[Paleoceanography and Paleoclimatology]

Supporting Information for

Tropical Sea Surface Temperatures following the Middle Miocene Climate Transition from Laser-Ablation ICP-MS analysis of glassy foraminifera

Michael G. Nairn[1], Caroline H. Lear[1], Sindia M. Sosdian[1], Trevor R Bailey[2], and Simon Beavington-Penney[3]

[1]School of Earth and Environmental Sciences, Cardiff University, Cardiff, UK,
[2]Department of Natural Sciences, Amgueddfa Cymru, National Museum Wales, Cathays Park, Cardiff, [3] BG Group, 100 Thames Valley Park Drive, Reading, RG6 1PT, UK*

*Current address: Department of Earth and Environmental Sciences, The University of Manchester, Williamson Building, Oxford Road, Manchester, M13 9PL, UK.

Contents of this file

Additional Supporting Information (Files uploaded separately)

Tables S1 to S3, and S5 to S11.

Introduction

This supporting information contains the age-depth model for the Sunbird-1 well used in this study, a figure comparing Mg/Ca ratios from solution-based and laser-ablation ICP-MS, a figure showing the relationship between Mg/Ca ratios and those of Al/Ca and Mn/Ca from a LA-ICP-MS sample, a figure showing the seawater Mg/Ca curve used to correct Mg/Ca for changes in seawater Mg/Ca, a figure showing the surface pH record used to correct Mg/Ca for changes in the carbonate system, a figure comparing SST estimates using both the *Anand et al.* (2003) and the *Evans et al.* (2016) approaches, a figure showing the covariance between solution-based

Mg/Ca ratios and those of Mn/Ca, Al/Ca, and U/Ca at Sunbird-1, a version of Figure 5 using the alternative approach of *Evans et al.* (2016) to calculate SST, a version of Figure 6 using the alternative approach of *Evans et al.* (2016) to calculate SST, and a figure showing *D. altispira* mean test weights.

There are 11 data tables, with all but Table S4 uploaded separately. Tables S1 to S3 show downcore % coarse fraction, $\delta^{18}O$, and solution-based ICP-MS data from Sunbird-1. Table S4 shows the LA-ICP-MS parameters used. There are further tables of the LA-ICP-MS trace metal data for all profiles from the 1551-1554m sample, the downcore LA-ICP-MS Mg/Ca ratios for all samples, a data table indicating the age range of pooled samples, and the downcore LA-ICP-MS Mg/Ca ratios distinguishing between pooled and unpooled samples. There are then data tables for the alternative sea surface temperature downcore record from LA-ICP-MS Mg/Ca data, and from the $\delta^{18}O$ data. The final data table provides *D. altispira* mean test weights.

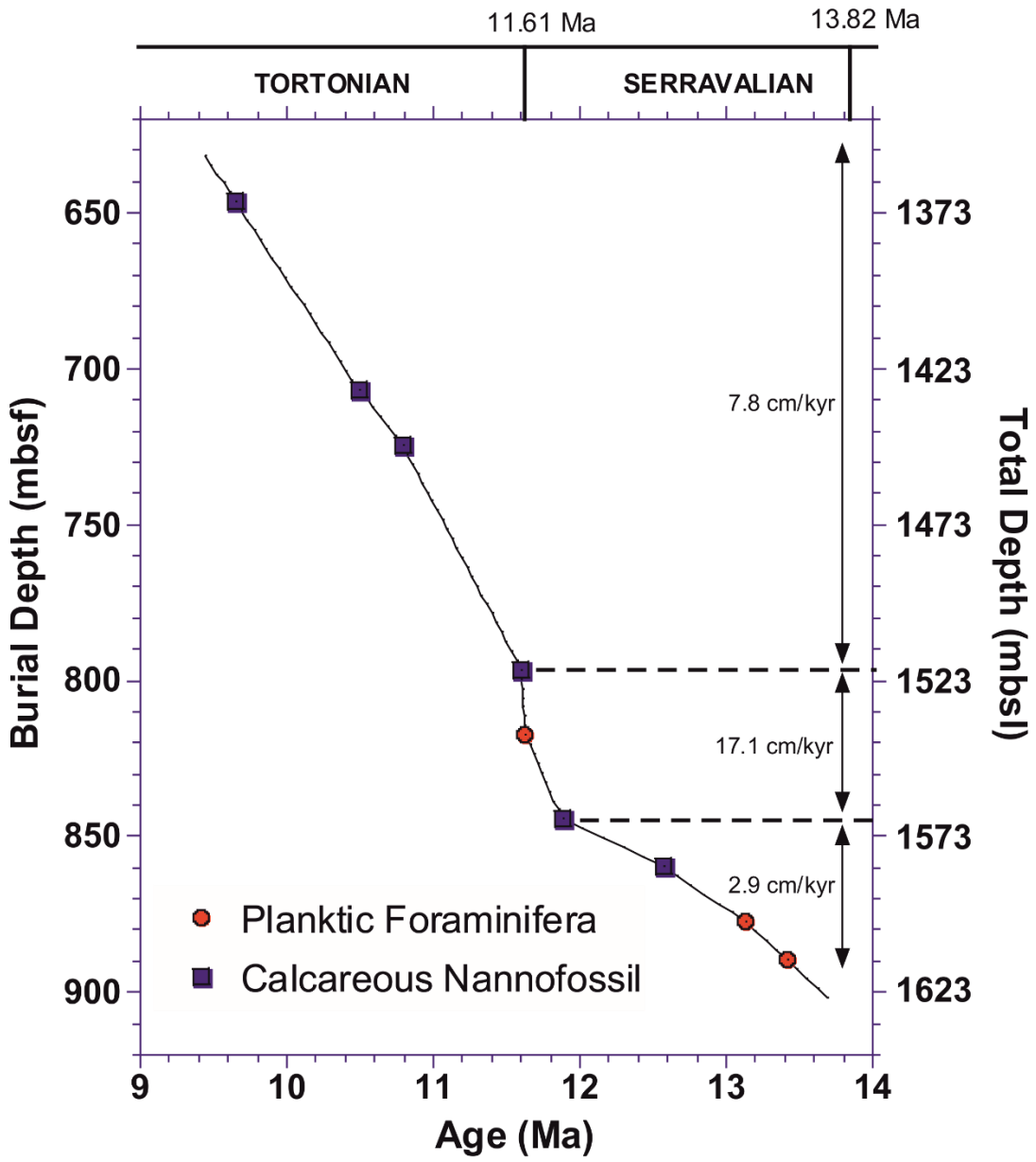

Figure S1. Age-depth model for Sunbird-1 using the biostratigraphic zonations of *Wade et al.* (2011) and *Backman et al.* (2012) updated in the astronomically tuned timescale of *Raffi et al.* (2020) using linear interpolation between reliable biostratigraphic datums. Burial depth in the sediment and the total depth below the sea surface are given (water depth =723m). Micropaleontological and calcareous nannoplankton assemblages for Sunbird-1 were analyzed by Haydon Bailey and Liam Gallagher of Network Stratigraphic Consulting.

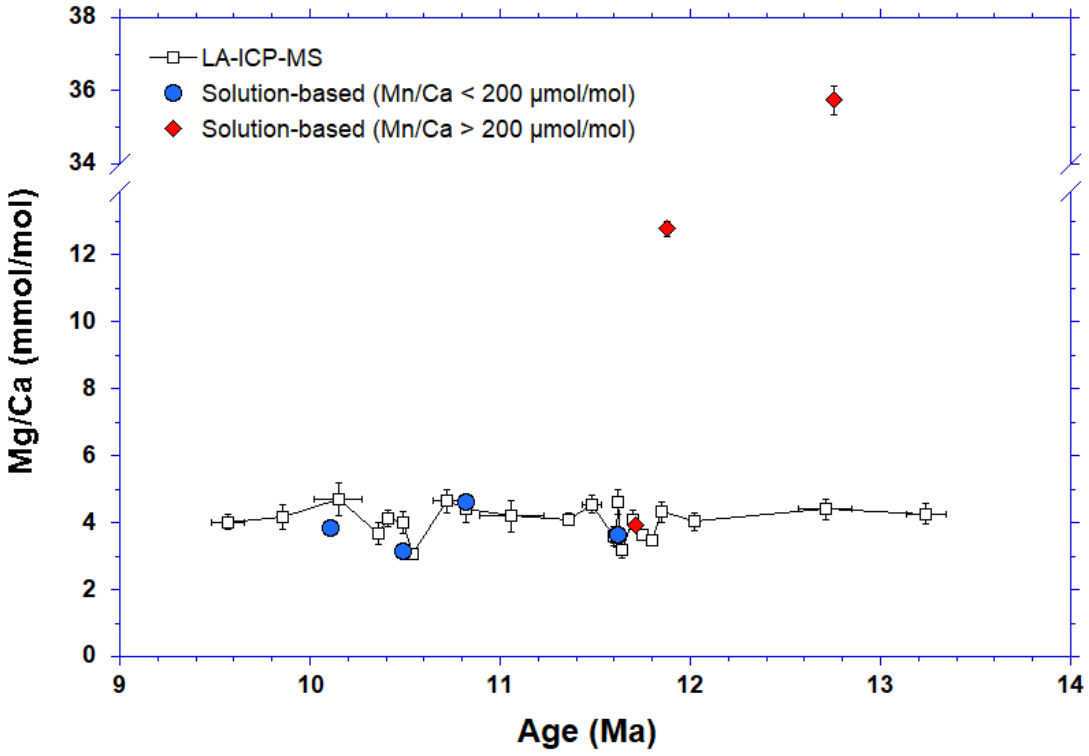

Figure S2. Comparison of Sunbird-1 *D. altispira* Mg/Ca results from LA-ICP-MS analysis (white squares) and reductively cleaned, solution-based analysis where blue circles represent values with Mn/Ca < 200 µmol/mol and red diamonds represent values with Mn/Ca > 200 µmol/mol. Error bars on the LA-ICP-MS data denote the age range for pooled samples and the ± 2SE of Mg/Ca from all depth profiles in the sample. Error bars on the solution-based data denote the ± 2SD from the analysis. Note the break between 13.9 mmol/mol and 34 mmol/mol.

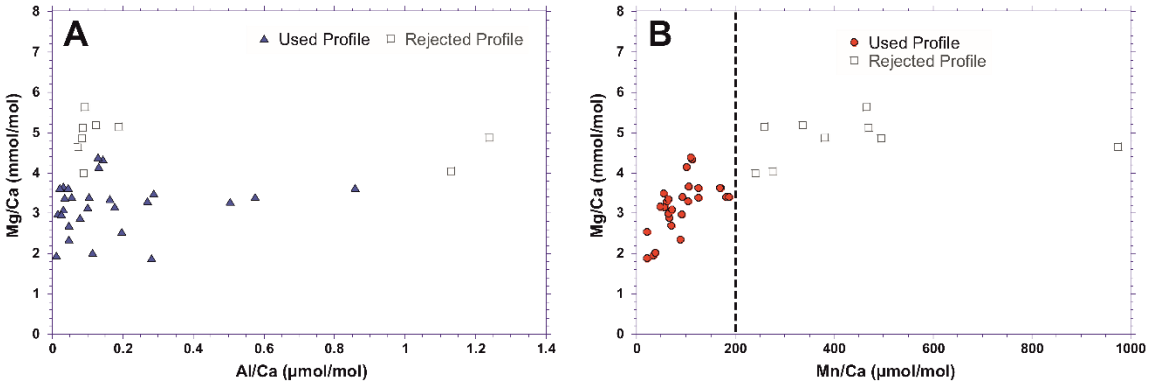

Figure S3. Covariance between *D. altispira* Mg/Ca and (a) Al/Ca, and (b) Mn/Ca from LA-ICP-MS profiles from the 1539-1542 m sample. Used profiles are filled blue triangles and red circles, respectively, whereas profiles excluded during screening are open squares.

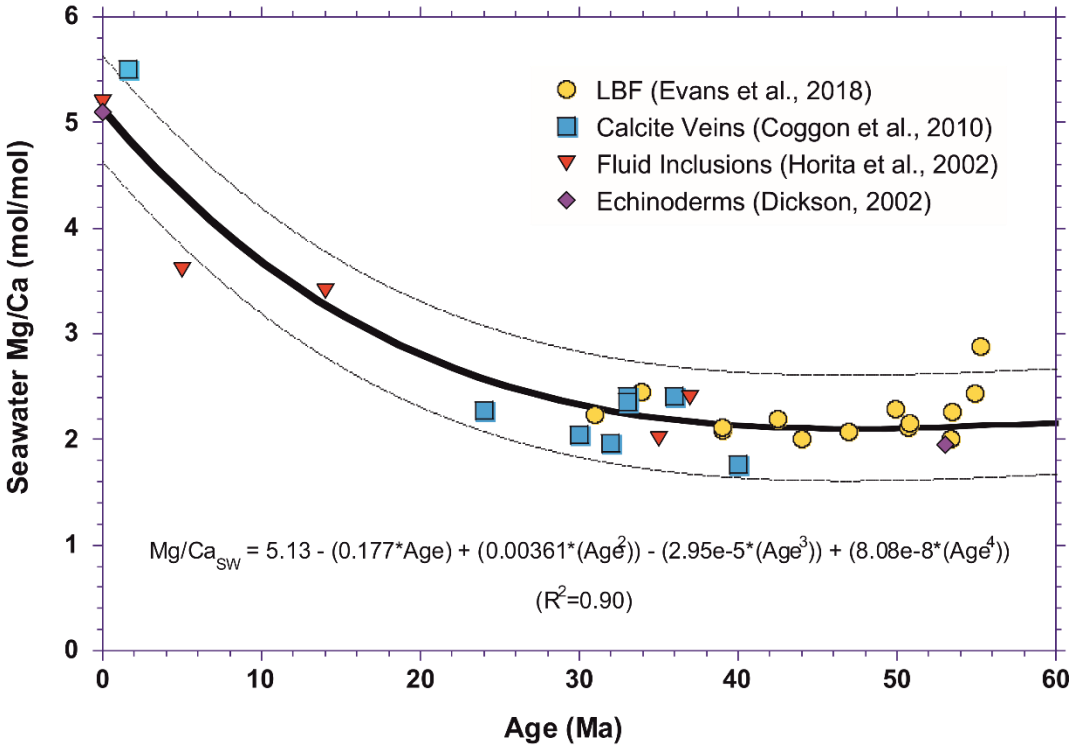

Figure S4. The evolution of seawater Mg/Ca (Mg/Ca_{SW}) through the Cenozoic from records of large benthic foraminifera (LBF) (*Evans et al.*, 2018) (yellow circles), calcite veins (*Coggon et al.*, 2010) (blue squares), fluid inclusions (*Horita et al.*, 2002) (red triangles), and echinoderms (Dickson, 2002) (purple diamonds). Fourth order polynomial fit (thick black line) through the compiled data. The thin lines represent a ±0.5 mol/mol uncertainty window used in the following temperature calculations.

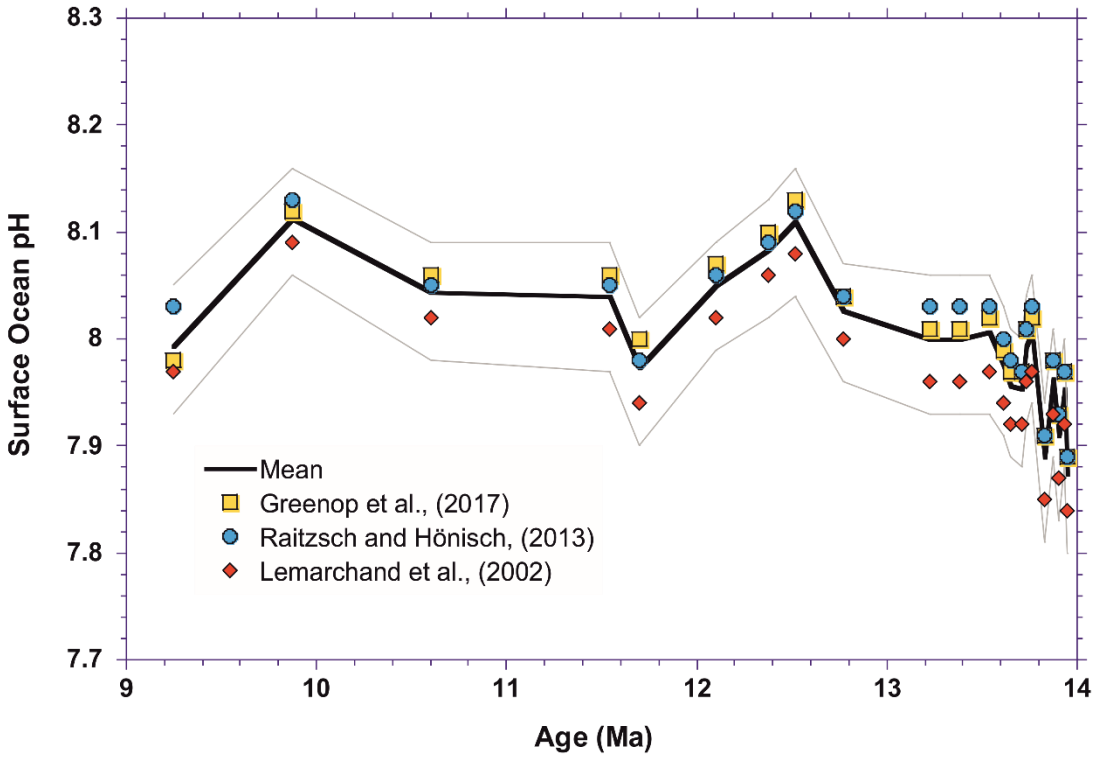

Figure S5. Surface ocean pH determined using $\delta^{11}B$ measurements on planktic foraminifera from a global distribution of open ocean sites (Sosdian et al., 2018). Three $\delta^{11}B_{SW}$ scenarios are used (*Greenop et al.*, 2017, *Lemarchand et al.*, 2002, *Raitzsch and Hönisch*, 2013). Uncertainty envelopes denote the maximum and minimum pH at the 17% and 83% confidence interval, independent of the $\delta^{11}B_{SW}$ scenario.

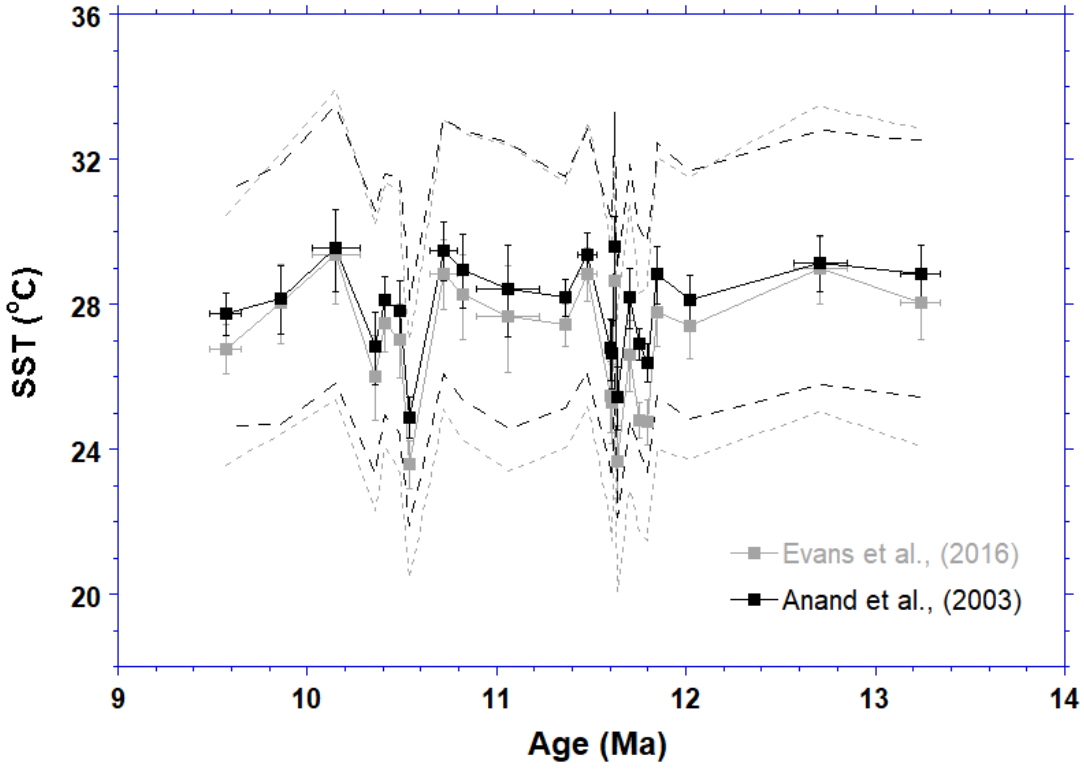

Figure S6. Sea surface temperature record at Sunbird-1 from LA-ICP-MS Mg/Ca using the preferred approach of *Anand et al.*(2003), without a pH correction (black squares), and the alternative approach of *Evans et al.* (2016) (grey squares). Vertical error bars denote the sample uncertainty (± 2SE) and horizontal error bars denote the age range of pooled samples. Dashed black and grey lines denote the full uncertainty on the temperature estimates, including that derived from the calibration uncertainty.

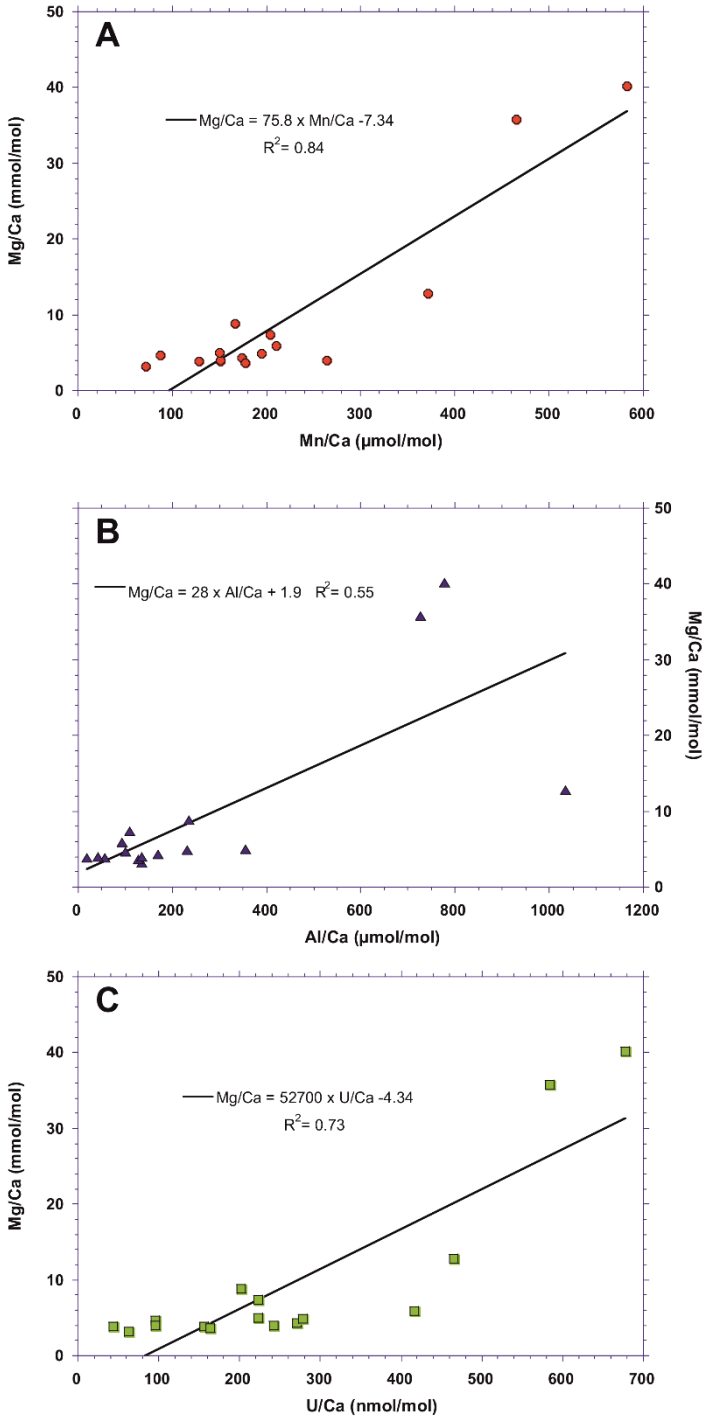

Figure S7. Covariance plots between *D. altispira* Mg/Ca and (a) Mn/Ca (red circles), (b) Al/Ca (blue triangles), and (c) U/Ca (green squares) from solution-based ICP-MS. R2 correlations for all plots are given.

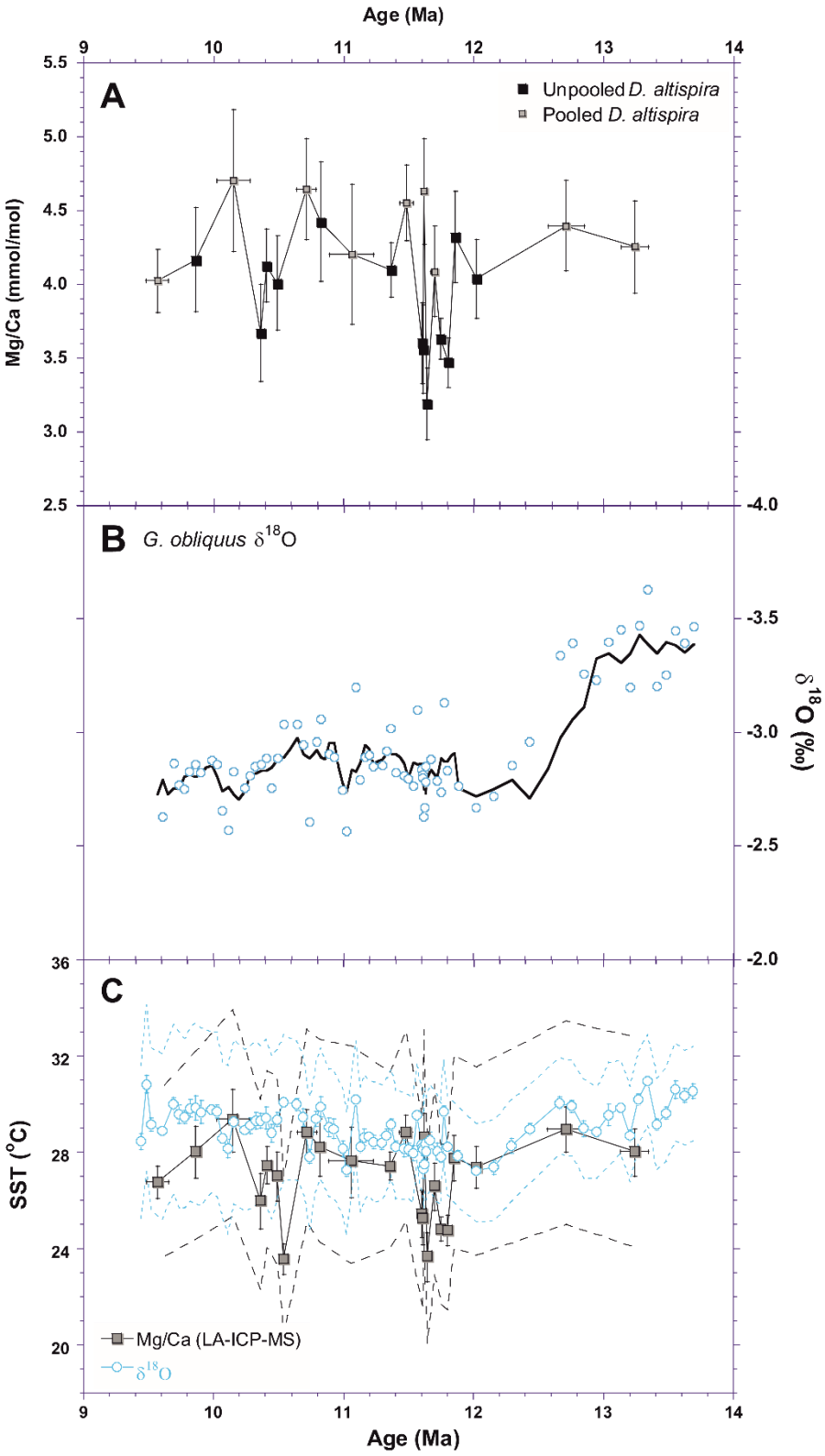

Figure S8. (a) Mean *D. altispira* LA-ICP-MS Mg/Ca ratios (mmol/mol) for unpooled (black squares) and pooled (grey squares) samples from Sunbird-1. Error bars denote the age range for

pooled samples, and the ± 2SE of Mg/Ca from all depth profiles in the sample. (b) *G. obliquus* $\delta^{18}O$ from Sunbird-1. Solid line is a five-point moving average. (c) Sea surface temperature records at Sunbird-1 from planktic foraminiferal δ18O, and LA-ICP-MS Mg/Ca using the alternative approach of *Evans et al.* (2016). Symbols are the same as in (a) and (b). Error bars on the $\delta^{18}O$ record denote the analytical uncertainty (± 2SD), and error bars on the Mg/Ca record denote the sample uncertainty (± 2SE). As in (a), pooled Mg/Ca samples also have horizontal error bars denoting the sample age range. Dashed blue and black lines denote the full uncertainty on the temperature estimates, including that derived from the calibration uncertainty, for $\delta^{18}O$ and LA-ICP-MS Mg/Ca respectively. Figure 5 provides LA-ICP-MS Mg/Ca sea surface temperatures using the preferred approach of *Anand et al.* (2003) without a pH correction.

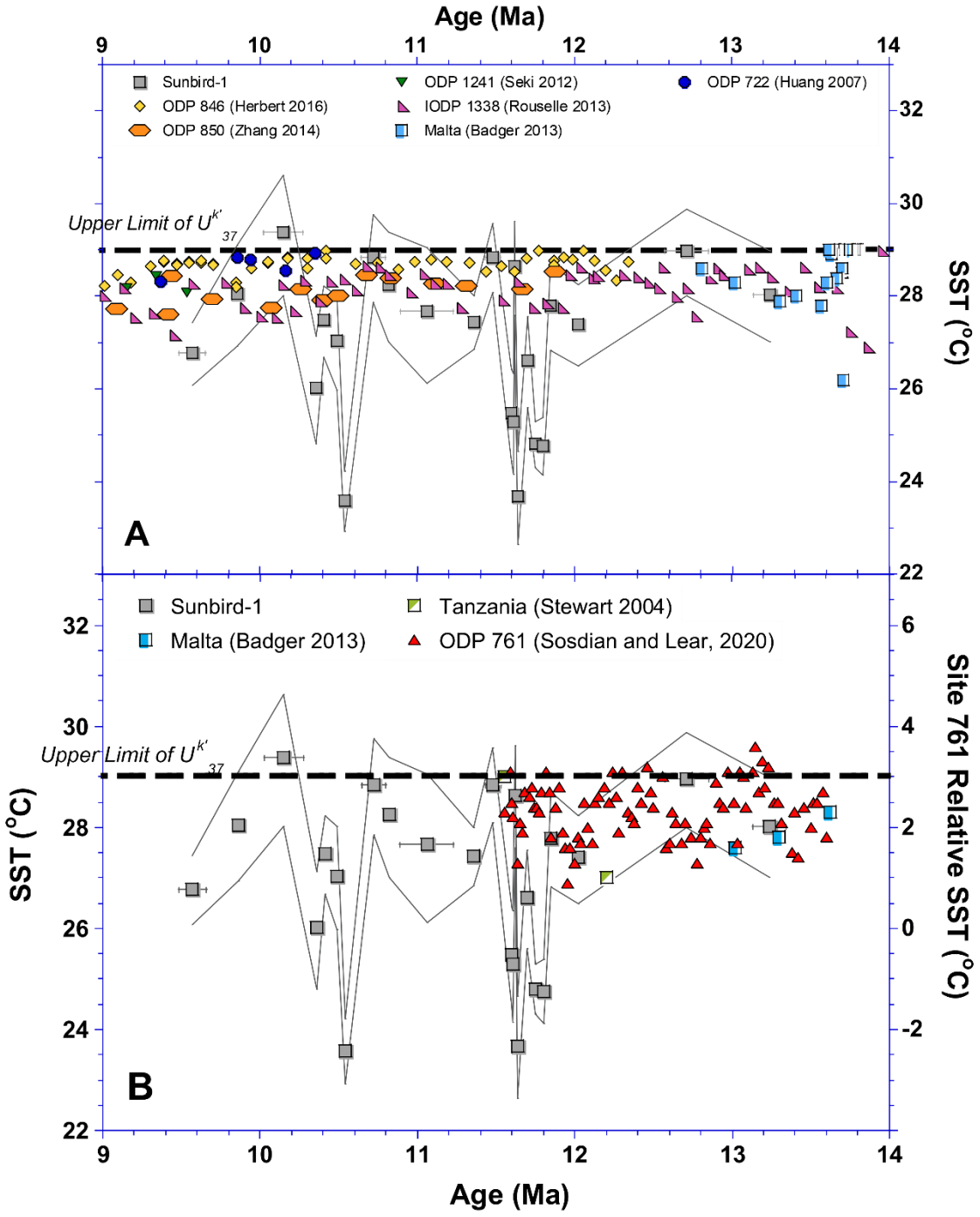

Figure S9. Sunbird-1 LA-ICP-MS Mg/Ca derived SST using the approach of *Evans et al.* (2016) compared to SST estimates at contemporaneous sites from (a) Uk37, and (b) foraminiferal geochemistry. Estimates applying Uk37 are from ODP Site 722 (*Huang et al.*, 2007) in the Arabian Sea, ODP & IODP Sites 846 (*Herbert et al.*, 2016), 850 (*Zhang et al.*, 2014), 1241 (*Seki et al.*, 2012), and U1338 (*Rousselle et al.*, 2013) in the Eastern Equatorial Pacific, and terrestrial outcrops in Malta (*Badger et al.*, 2013). Estimates applying the foraminiferal Mg/Ca proxy are

from ODP Sites 761 (*Sosdian and Lear*, 2020) and terrestrial outcrops in Malta (*Badger et al.*, 2013). ODP Site 761 is displayed on an alternative axis as SST anomalies relative to the baseline average from 16.0 – 15.5 Ma. Two temperature estimates using the $\delta^{18}O$ of exceptionally preserved foraminifera from Tanzania are also shown (*Stewart et al.*, 2004). The upper limit for the Uk37 proxy (29^{0}C) is marked by the thick dashed black line. All previously published records used for comparison are kept on their original age models.

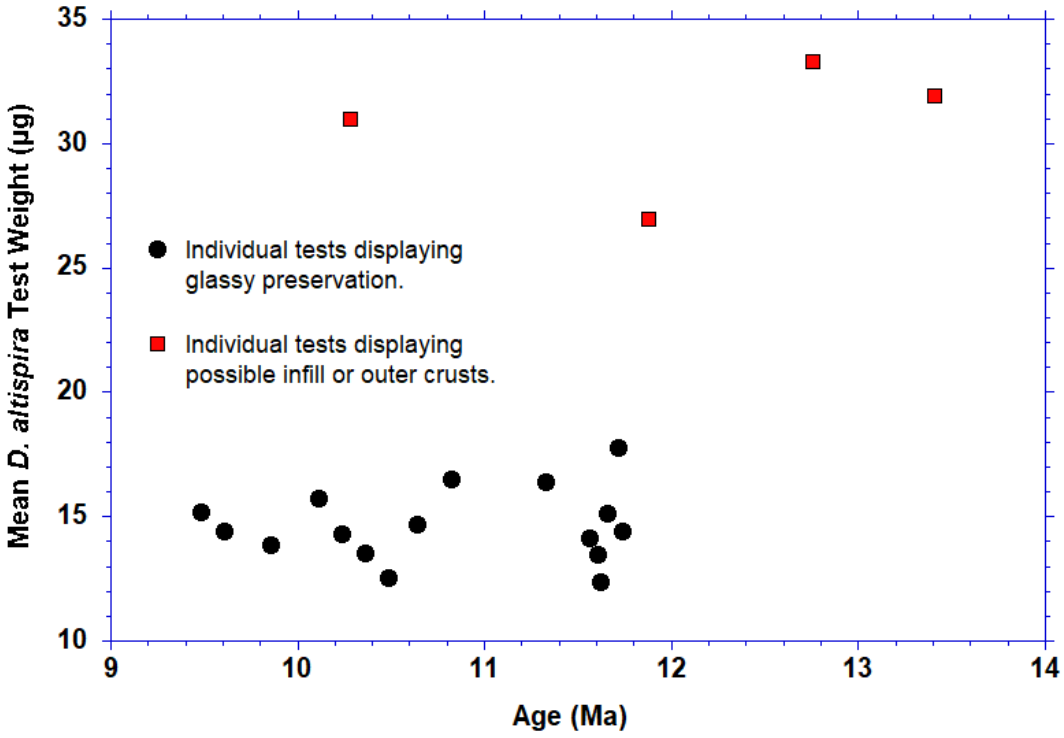

Figure S10. Mean *D. altispira* test weight (µg) for samples measured by solution ICP-MS (Supplementary Table S3) in the Sunbird-1 core. Samples noted to have individuals displaying either infill or outer crusts prior to chemical cleaning are displayed as red squares.

Table S1: Weighed coarse fraction (% >63µm) in the Sunbird-1 core. The 1353-1356m, 1356-1359m, and 1575-1578m samples (marked by an asterisk) were rejected due to the presence of concrete, emplaced by the drilling process, artificially raising the % coarse fraction.

Table S2: *Globigerinoides obliquus* $\delta^{18}O$ ratios in the Sunbird-1 core. Foraminiferal abundance from thirteen samples (marked with an asterisk) was insufficient for analysis.

Table S3: Solution-based *Dentoglobigerina altispira* trace metal/calcium ratios from Sunbird-1. We distinguish between those cleaned with and without the reductive cleaning step**.**

ICP-MS: Thermo Element XR

RF Power	1300 Watts
Torch Position (X, Y, Z)	2.5, -0.2, -4.5 mm
Argon Carrier Flow (optimised daily)	~0.90 l/min
Argon Coolant Flow	14 l/min
Argon Auxiliary Flow	0.80 l/min
Sweep Time	350 ms
Cones	Ni

Laser Ablation System: RESOlution S-155

Helium Flow	350 ml/min
N_2 Flow	4 ml/min
Spot Size	50 µm
Scan Speed	3 μms^{-1}
Fluence	3.5 Jcm^{-2}
Repetition Rate	2.0 Hz
ThO^+/Th^+	<0.4%
U^+/Th^+	~1

Table S4. Operating parameters of LA-ICP-MS for *Dentoglobigerina altispira* analyses. ICP-MS parameters were optimized daily during tuning, and typical operating values are stated.

Table S5. *Dentogloboquadrina altispira* LA-ICP-MS Mg/Ca ratios from the 1551-1554m sample in the Sunbird-1 core. Up to 10 profiles through 10 tests were analyzed for each species. Highlighted samples were excluded due to elevated Mn/Ca and/or Al/Ca ratios.

Table S6. Summary of *Dentogloboquadrina altispira* Mg/Ca ratios in the Sunbird-1 core from LA-ICP-MS analyses. Highlighted samples do not contain the required number of profiles for the Mg/Ca value to be considered representative for the sample.

Table S7. Age range and the number of samples, specimens, and profiles combined for each pooled sample of D. altispira from Sunbird-1.

Table S8. Summary of pooled and unpooled *Dentogloboquadrina altispira* mean Mg/Ca ratios in the Sunbird-1 core from LA-ICP-MS analyses. Minimum and maximum age refer to the age range of the pooled samples (Supplementary Table S7).

Table S9. Sea Surface Temperatures calculated from the unpooled and pooled *Dentogloboquadrina altispira* mean Mg/Ca ratios in the Sunbird-1 core from LA-ICP-MS analyses (Supplementary Table S8). Minimum and maximum age refer to the age range of the pooled samples (Supplementary Table S7). pH is calculated by linear interpolation between the pH measurements of *Sosdian et al.* (2018) (Supplementary Figure S5). pH corrected Mg/Ca is calculated using the multi-species calibration of *Evans et al*. (2016) (Equation 3). Seawater Mg/Ca is calculated from this study using Supplementary Figure S4. The pre-exponential (B) and exponential (A) constants of the Mg/Ca-temperature calibration are calculated using the calibration of *Evans et al.* (2016b), (Equation 4 and 5). Temperature is calculated as ln((Mg/Ca)/B)/A, using the values of B and A calculated in the previous columns. Maximum and Minimum temperatures refer to the full range of absolute temperatures derived incorporating the analytical and calibration uncertainty. Analytical Error Only Maximum and Minimum temperatures refer to the range of temperatures derived from the analytical and analytical uncertainty only.

Table S10. Supplementary Table S10: Sea Surface Temperatures calculated from *Globigerinoides obliqus* $\delta^{18}O$ ratios in the Sunbird-1 core (Supplementary Table S2) using the calibration of *Bemis et al.* (1998) (Equation 4). Calibration uncertainty includes ± 0.091 ‰ due to any potential influence of salinity (*LeGrande and Schmidt,* 2006) and seawater $\delta^{18}O$ (*Cramer et al.* 2011). This $\delta^{18}O_{SW}$ was converted from VSMOW to VPDB by incorporating a -0.27‰

correction (*Hut*, 1987). Maximum and Minimum temperatures refer to the full range of absolute temperatures derived incorporating the analytical and calibration uncertainty. Analytical Error Only Maximum and Minimum temperatures refer to the range of temperatures derived from the analytical uncertainty only**.**

Table S11. Supplementary Table S11: Mean *Dentoglobigerina altispira* test weight (µg) for samples measured by solution ICP-MS (Supplementary Table S3) in the Sunbird-1 core. Samples at 1413-1416m, 1566-1569m, 1587-1590m, and 1611-1614m depths (marked by an asterisk) were noted to have individuals displaying either infill or outer crusts, prior to chemical cleaning.