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Supporting Information for "Dynamic intermediate waters across the late glacial revealed by paired radiocarbon and clumped isotope temperature records"

Sophia K. V. Hines[1,2], John M. Eiler[1], John R. Southon[3], and Jess F. Adkins[1]

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Corresponding author: S.K.V. Hines, Lamont-Doherty Earth Observatory of Columbia University, 61 Route 9W, Palisades, NY, 10964, USA. (shines@ldeo.columbia.edu)

[1]California Institute of Technology, Pasadena, CA, USA.

[2]LDEO, Palisades, NY, USA.

[3]University of California Irvine, Irvine, CA, USA.

1. Culled clumped isotope samples

Out of 402 individual measurements on 61 samples, 43 measurements were culled and excluded from averages. There are four reasons why measurements were culled: mass-48 excess (14 measurements), proximity to standards with unusually high residuals (25 measurements), physically impossible temperatures (2 measurements), and statistical outliers that were more than 3σ from the sample mean (2 measurements). Mass-48 excess is determined by regressing a line through heated gases for a particular week in δ_{48} versus Δ_{48} space. The deviation of each sample from this '48 line' is measured, and samples with $|48\,\text{excess}| > 1$ are flagged. Unusually high standard residuals are defined as standard residuals more than 2σ from zero, or a residual of $> \pm 0.053$. Samples that were measured immediately before or after these high-residual standards were culled. In addition to these 39 samples, two samples were marked for physically impossible temperatures. These two samples have uncorrected temperatures of -10.8 and -9.7 °C and corrected temperatures of -7.2 and -3.6 °C respectively, below the freezing point of seawater. Additionally, these samples fall more than 2σ away from the sample mean.

2. Converting samples to the Absolute Reference Frame using a secondary transfer function

Converting samples to the clumped isotope absolute reference frame requires both 'heated gases' (1000 °C) and 'equilibrated gases' (25 °C) (*Dennis, Affek, Passey, Schrag, and Eiler*, 2011). Since the absolute reference frame was developed after N. Thiagarajan ran her deep-sea coral samples, we must resort to secondary method of retroactively transferring her values into the absolute reference frame using carbonate standards in order to compare our two deep-sea coral datasets. Because different carbonate standards were measured during different measurement sessions, we have decided to transfer averaged temperatures for each deep-sea coral from the Caltech reference frame (CRF) into the absolute reference frame (ARF) (Figure S4). The secondary transfer function was made using three materials: heated gas, carbonate standard NBS 19, and deep-sea coral standard 45923. Accepted ARF values for heated gases and these carbonate standards are from *Dennis et al.* (2011) (N.B. the corrected acid digestion fractionation was not used in the *Dennis et al.* (2011) paper, so 0.011 was added to the published Δ_{47} values for the carbonate standards to account for this error).

Once the samples are in the ARF, we also apply a carbonate correction, to account for long-term reproducibility. Since the same carbonate standards were not run with our deep-sea corals and with those of N. Thiagarajan, we apply the same carbonate standard offset correction to the fossil deep-sea coral data as was applied to the modern deep-sea coral data for our new modern calibration, since all of these samples were run around the same time.

3. Long-term clumped isotope temperature accuracy

Five carbonate standards with different formation temperatures, TV03, TV04, CIT-Carrara, LB-001, and LB-002, were measured repeatedly with every sample session. CIT-Carrara is a marble with an accepted Δ_{47} ARF value of 0.408, TV03 and TV04 are travertines with accepted Δ_{47} ARF values of 0.707 and 0.655 respectively (TV04 replaced TV03 when it ran out in December 2015), and LB-001 and LB-002 are deep-sea corals. LB-001 was collected live from south of Tasmania in 2009 and was measured throughout the entire measurement interval. LB-002 was also collected live in 2009 from the same location as LB-001 and was established in January 2017 as a new low-temperature lab standard. Over the course of the entire measurement interval (from April 2014–June 2017), there were temporally coherent shifts in the offset of these carbonate standards from their accepted values (Supplemental Figures 2 and 3). Because of this, unknown deep-sea coral Δ_{47} values were corrected for this week-to-week instrument variability using the average offset of consistency standard LB-001 from its accepted value for that week. LB-001 was used to correct unknown deep-sea coral samples because it has a similar Δ_{47} value.

Accepted values for carbonate standards TV03, TV04, and CIT-Carrara were established by repeatedly measuring these standards over the course of several weeks and averaging the measurements. For deep-sea coral standards LB-001 and LB-002, we have *a priori* information about the growth temperature of the samples, since we know their collection locations. Using the ODV 3D interpolation function, the growth temperature for these samples was determined to be 2.15 ± 0.05 °C. Converting this temperature to a Δ_{47} value requires a calibration, however, and our new deep-sea coral calibration relies on carbonate corrected data. In order to avoid circularity and to be consistent with other carbonate standards, we have determined an accepted Δ_{47} value of 0.835 (n=15) using the average Δ_{47} from the first three weeks of measurement (see Supplemental Figure 3). We believe this is the best way forward to maintain long-term reproducibility while still ensuring that our samples are anchored to real temperatures through our new modern coral calibration.

Deep-sea corals run by N. Thiagarajan (between 2009 and 2012) were also corrected for week-to-week variability using carbonate standards run during the same week, including a modern deep-sea coral 45923 from 1318 m water depth, 7.558 °N 56.417 °W. Using the same 3D interpolation method, we have determined a modern temperature of 4.73 ± 0.10 °C. Unfortunately, there was only one week where both modern corals (45923 and LB-001) were measured, because 45923 ran out. For this week, the average measured Δ_{47} value for LB-001 was 0.846 with a standard deviation of 0.005 (1σ, n=5) and the average measured Δ_{47} value for 45923 was 0.809 with a standard deviation of 0.015 (1σ, n=7). The difference between the measured Δ_{47} values, 0.038, is more than twice the expected difference based on growth temperature (using our deep-sea coral calibration), 0.013. While this Δ_{47} is larger than expected, we cannot rule out the possibility that this result is an analytical artifact.

As an additional accuracy check, we ran a deep-sea coral (sample SH-A008-S5) that was collected live from the same location as LB-001. It's standard-corrected average Δ_{47} value, 0.848±0.018, overlaps with the average Δ_{47} values of LB-001, 0.863±0.009, for weeks that they were run together within 2σ SE (and is barely outside 1σ SE).

References

Dennis, K. J., H. P. Affek, B. H. Passey, D. P. Schrag, and J. M. Eiler (2011), Defining an absolute reference frame for 'clumped' isotope studies of CO2, *Geochimica et Cosmochimica Acta*, *75*(22), 7117–7131.

Thiagarajan, N., D. Gerlach, M. L. Roberts, A. Burke, A. P. McNichol, W. J. Jenkins, A. Subhas, R. Thresher, and J. F. Adkins (2013), Movement of deep-sea coral populations on climatic timescales, *Paleoceanography*, *28*, 227–236.

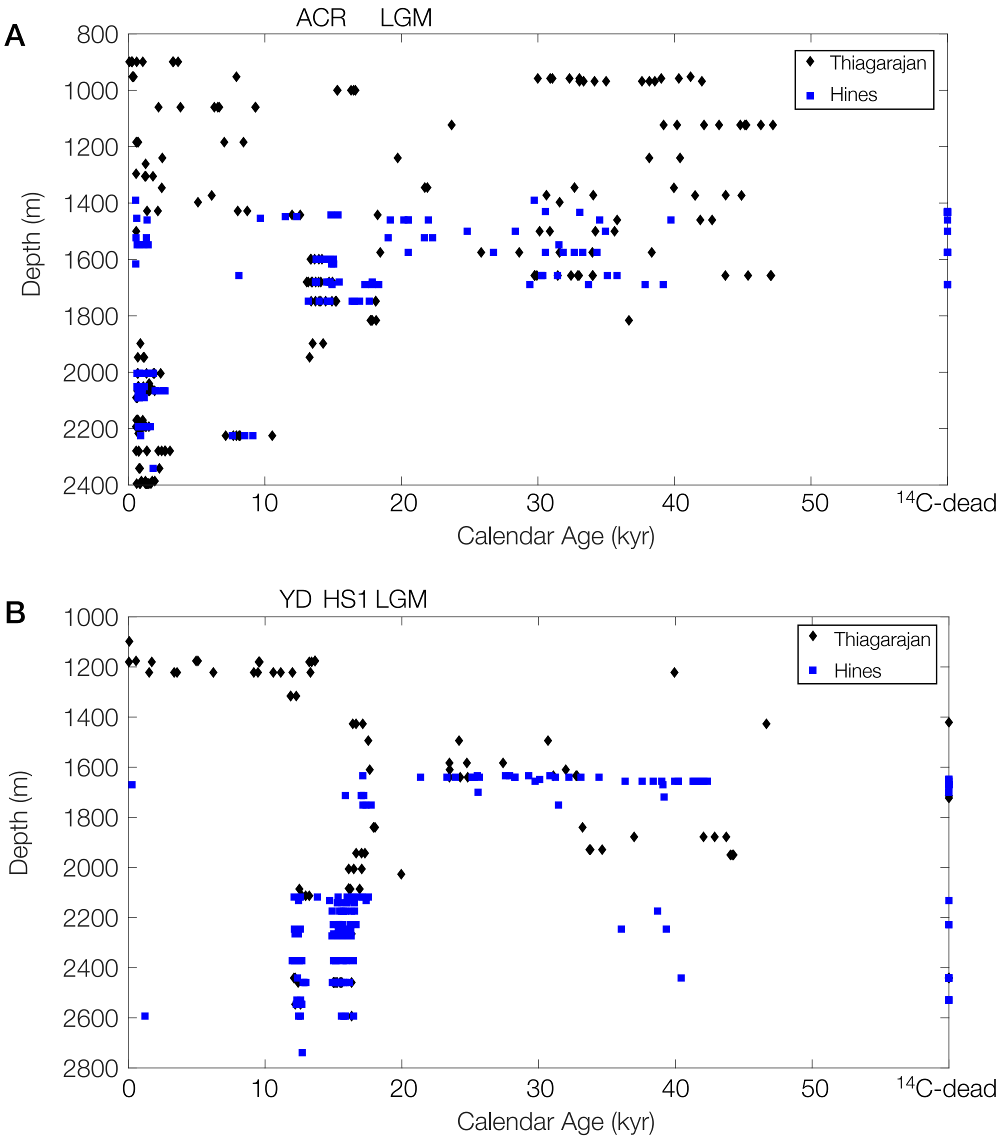

Figure S1. Age versus depth plot for Southern Ocean (A) and North Atlantic (B) deep sea corals, including data from *Thiagarajan et al.* (2013).

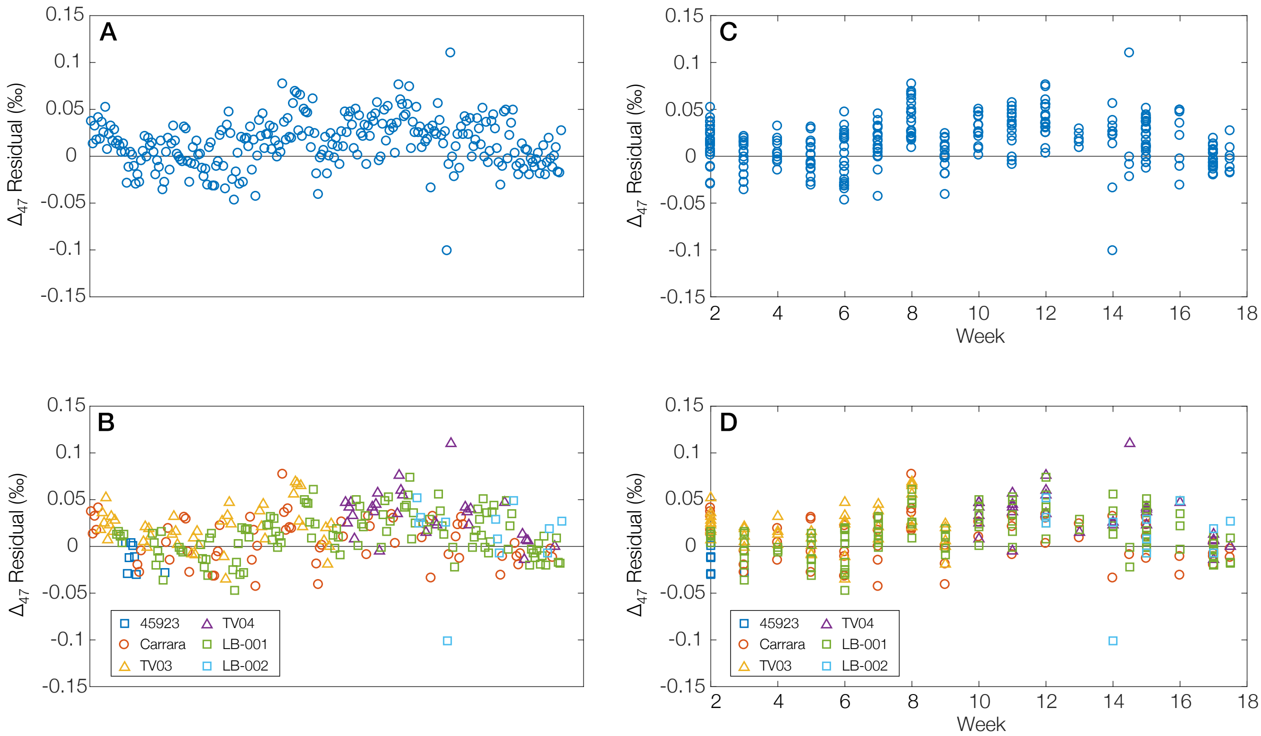

Figure S2. Summary of carbonate standard data. A) Plot of standard residuals in the absolute reference frame on an arbitrary time axis, where the standard residual is defined as: measured Δ_{47}−accepted Δ_{47}. B) Same data as in A, but colored by carbonate standard type. C and D) Same as A and B, but grouped by measurement week.

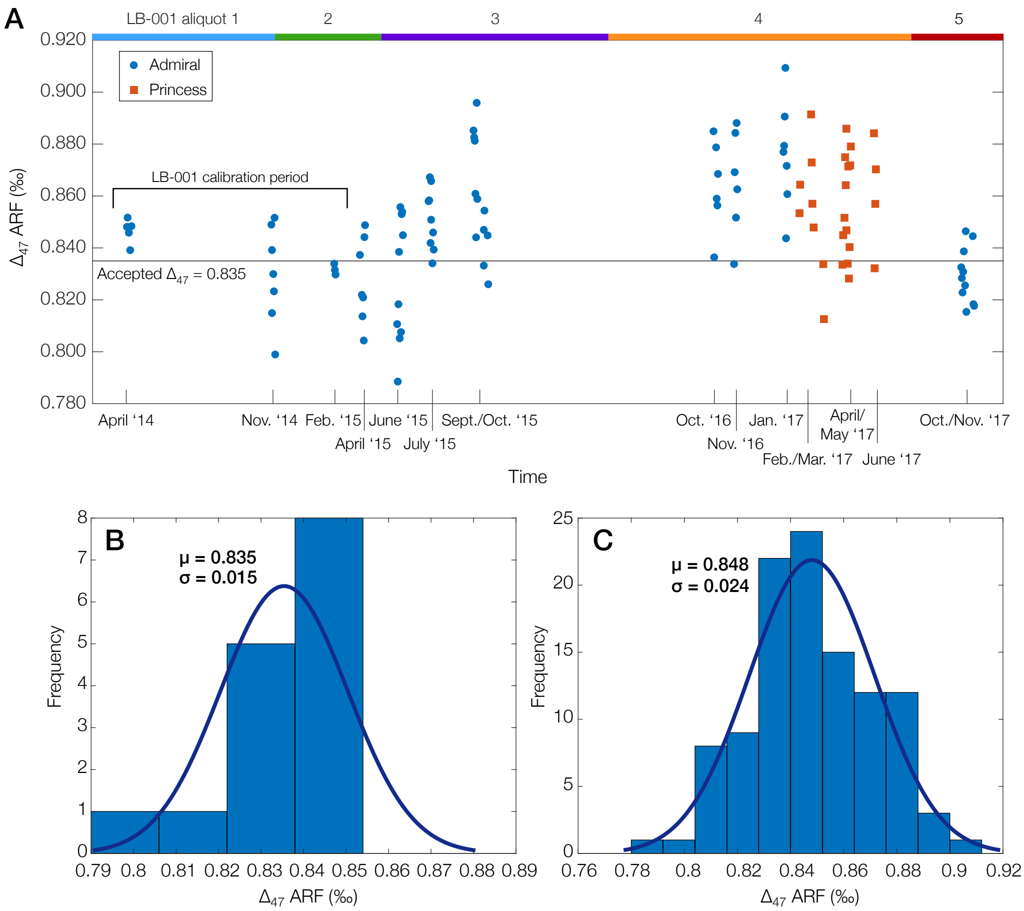

Figure S3. Deep-sea coral standard LB-001. A) Δ_{47} data for deep-sea coral standard LB-001 versus time, with measurement intervals labeled. Solid horizontal line is the accepted Δ_{47} value in the absolute reference frame for LB-001, 0.835. Blue points were measured on the instrument 'Admiral Akbar' and red points were measured on the instrument 'Princess Leia'. Colored bars at the top of the plot indicate five separate aliquots of the coral that were cut and measured—long-term variation in measured Δ_{47} does not correspond to times when new aliquots were taken. B) Histogram of data from LB-001 calibration period (first three measurement sessions) with mean and standard deviation of data. C) Histogram of all LB-001 data with mean and standard deviation.

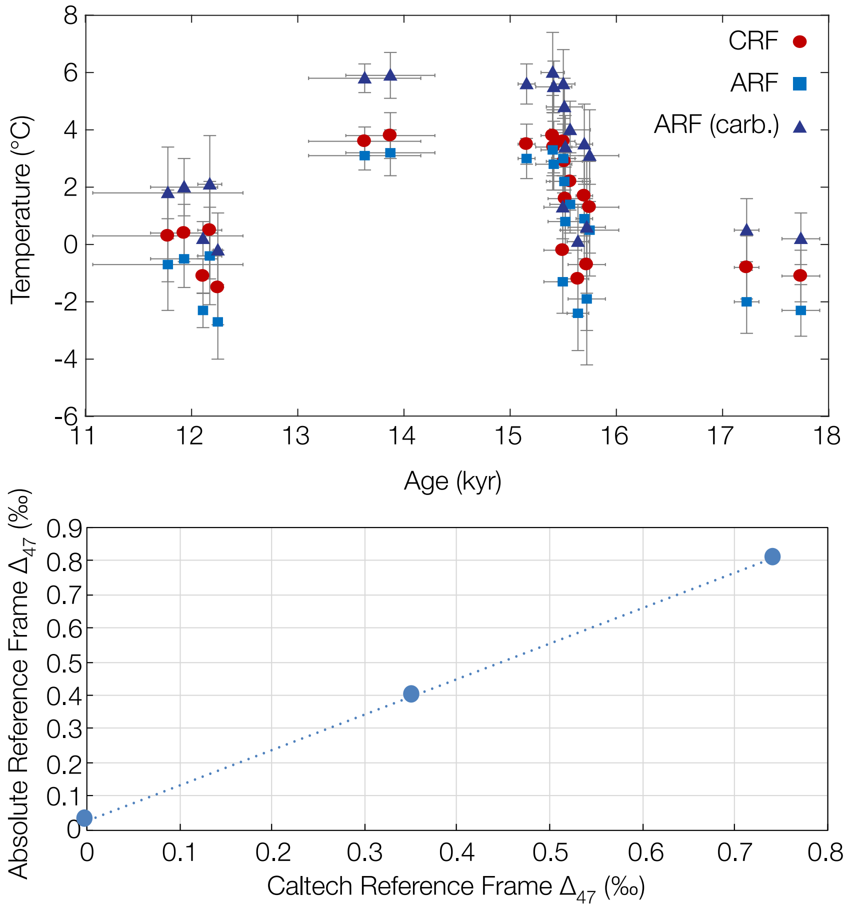

Figure S4. Transferring deep-sea corals run by N. Thiagarajan into the ARF. Secondary transfer function and deep-sea coral temperatures converted into the absolute reference frame.

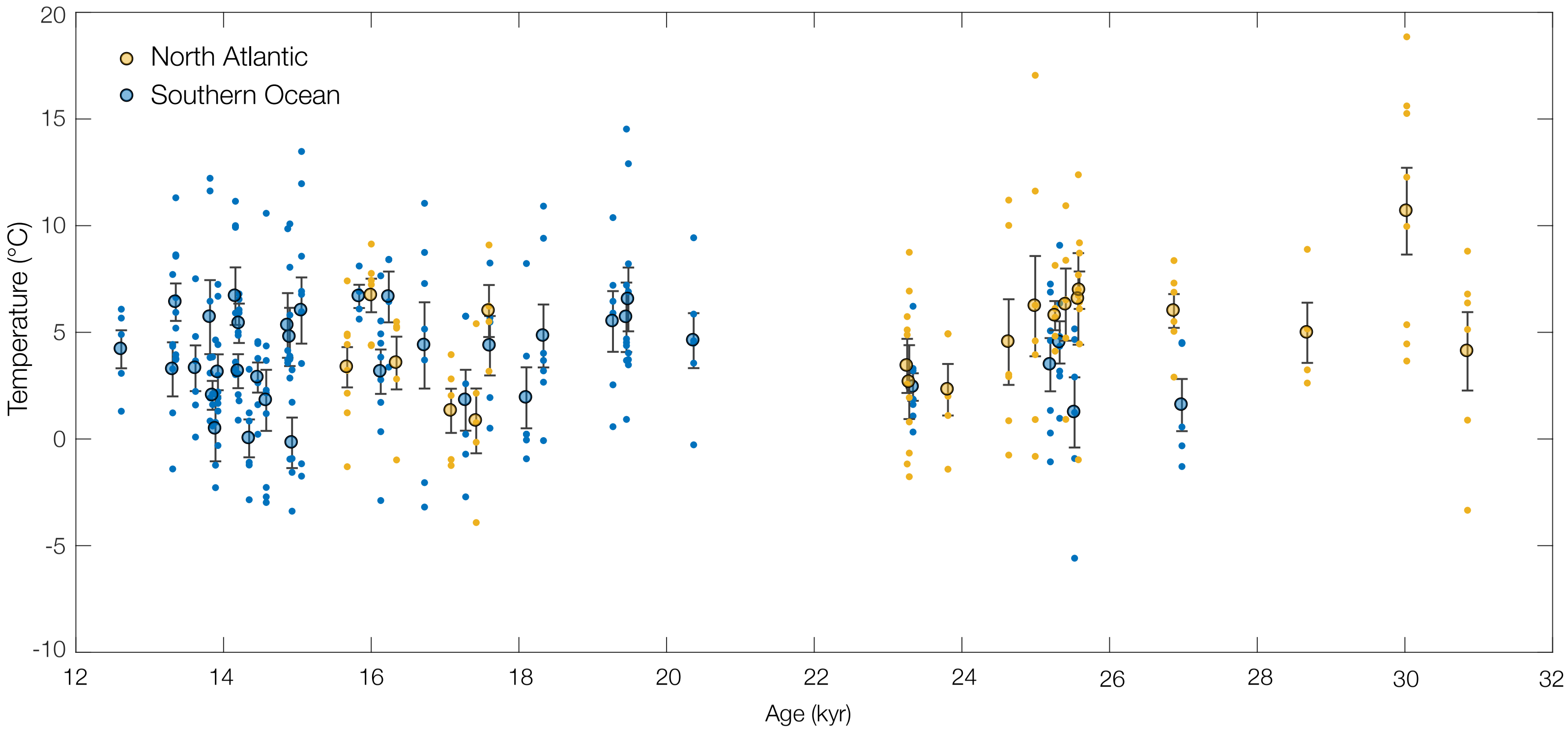

Figure S5. Summary of all clumped isotope temperature measurements for the North Atlantic (yellow) and Southern Ocean (blue). Means and 1σ SE are plotted as well.