *Rapid Communications in Mass Spectrometry* **30,** 2285-2300.

Kim, S.T., Mucci, A. and Taylor, B.E. (2007) Phosphoric acid fractionation factors for calcite and aragonite between 25 and 75 ˚C: Revisited. *Chemical Geology* **246,** 135-146.

Meckler, A.N., Ziegler, M., Millan, M.I., Breitenbach, S.F.M. and Bernasconi, S.M. (2014) Long-term performance of the Kiel carbonate device with a new correction scheme for clumped isotope measurements. *Rapid Communications in Mass Spectrometry* **28,** 1705-1715.

Schmid, T.W., Radke, J. and Bernasconi, S.M. (2012) Clumped-isotope measurements on small carbonate samples with a Kiel IV carbonate device and a MAT 253 mass spectrometer. *Thermo Fisher Application Note*.

Wang, Z., Schauble, E.A. and Eiler, J.M. (2004) Equilibrium thermodynamics of multiply substituted isotopologues of molecular gases. *Geochimica et Cosmochimica Acta* **68,** 4779-4797.