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

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Key Points:

- Laser-Ablation ICP-MS facilitates absolute sea surface temperature reconstructions using foraminifera with diagenetic coatings.
- Tropical sea surface temperatures remained relatively stable at 24-31°C following the Miocene Climate Transition.
- An increased latitudinal temperature gradient developed through the mid-to-late Miocene.

Abstract

The unipolar icehouse world of the mid-late Miocene is a poorly understood interval in the evolution of Cenozoic climate, and the sparse proxy-based climate reconstructions are associated with large uncertainties. In particular, tropical sea surface temperature (SST) estimates largely rely on the unsaturated alkenone U^{k}_{37} proxy, which fails to record temperatures higher than 29˚C, and Mg/Ca ratios of poorly preserved foraminifera. We reconstruct robust, absolute, SSTs between 13.5 Ma and 9.5 Ma from the South West Indian Ocean (paleolatitude ~5.5˚S) using Laser-Ablation (LA-) ICP-MS microanalysis of glassy planktic foraminiferal Mg/Ca. Employing this microanalytical technique, and stringent screening criteria, permits the reconstruction of robust paleotemperatures from Mg/Ca thermometry using foraminifera which although glassy, are contaminated by authigenic coatings. Our absolute estimates of 24-31ºC suggest that SST in the tropical Indian Ocean was relatively constant between 13.5 and 9.5 Ma, similar to those reconstructed from the tropics using the U^{k}_{37} alkenone proxy. This suggests an interval of enhanced polar amplification between 10 and 7.5 Ma, immediately prior to the global late Miocene Cooling. The mid-to-late Miocene is proposed as a key interval in the transition of the Earth's climate state towards that of the modern-day.

1 Introduction

The mid-late Miocene is an important interval in the evolution of global climate through the Cenozoic, representing a key period in the transition out of the warm, dynamic climate state of the Miocene Climatic Optimum (MCO) into a more stable unipolar icehouse world (*Badger et al.*, 2013; *Foster et al.*, 2012; *Greenop et al.*, 2014; *Sosdian et al.*, 2018). Despite being characterized by similar to modern day atmospheric CO_2 concentrations (*Gavin L. Foster et al.*, 2012; *Sosdian et al.*, 2018; *Super et al.*, 2018), middle Miocene mean global temperatures were likely significantly warmer than the modern day (*Pound et al.*, 2011; *Rousselle et al.*, 2013). This has been used to suggest a decoupling of global temperature and atmospheric CO_2 forcing (*LaRiviere et al.*, 2012; *Pagani et al.*, 1999), a characteristic which general circulation models struggle to simulate (*Knorr et al.*, 2011; *von der Heydt and Dijkstra*, 2006). It has also been suggested that the late Miocene was an additional important key step in the transition to our modern climate state, as high latitudes cooled more than low latitudes, leading to a marked steepening of latitudinal temperature gradients (*Herbert et al.*, 2016). The late Miocene Cooling (LMC) between ~ 7.5 and 5.5 Ma was a global phenomenon (*Herbert et al.*, 2016) perhaps associated with decreasing atmospheric pCO_2 (*Stoll et al.*, 2019). The increase in the equator to pole surface temperature gradients was not associated with an increase in the benthic foraminiferal oxygen isotope record, implying that it occurred in the absence of a large increase in continental ice volume (*Herbert et al.*, 2016). Polar amplification in the LMC is consistent with estimates for other time intervals (e.g., *Cramwinckel et al.* (2018)). However, the LMC was also preceded by a significant cooling of mid to high southern and northern latitudes, a heterogenous cooling at high northern latitudes, and a muted, limited cooling in the tropics (*Herbert et al.*, 2016). This perhaps suggests an unusually high polar amplification factor for the interval immediately preceding the LMC. Potential changes in the Earth System that could impact the magnitude of polar amplification include for example sea ice extent, vegetation induced changes in albedo, cloud cover, or ocean-atmosphere heat transport. Constraining the magnitude and timing of the steepening of latitudinal temperature gradients is therefore important for understanding the factors driving the late Miocene surface cooling specifically, and Earth System feedbacks more generally. Ideally, this would be achieved through a combined data-modelling approach using multi-proxy temperature reconstructions spanning a range of latitudes to increase confidence in calculated changes in temperature gradients.

Despite the significance of this climate interval, the evolution of global sea surface temperatures (SST) and hence temperature gradients during the mid-late Miocene is relatively poorly constrained due to a paucity of complete well-preserved sedimentary successions (*Lunt et al.*, 2008). The widespread carbonate dissolution, which dramatically reduced the sediment carbonate content and preservation quality in deep marine sediments, is termed the middle-late Miocene carbonate crash (*Farrell et al.*, 1995; *Jiang et al.*, 2007; *Keller and Barron*, 1987; *Lübbers et al.*, 2019; *Lyle et al.*, 1995). In addition to these dissolution issues, the majority of foraminifera-bearing Miocene sections are comprised of carbonate rich sediments which have undergone some degree of recrystallisation. The oxygen isotopic composition of planktic foraminifera that have undergone recrystallisation in seafloor sediments has been shown to be biased to colder temperatures (*Pearson et al.*, 2001). While planktic foraminiferal Mg/Ca appears to be less affected than $\delta^{18}O$, the impact of recrystallisation on reconstructed Mg/Ca sea surface temperatures remains an additional source of uncertainty (*Sexton et al.*, 2006). As a consequence, many mid-late Miocene absolute sea surface temperature reconstructions are restricted to estimates based on the unsaturated alkenone proxy (*Herbert et al.*, 2016; *Huang et al.*, 2007; *LaRiviere et al.*, 2012; *Rousselle et al.*, 2013; *Seki et al.*, 2012; *Zhang et al.*, 2014). These records show a cooling in the late Miocene which begins around 10 Ma at high northern and southern latitudes. However, significant cooling in the tropics is not apparent in the alkenone records until ~7.5 Ma, while atmospheric pCO_2 reconstructions also suggest a significant decline from this time (*Sosdian et al.*, 2018; *Stoll et al.*, 2019). At face value therefore, these records imply an interval of enhanced polar amplification between 10 Ma and 7.5 Ma in the absence of significant drawdown of CO_2 or increase in ice volume (*Herbert et al.*, 2016; *Sosdian et al.*, 2018). One significant caveat to this interpretation is that the Uk_{37} alkenone proxy becomes saturated above 28ºC (*Müller et al.*, 1998) and the late Miocene tropical SSTs prior to 7.5 Ma are at this limit (*Herbert et al.*, 2016). Therefore, an alternative interpretation of the data would be that the high latitudes and the tropics cooled synchronously from ~10 Ma, but the initial cooling in the tropics was not able to be recorded by the Uk_{37} alkenone proxy. Corroboration of the absolute Uk_{37} alkenone temperatures by an independent proxy would therefore confirm the timing of the global late Miocene Cooling and the possible interval of enhanced polar amplification between 10 Ma and 7.5 Ma.

Here we present a new planktic foraminiferal Mg/Ca record from the Sunbird-1 industry well cored offshore Kenya by BG Group. Critically, middle to late Miocene sediments in Sunbird-1 are hemipelagic clays, which has resulted in glassy preservation of the foraminifera. However, the foraminifera are coated with metal-rich authigenic coatings, which are not removed by standard cleaning techniques. Planktic foraminifera were therefore analyzed by laser ablation ICP-MS to obtain pristine Mg/Ca of the foraminiferal test carbonate and hence enable estimation of absolute SSTs.

2 Materials and Methods

2.1 Site location, stratigraphy, and age control

This study utilizes 91 cuttings, spanning 273 meters at burial depths ranging from 630 m to 903 m, recovered by BG Group from the Sunbird-1 well offshore Kenya (04° 18' 13.268" S, 39° 58' 29.936" E; 723.3 m water depth) (Figure 1, Supplementary Table S1). Sedimentation at Sunbird-1 through the studied interval (9.5-13.5 Ma) is dominated by clays; the fraction of the sediment >63μm averages 11.5% (Supplementary Table S1), much lower than typical carbonate-rich deep-water sites. The impermeable nature and chemical composition of clay-rich sediment reduces diagenetic alteration of primary foraminiferal calcite, making them ideal targets for geochemical analysis (*Pearson et al.*, 2001; *Sexton et al.*, 2006). Tests displaying the desired exceptional preservation appear glassy and translucent under reflected light, and SEM imaging shows retention of the foraminiferal original microstructure (*Pearson and Burgess*, 2008). This style of preferential glassy preservation, as displayed in the Sunbird-1 well, is rare to absent in published records from Miocene foraminifera.

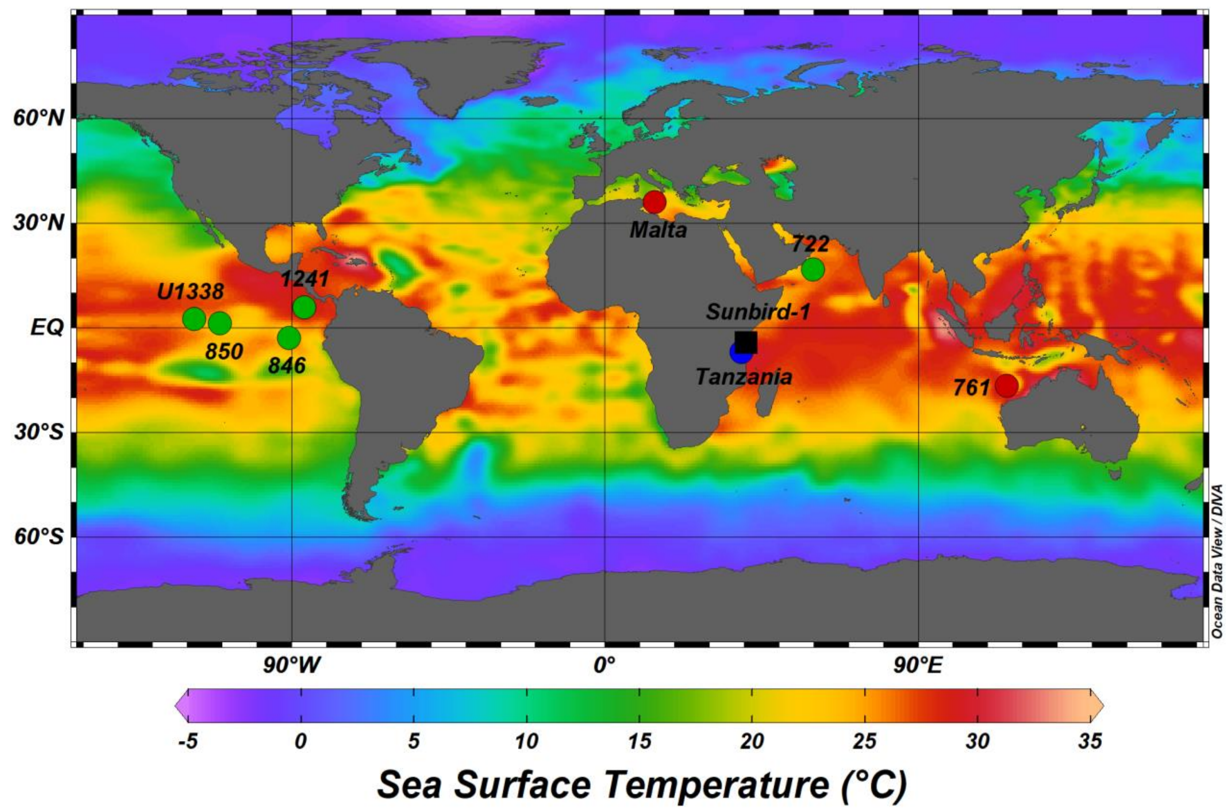


Figure 1: Location of the Sunbird-1 study site (black square). Other sites for which there are mid to late Miocene sea surface temperature reconstructions from Mg/Ca (red circles), $\delta^{18}O$ (blue circles), and unsaturated alkenones (green circles) are shown. Figure produced using Ocean Data

Viewer (*Schlitzer, R.*, 2018) using modern-day sea surface temperature data from the World Ocean Database.

Micropaleontological and calcareous nannoplankton assemblages for Sunbird-1 were analyzed by Haydon Bailey and Liam Gallagher of Network Stratigraphic Consulting. Biostratigraphic datums, correlated with the astronomical timescale of *Gradstein et al.* (2004), are based on the planktic foraminifera zonations of *Wade et al.* (2011) and calcareous nanofossil zonations of *Backman et al.* (2012). An age model was constructed by linear interpolation between these biostratigraphic datums (Figure S1). Sedimentation rates were ~3 cm/kyr immediately following the middle Miocene Climate Transition (MMCT), and subsequently increased to ~17 cm/kyr between 11.8 and 11.5 Ma, before decreasing to ~8 cm/kyr until 9.5 Ma.

2.2 Foraminiferal stable isotope analysis

Up to 12 individual tests of the planktic foraminifer *Globigerinoides obliquus* showing glassy preservation were used. *G. obliquus* is an extinct, symbiont bearing species with a tropical to subtropical paleogeographical distribution, and is interpreted as being a surface mixed-layer dweller (*Aze et al.*, 2011; *Keller*, 1985). The assertion that *G. obliquus* inhabits and calcifies in the surface mixed layer (*Aze et al.*, 2011; *Keller*, 1985) is supported by multispecies analyses from a 10.0 Ma sediment sample from the Indian Ocean offshore Tanzania showing *G. obliquus* to have the most negative $\delta^{18}O$ (-2.5‰) of all species (Paul Pearson, personal communication, 2019). Tests were crushed between two glass plates ensuring all chambers were opened. Any visible infill was removed using a fine paintbrush under a binocular microscope. Fine clays and other detrital material on the outer surface of the test were removed by rinsing three times in 18.2 MΩ DI water, ultrasonicating for 5-10 seconds in analytical grade methanol, and finally rinsing a further time in 18.2 MΩ DI water. Samples were analyzed at Cardiff University on a ThermoFinnigan MAT253 with online sample preparation using an automated Kiel IV carbonate device. Results are reported relative to Pee Dee Belemnite, and long-term uncertainty based on repeat analysis of NBS-19 is ±0.08 ‰ (n=469, 2 standard deviations) and on repeat analysis of BCT63 is ±0.07 ‰ (n=310, 2 standard deviations). Data is available in Supplementary Table S2.

2.3 Solution ICP-MS trace metal analysis

Between 10 and 15 individuals of the planktic foraminifer *Dentoglobigerina. altispira* were crushed between two glass plates ensuring all chambers were opened. Due to the low foraminiferal abundance it was not possible to analyze the same species for stable isotope and trace metal composition. Any visible infill was removed using a fine paintbrush under a binocular microscope. Fragments were cleaned to remove clays and organic matter following the standard protocol (*Barker et al.*, 2003; *Boyle and Keigwin*, 1985). Due to the clay rich nature of the sediment the clay removal procedure was conducted twice. To test for the possible presence of metal oxides half of the samples were reductively cleaned between the clay removal and oxidative cleaning steps. Samples were dissolved in trace metal pure 0.065 M HNO_3 and diluted with trace metal pure 0.5M HNO_3 to a final volume of 350 µl. Samples were analyzed at Cardiff University on a Thermo Element XR ICP-MS using standards with matched calcium concentrations to reduce matrix effects (*Lear et al.*, 2010; *Lear et al.*, 2002). Together with Mg/Ca, several other ratios (Al/Ca, Mn/Ca, and U/Ca) were analyzed to screen for potential contaminant phases. Data are available in Supplementary Table S3. Long-term analytical precision for Mg/Ca throughout the study is better than 2%.

2.4 Laser ablation-ICP-MS analysis

Direct sampling of solid phase material via laser ablation (LA-) allows for geochemical analyses through individual foraminiferal tests at the sub-micron scale when coupled to an inductively-coupled-plasma mass spectrometer (ICP-MS) (*Detlef et al.*, 2019; *Eggins et al.*, 2004; *Evans et al.*, 2015; *Fehrenbacher et al.*, 2015; *Hines et al.*, 2017; *Petersen et al.*, 2018; *Reichart et al.*, 2003). A key advantage of analyzing the trace element composition of foraminifera using LA-ICP-MS over the more traditional solution based ICP-MS is the ability to recognize the diagenetically altered portions of the tests, allowing identification of the primary calcite (*Creech et al.*, 2010; *Hasenfratz et al.*, 2016; *Pena et al.*, 2005). The elemental composition of this primary calcite can provide uncompromised information about palaeotemperature (*Nooijer et al.*, 2017; *Eggins et al.*, 2003; *Pena et al.*, 2005) and other paleo-environmental conditions such as pH (*Mayk et al.*, 2020; *Thil et al.*, 2016) and oxygenation (*Koho et al.*, 2015; *Petersen et al.*, 2018).

Up to six specimens of *D. altispira* were selected from 44 depth intervals through the Sunbird-1 core for LA-ICP-MS analysis. Foraminiferal sample preparation included the removal of fine clays and other detrital material on the outer surface of the test using DI water and methanol, but the more aggressive oxidative and reductive steps (*Barker et al.*, 2003; *Boyle and Keigwin*, 1985), were not required for laser ablation analysis (*Vetter et al.*, 2013). The cleaned tests were mounted onto glass slides using double sided carbon tape and were allowed to dry before being mounted into the sample cell (*Evans et al.*, 2015; *Fehrenbacher et al.*, 2015; *Hines et al.*, 2017).

Analyses were performed using an ArF excimer (193nm) LA- system with dual-volume laser-ablation cell (RESOlution S-155, Australian Scientific Instruments) coupled to a Thermo Element XR ICP-MS. Optimized ablation parameters and analytical settings determined for analyzing foraminifera in the Cardiff University CELTIC laboratory (Supplementary Table S4; (*Detlef et al.*, 2019; *Nairn*, 2018)) were used for this study. Three cleaning pulses to remove any contaminant on the outer ~0.5 µm of the test surface were included prior to analysis. We analyzed ^{25}Mg, ^{27}Al, ^{43}Ca, ^{55}Mn and ^{88}Sr, each isotope having a constant 50 ms dwell time. Typically, intervals with elevated Mn and Al in concert with elevated Mg are interpreted as being contaminant phases (e.g., Fe-Mn oxides-hydroxides or clays), and are commonly found on the inner and outer test surface (*Barker et al.*, 2003; *de Nooijer et al.*, 2014; *Hasenfratz et al.*, 2016; *Koho et al.*, 2015; *Pena et al.*, 2005).

Where possible three laser spot depth profiles, each approximately 15 µm deep assuming that each laser pulse only ablates a very thin, ~0.1 µm, layer of calcite, were collected on each of the penultimate (f-1) and previous (f-2) chambers. However, this was not always possible such that older chambers were frequently used to ensure six laser spots per specimen were analyzed (*Nairn*, 2018). NIST SRM 610 glass standard was measured between every six laser profiles, and NIST SRM 612 at the beginning and end of analyses from each sample depth. The reference values for elemental concentrations in both silicate glass standards are taken from the GEOREM website (http://georem.mpch-mainz.gwdg.de/sample_query_pref.asp), updated from *Jochum et al.* (2011). NIST SRM 612 was used to determine long term external reproducibility using NIST SRM 610. For Mg/Ca NIST 612 (n=90) had an accuracy of 12.0% and a precision of 3.7% relative to the reported value. A similar ~12% negative offset relative to the reported value of NIST 610-calibrated NIST 612 has been observed over a much longer period of data collection (*Evans and Müller*, 2018). The NIST 610-calibrated data presented here supports the determination of *Evans and Müller* (2018) that the Mg values for both NIST 610 and NIST 612 require reassessment. A more thorough assessment of accuracy cannot be made at present, as a well-characterized calcite reference material, matrix matched to typical foraminiferal calcite, is not currently available (*Evans et al.*, 2015; *Evans and Müller*, 2018; *Fehrenbacher et al.*, 2015).

2.5 LA-ICP-MS data processing and screening

Each individual laser ablation profile was carefully inspected and processed using the SILLS data reduction software package (*Guillong et al.*, 2008) following the established protocol outlined in *Longerich et al.* (1996). First, a background signal of ~15 seconds, from data acquired when the laser was turned off prior to ablation, was selected for each profile. Following this the integration interval for the profile was selected based upon the following three criteria: (i) stable ^{43}Ca counts, indicating ablation of calcite, (ii) stable Mg/Ca signal, indicating a consistent primary calcite phase, (iii) flat Mn/Ca and Al/Ca signals, avoiding any peaks indicating intervals of contamination (Figure 2).

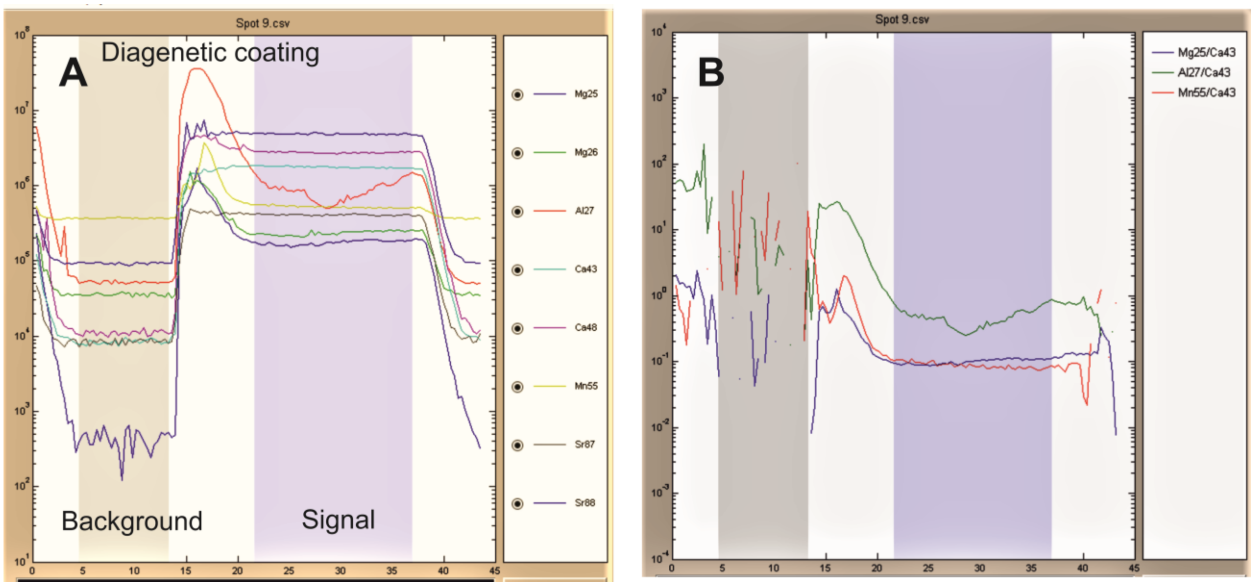


Figure 2: Representative LA-ICP-MS Mg, Al, and Mn profiles demonstrating the selection of background (grey panel) and sample (blue panel) signals, shown in raw isotopic counts (A), and ratios mode (B) where the isotopes of interest are relative to ^{43}Ca, the internal standard. In both panels the x axis is analysis time (seconds), and the y axis is the raw intensity of the isotopes (A) or ratios (B) on a log scale. The sample interval is selected to avoid the elevated Mg/Ca, Mn/Ca, and Al/Ca at the outer surface of the test.

Individual depth profiles were corrected by first subtracting the mean background signal. The repeated analysis of the NIST 610 standard reference material was used to linearly correct for any instrumental drift. Typically, this is small, <2%, because of the good counting statistics and stable data acquisition during ablation. The ablation profiles were normalized to ^{43}Ca as the internal standard and elemental concentrations (TM/Ca) were calculated, assuming 40 wt % for $CaCO_3$. Integrated depth profiles which display Mn/Ca > 200 µmol/mol were excluded, as these suggest potential contamination by Mn-oxides. Furthermore, integrated depth profiles with Al/Ca > 100 µmol/mol associated with elevated Mg/Ca were also excluded (e.g. Figure 3).

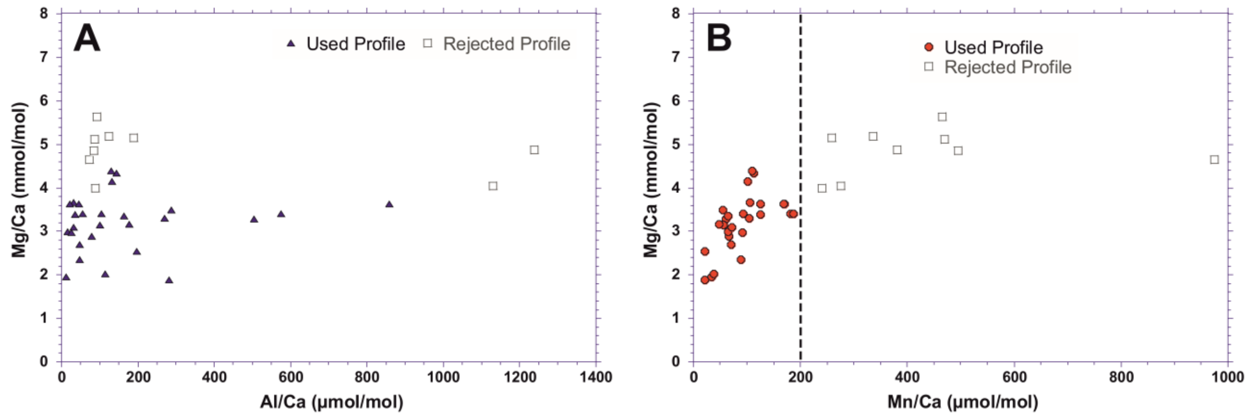


Figure 3: Covariance between *D. altispira* Mg/Ca and (a) Al/Ca, and (b) Mn/Ca from LA-ICP-MS profiles from the 1539-1542 m sample. Used profiles are filled blue triangles and red circles, respectively, whereas profiles excluded during screening are open squares.

2.6 Determination of mean foraminiferal test Mg/Ca by laser ablation

Geochemical heterogeneity exists both within an individual foraminiferal test and between foraminiferal tests from the same sample (*Eggins et al.*, 2004; *Fehrenbacher and Martin*, 2014; *Sadekov et al.*, 2008; *Sadekov et al.*, 2005). Therefore, several laser ablation profiles are required to produce a consistent Mg/Ca ratio for temperature reconstructions. Here we analyzed ten depth profiles through each of ten individual *D. altispira* tests from the 1551-1554 m (11.74 Ma) sample to determine representative inter-specimen variability for these samples (Figure 4). Approximately one third (n=28) of the 100 depth profiles were excluded during screening for elevated Al/Ca and Mn/Ca indicative of diagenetic contamination. The Mg/Ca value of individual depth profiles in *D. altispira* from the 1551-1554 m sample ranges from 2.67 mmol/mol to 5.23 mmol/mol, with a mean of 3.63 ± 0.14 mmol/mol (n=72) (Figure 4a; Supplementary Table S5). The mean Mg/Ca value from four specimens, a total of 28 profiles, is 3.41 ± 0.18 mmol/mol (Figure 4a). Averaging profiles from ten individual tests did therefore not produce significantly better accuracy or precision than averaging profiles from four individual tests (Figure 4b). Therefore, for a Mg/Ca ratio to be considered representative it must represent an average of at least 28 laser ablation profiles, from at least four specimens, with the analytical uncertainty (2 SE) indicating the intra- and inter-specimen variability this incorporates. To account for depth profiles excluded due to contamination, where possible the number of measurements per sample was increased to 36, six depth profiles per specimen and six specimens per sample. This result is in line with other LA-ICP-MS studies (*Rathmann et al.*, 2004; *Sadekov et al.*, 2008). Future studies are advised to conduct similar testing to determine the number of measurements required for a mean sample Mg/Ca to be representative, as this will likely be site dependent.

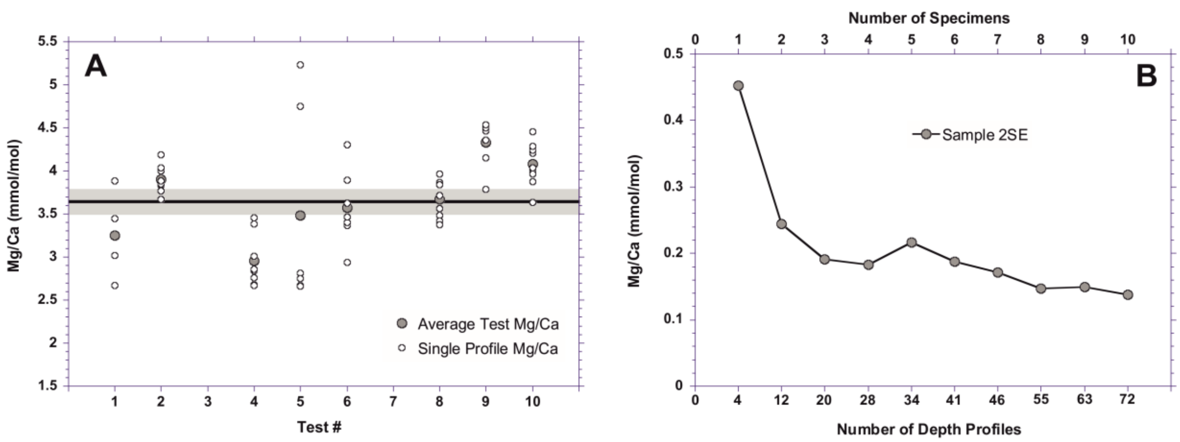


Figure 4: Distribution of *D. altispira* Mg/Ca values from LA-ICP-MS profiles of the 1551-1554 m sample. (A) A summary of all Mg/Ca values, where open circles denote individual measurements, and filled circles denote mean Mg/Ca values for each specimen. The horizontal black line is the mean of all depth profiles from the sample, and the grey bar the ±2 SE sample uncertainty. (B) The evolution of the sample 2 SE with increasing specimens. Only profiles that passed data screening are included (n=72). Data is from Supplementary Table S5.

2.7 Mg/Ca paleo-sea surface temperature calculations

The influence of calcification temperature (T) on the Mg/Ca ratio of foraminiferal calcite can be explained by an exponential curve of general form Mg/Ca = Bexp^{AT} where the pre-exponential constant (B) and exponential constant (A) are species specific (*Anand et al.*, 2003; *Lear et al.*, 2002; *Nürnberg et al.*, 1996; *Rosenthal et al.*, 1997). To convert raw Mg/Ca ratios to absolute temperatures, several secondary controls on Mg/Ca must be considered, and accounted for (*Gray et al.*, 2018; *Hollis et al.*, 2019; *Lear et al.*, 2015).

Planktic foraminiferal Mg/Ca is influenced by changes in the carbonate system, the ratio increasing with decreased pH and/or $\Delta[CO_3^{2-}]$ (*Evans et al.*, 2016; *Gray and Evans*, 2019; *Gray et al.*, 2018; *Russell et al.*, 2004; *Yu and Elderfield*, 2008). However, the ultimate driver of this effect is not certain, and it has been shown that for *Orbulina universa* DIC plays a role in test Mg/Ca variability (*Holland et al.*, 2020). We follow recent results which interpret pH, as opposed to $\Delta[CO_3^{2-}]$ or DIC, as the parameter which controls the carbonate system's influence on Mg/Ca (*Evans et al.*, 2016; *Gray et al.*, 2018). Furthermore, unlike with $\Delta[CO_3^{2-}]$, it is possible to reconstruct pH through the Neogene using boron isotopes in foraminifera (*Foster and Rae*, 2015; *Greenop et al.*, 2014; *Henehan et al.*, 2013; *Sosdian et al.*, 2018). Here we use the recent Neogene boron isotope compilation of *Sosdian et al.* (2018), which provides well constrained estimates of pH across this time interval (Figure S2). Linear interpolation between these pH values allows us to estimate a mean pH value, and associated uncertainty envelope, for each Sunbird-1 sample, where the uncertainty envelope is maximum and minimum pH at the 17% and 83% confidence interval (~± 0.06 pH units). Measured planktic foraminiferal Mg/Ca values are corrected for this influence of pH using the equation of *Evans et al.* (2016) (Equation 1).

$$\textbf{Equation 1}: \ \mathbf{Mg}\Big/\mathbf{Ca}_{\mathbf{CORRECTED}} = \frac{\mathbf{Mg/Ca_{MEASURED}}}{\frac{\mathbf{0.66}}{\mathbf{1+exp(6.9(pH-8.0))}}+\mathbf{0.76}}$$

Fluxes of Mg^{2+} and Ca^{2+} into and out of the oceans means seawater Mg/Ca (Mg/Ca_{sw}) experiences secular variation. This variability must be accounted for when determining absolute sea surface temperatures on Cenozoic timescales (*Hollis et al.*, 2019). Reconstructions of Mg/Ca_{sw} based on large benthic foraminifera (*Evans et al.*, 2018), calcite veins (*Coggon et al.*, 2010), fluid inclusions (*Horita et al.*, 2002), and echinoderms (*Dickson*, 2002) have constrained this variability through the Cenozoic (Figure S3). The Eocene-Oligocene demonstrates relatively stable values of 2.0-2.5 mol/mol (*Coggon et al.*, 2010; *Evans et al.*, 2018). However, only one data point exists from the Miocene, through which Mg/Ca_{sw} more than doubles from ~2.2 mol/mol in the late Oligocene (*Coggon et al.*, 2010) to the well constrained value of 5.2 mol/mol in the modern ocean (*Broecker et al.*, 1982; *Dickson*, 2002; *Horita et al.*, 2002; *Kısakürek et al.*, 2008). Therefore, the method of *Lear et al.* (2015) is followed by fitting the fourth-order polynomial curve fit through the compiled seawater Mg/Ca (Mg/Ca_{sw}) proxy records (Figure S3). We use a ±0.5 mol/mol uncertainty window in the following temperature calculations, this error envelope incorporating the majority of the spread in the proxy data (Figure S3). The preferred equation of (*Evans et al.*, 2016) is used to account for the influence of changing Mg/Ca_{sw} when estimating SST. These authors determined that the best fit to culture-derived calibration lines is when both the pre-exponential (B) and exponential (A) coefficients vary quadratically with Mg/Ca_{sw} (Equation 2 and 3).

$$\textbf{Equation 2:}\ \mathbf{B = (0.019 \times Mg/Ca_{sw}^{2}) - (0.16 \times Mg/Ca_{sw}) + 0.804}$$

$$\textbf{Equation 3:}\ \mathbf{A = (-0.0029 \times Mg/Ca_{sw}^{2}) + (0.032 \times Mg/Ca_{sw})}$$

We substitute these equations into the general exponential calibration, $Mg/Ca = B\exp^{AT}$, to account for changing Mg/Ca_{sw}. Although the *Evans et al.* (2016b) equation is specific to *Globigerinoides ruber*, this species inhabits a shallow water depth of 0-50m (*Schiebel and Hemleben*, 2017) similar to the inferred mixed-layer habitat depth *D. altispira* (*Aze et al.*, 2011). Furthermore, as with *G. ruber*, *D. altispira* was a tropical/subtropical species, with symbionts (*Aze et al.*, 2011).

Salinity can exert a secondary effect on foraminiferal Mg/Ca, sensitivity measurements from culture and core-top studies show this to be ~3-5% per practical salinity unit (psu) (*Gray et al.*, 2018; *Hollis et al.*, 2019; *Hönisch et al.*, 2013; *Kısakürek et al.*, 2008). In the absence of a robust, independent salinity proxy (although we do note the promise of Na/Ca (*Bertlich et al.*, 2018; *Geerken et al.*, 2018)) and the relatively minor effect of salinity on foraminiferal Mg/Ca, this potential secondary control is not empirically accounted for. Sunbird-1 was located in a coastal setting and likely experienced a highly variable hydrological cycle due to changes in the position of the ITCZ making it susceptible to changes in salinity. Therefore, an error of ± 0.5ºC is incorporated into the final sea surface temperature estimates, equivalent to an assumed salinity variability of ~± 1 PSU.

The uncertainties (± 2SE) associated with the conversion from Mg/Ca to absolute SST estimates incorporates the uncertainty in the pH correction, the uncertainty on the Mg/Ca_{sw} record, and a potential uncertainty due to varying salinity. This is termed the calibration uncertainty and is considerably greater than the independent analytical uncertainty.

2.8 $\delta^{18}O$ paleo-sea surface temperature calculations

Due to the limited sampling resolution of the trace metal data, SST is also calculated using foraminiferal $\delta^{18}O$. Foraminiferal $\delta^{18}O$ ($\delta^{18}O_{calcite}$) is converted to temperature (T) using the palaeotemperature equation of *Bemis et al.* (1998) (Equation 4), changes in global ice volume being corrected using the $\delta^{18}O_{sw}$ value from the nearest 0.1 Myr time interval in the compilation of *Cramer et al.* (2011).

$$\textbf{Equation 4}: \ (\boldsymbol{\delta^{18}O_{calcite}} - \boldsymbol{\delta^{18}O_{sw}} + \mathbf{0.27}) = -\mathbf{0.21} \pm \mathbf{0.003\ T} + \mathbf{3.10} \pm \mathbf{0.07}$$

The absence of a robust, independent salinity proxy makes any quantitative attribution of its influence on foraminiferal $\delta^{18}O$ challenging. Therefore, we incorporate potential $\delta^{18}O$ variability due to salinity into any temperature estimate uncertainty. Salinity of the upper water column in a 0.75° x 0.75° grid square around the modern-day study site varies between 34.9 and 35.4 PSU (*Boyer et al.*, 2013). Using the Indian Ocean $\delta^{18}O_{sw}$-salinity relationship of *LeGrande and Schmidt* (2006) (Equation 5) this equates to a maximum $\delta^{18}O_{sw}$ uncertainty of ±0.091‰. Using Equation 4 this equates to a 0.4 ºC uncertainty in the calculated surface temperature.

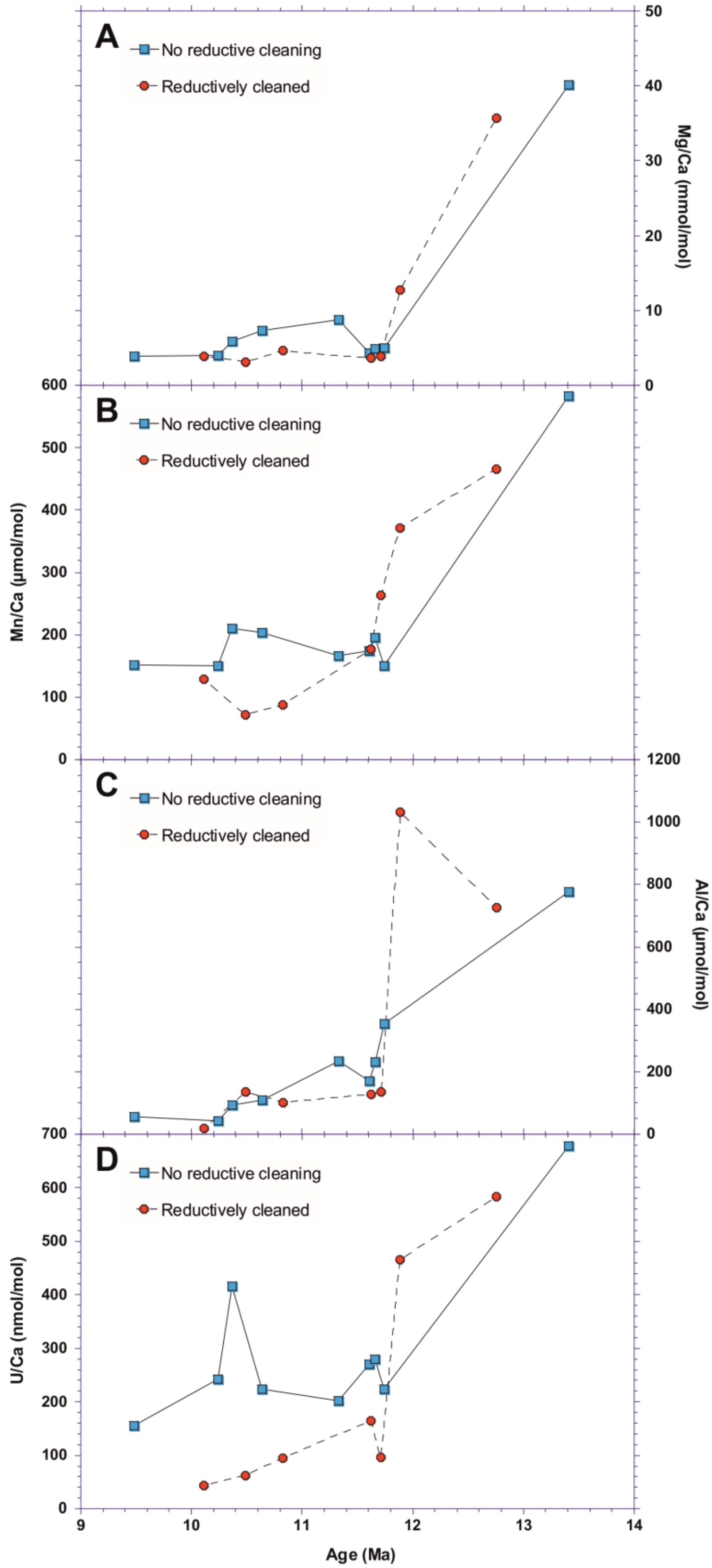
$$\textbf{Equation 5}: \boldsymbol{\delta^{18}O_{sw}}(\mathbf{SMOW}) = (\mathbf{0.16} \pm \mathbf{0.004\ x\ Salinity}) - \mathbf{5.31} \pm \mathbf{0.135}$$

We acknowledge the likelihood of increased variability in sea surface salinity in this downcore record, more than the modern-day calibration accounts for. We use the paleolatitude calculator of *van Hinsbergen et al.* (2015) to calculate a paleolatitude for Sunbird-1 at 10 Ma of approximately 5.5 °S. Using the latitudinal correction of *Zachos et al.* (1994), this gives a $\delta^{18}O_{sw}$ of 0.1‰. The absence of a significant offset from ‰SMOW (0‰) suggests that this will have a negligible influence on the isotopic SST reconstructions.

3 Results

3.1 Solution ICP-MS trace element chemistry

D. altispira Mg/Ca measured by solution ICP-MS ranges from 3.15 ± 0.1 to 40.2 ± 0.2 mmol/mol (Figure 5a), translating to unrealistically high reconstructed sea surface temperatures. The high Mg/Ca ratios strongly suggest the addition of magnesium from a secondary, post-depositional source, prior to 11.75 Ma. The elevated Mg/Ca ratios are associated with correspondingly high Mn/Ca, Al/Ca, and U/Ca (Figure 5b-d). All but two of the Mn/Ca ratios are in excess of the proposed 100 µmol/mol threshold above which its role as a potential contaminant must be assessed (*Boyle*, 1983). Furthermore, every foraminiferal U/Ca ratio is considerably higher than typical U/Ca ratios of primary foraminiferal calcite, which range from ~3-23 nmol/mol (*Chen et al.*, 2017; *Raitzsch et al.*, 2011; *Russell et al.*, 2004). In addition, foraminiferal Al/Ca exceeds the commonly applied 100 µmol/mol threshold in all but the four youngest samples.


A
No reductive cleaning
Reductively cleaned
Mg/Ca (mmol/mol)
50
40
30
20
10
0
B
No reductive cleaning
Reductively cleaned
Mn/Ca (µmol/mol)
600
500
400
300
200
100
0
C
No reductive cleaning
Reductively cleaned
Al/Ca (µmol/mol)
1200
1000
800
600
400
200
0
D
No reductive cleaning
Reductively cleaned
U/Ca (nmol/mol)
700
600
500
400
300
200
100
0
9
10
11
12
13
14
Age (Ma)

404

Figure 5: Downcore (a) Mg/Ca, (b) Mn/Ca, (C) U/Ca, and (d) Al/Ca records for *D. altispira* in the Sunbird-1 core, distinguishing between sample that were reductively cleaned (red circles) and those that were not (blue squares).

The presence of elevated foraminiferal Mn/Ca, Al/Ca, and U/Ca ratios does not necessarily mean that the Mg/Ca ratios are contaminated. However, the downcore, point to point correlation (Figure 5) and covariance (Supplementary Figure S4) between Mg/Ca and contaminant indicators suggest a strong association. This downcore association between Mg/Ca and contaminant indicators, despite a rigorous chemical cleaning protocol, suggests one of two things; (i) the chemical cleaning protocol is not fully effective at removing contaminant coatings, and/or (ii) an Mg-rich contaminant phase is pervasive throughout the calcite test.

Including the reductive cleaning step lowers Mg/Ca, Mn/Ca, and U/Ca ratios in the post 11.8 Ma portion of the record, but has a negligible effect on Al/Ca. Neither cleaning protocol is effective at removing the authigenic coatings on the Sunbird-1 foraminifera in the pre 11.8 Ma portion of the record (Figure 5). For this reason, we also analyzed Sunbird-1 planktic foraminifera by laser ablation ICP-MS.

3.3 Downcore Laser Ablation ICP-MS Mg/Ca

Our laser ablation profiles clearly demonstrate that the metal-rich contaminant is present as an authigenic surface coating on the glassy foraminifera (e.g., Figure 2). Because the alteration is not pervasive throughout the calcite test, laser ablation ICP-MS is an ideal approach to determine pristine test Mg/Ca on these coated samples (section 2.6). *D. altispira* Mg/Ca determined by laser-ablation ICP-MS ranges from 3.03 to 5.07 mmol/mol, with an average value of 4.18 ± 0.40 mmol/mol, and errors (±2SE) range from 0.10 to 1.04 mmol/mol (Supplementary Table S6). However, due to elevated Al/Ca and Mn/Ca ratios, only 14 of the 44 samples are represented by at least 28 laser profiles. To alleviate this problem, adjacent samples have been combined into longer time slices to ensure that the absolute mean Mg/Ca measurements are robust (Table 1). Samples comprising the mean of at least 28 laser profiles are termed “un-pooled samples”. Samples pooled to achieve a minimum of 28 laser profiles are termed “pooled samples”. It is acknowledged that by combining adjacent samples, which span up to 420 kyr, could incorporate orbital scale climatic variability into these pooled samples. However, we do not infer climatic variability on orbital timescales because the coarse sampling resolution could incorporate aliasing of any precessional or obliquital periodicity into longer term eccentricity cycles (*Pisias and Mix*, 1988). In fact, by combining adjacent samples to generate a representative mean Mg/Ca for a longer time-slice could in fact smooth orbital scale variability, reducing uncertainty and assisting the interpretation of longer-term climatic trends.

Average Age (Ma)	Minimum Age (Ma)	Maximum Age (Ma)	# Samples Pooled	# Specimens Used	# Profiles used	Sample Mean Mg/Ca (mmol/mol)	Sample 2 SE
9.57	9.48	9.65	3	13	51	4.02	0.21
10.15	10.03	10.28	2	8	24	4.70	0.48
10.72	10.64	10.79	2	9	39	4.65	0.34
11.06	10.89	11.23	5	11	22	4.20	0.48
11.48	11.43	11.53	3	13	40	4.55	0.26
11.70	11.67	11.72	2	9	35	4.09	0.31
12.71	12.57	12.85	4	12	50	4.40	0.31
13.24	13.13	13.34	3	7	25	4.26	0.31

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

The mean Mg/Ca of representative samples after incorporating the nine pooled Mg/Ca samples with the 14 un-pooled samples ranges from 3.08 to 4.70 mmol/mol, with an average value of 4.04 ± 0.29 mmol/mol, and errors (±2SE) range from 0.14 to 0.48 mmol/mol (Supplementary Table S7). These values are in good agreement with the reductively cleaned solution ICP-MS data for the post-11.8 Ma portion of the record (Figure 6a). However, we can be more confident that the laser ablation data are not biased by authigenic coatings, and the laser-ablation approach has the advantage that we can also determine original test Mg/Ca in the older part of the record (Figure 6b).

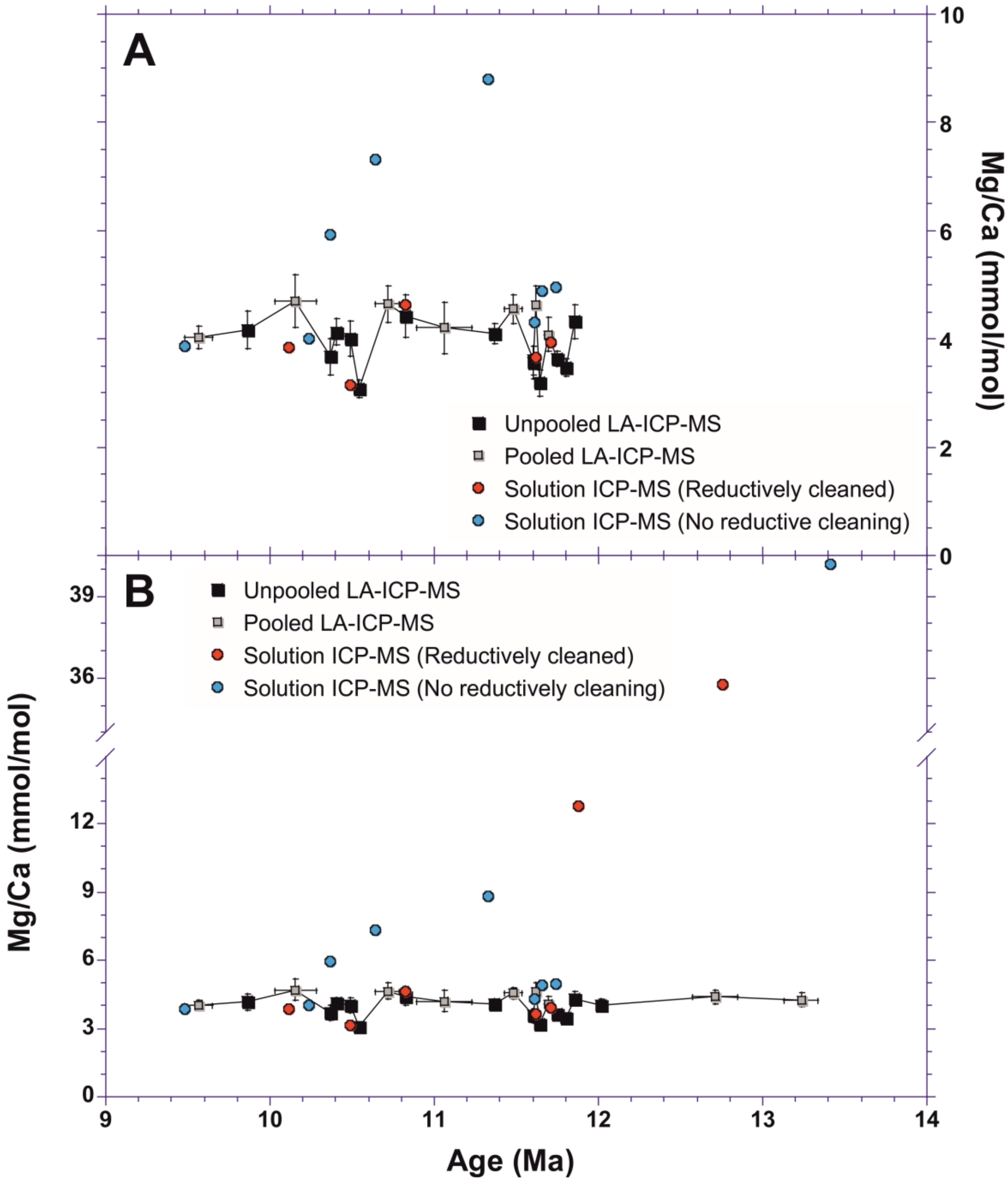
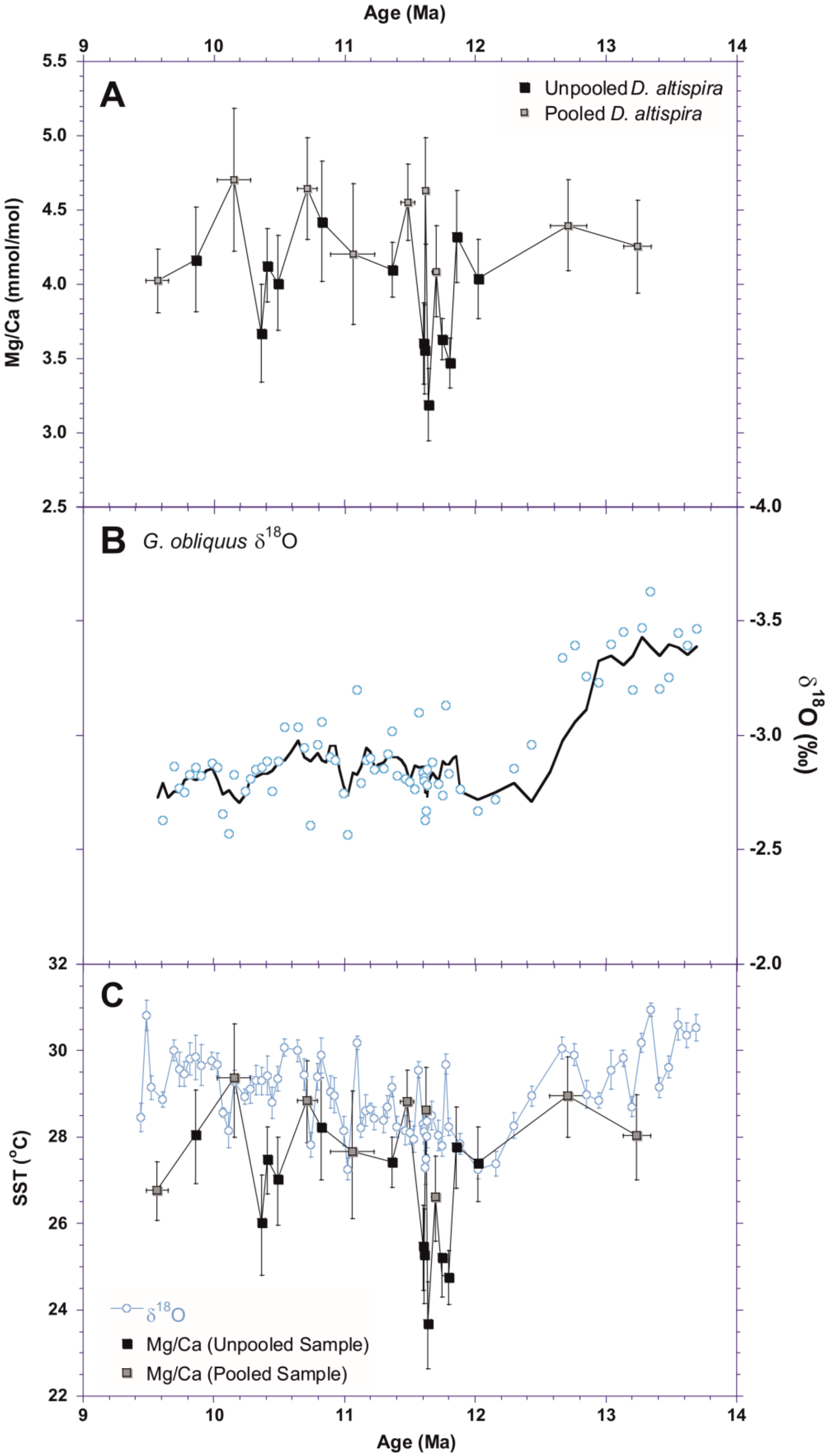


Figure 6: Comparison of solution based (red circles with reductive cleaning, and blue circles without reductive cleaning) and LA-ICP-MS (black squares denoting unpooled samples, and grey squares denoting pooled samples) *D. altispira* Mg/Ca at Sunbird-1 from the intervals (a) after 11.8 Ma, and (b) the full record. 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. Note the break between 13 mmol/mol and 35 mmol/mol in (b).

There is no obvious long-term trend in Mg/Ca through the interval (Figure 7a). Between 11.8 Ma and 11.7 Ma there is a 0.7-0.8 mmol/mol decrease in Mg/Ca followed by a recovery to approximately previous values at 11.5-11.4 Ma. There is a Mg/Ca decrease of similar magnitude from between 10.7 Ma and 10.36 Ma, recovering by 9.85 Ma. We acknowledge that the coarse sampling frequency, and the combining of samples could be obscuring similar variability through the rest of the record.

3.4 G. obliquus $\delta^{18}O$

G. obliquus $\delta^{18}O$ ranges from -3.63‰ to -2.34‰ with a mean value of -2.92‰. The $\delta^{18}O$ record shows very little variability, values remaining stable at -3.4‰ prior to a positive 0.6‰ shift at ~12.5 Ma, and -2.7‰ after (Figure 7b). This translates to a stable $\delta^{18}O$ SST record, temperatures ranging between 27°C and 31°C with the only distinctive trend being a ~3°C decrease between ~12.7 Ma and 12.0 Ma.


Age (Ma)
A
Unpooled D. altispira
Pooled D. altispira
Mg/Ca (mmol/mol)
B
G. obliquus δ18O
δ18O (‰)
C
SST (°C)
δ18O
Mg/Ca (Unpooled Sample)
Mg/Ca (Pooled Sample)
Age (Ma)

479

Figure 7: (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 $\delta^{18}O$ and LA-ICP-MS Mg/Ca. 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 age range the sample incorporates.

4 Discussion

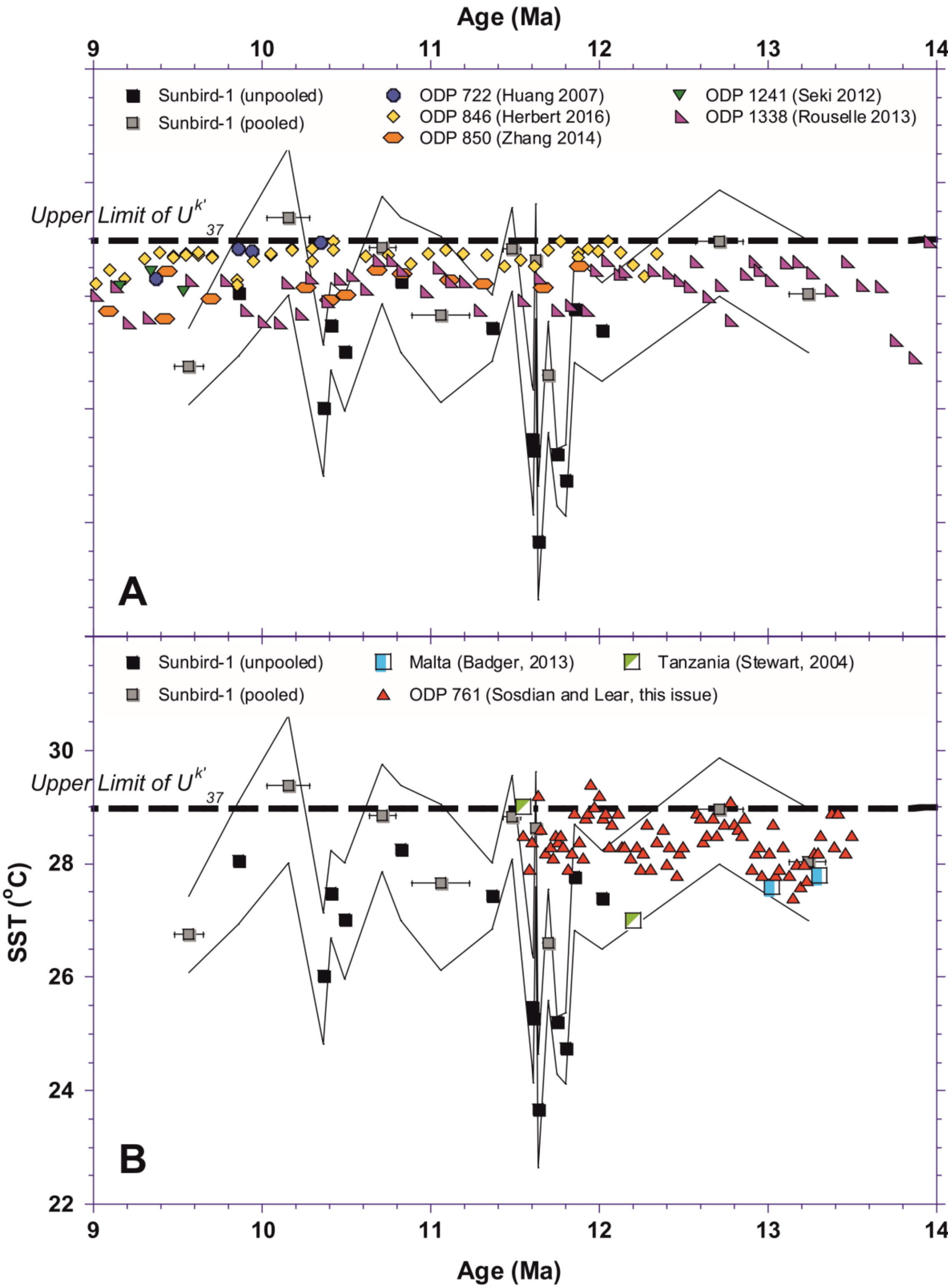
4.1 Reconstructing sea surface temperature from diagenetically altered foraminifera using laser ablation ICP-MS

Robust paleotemperature reconstructions using foraminiferal Mg/Ca ratios are reliant upon the Mg/Ca ratio recording a primary environmental signal, unaltered by diagenetic alteration. Despite employing a thorough cleaning protocol (*Barker et al.*, 2003; *Boyle and Keigwin*, 1985), our Mg/Ca ratios from solution-based ICP-MS analysis in the >11.8 Ma portion of the record are clearly influenced by a diagenetic contaminant phase containing elevated magnesium (Figure 4). The application of LA-ICP-MS to collect high resolution elemental profiles through the foraminiferal tests, excluding regions displaying diagenetic contamination, has facilitated the identification of what we interpret to be primary paleotemperatures from diagenetically altered foraminifera (*Hines et al.*, 2017; *Hollis et al.*, 2015).

The Sunbird-1 $\delta^{18}O_{PF}$ SST record from *G. obliquus* reconstructs very similar absolute temperatures to the planktic foraminiferal Mg/Ca SST record (Figure 7c, Supplementary Table S8 and S9). Mean SST from the Sunbird-1 $\delta^{18}O_{PF}$ record (29^{0}C) is 2^{0}C higher than mean SST from the Mg/Ca record (27^{0}C), although with the exception of the two transient decreases in Mg/Ca reconstructed SST initiating at 11.8 Ma and 10.7 Ma the records are within error. The similarity of the absolute SSTs reconstructed by the two proxies, strengthens the case for the LA-ICP-MS Mg/Ca SST record recording a primary temperature signal and that these absolute sea surface temperatures at Sunbird-1 should be considered primary.

4.2 Mid-late Miocene sea surface temperatures in the equatorial Indian Ocean

The results from Sunbird-1 indicate that SST in the equatorial Indian Ocean remained stable at ~27ºC-29ºC through the 13.3 Ma to 9.5 Ma interval (Figure 7c). This suggests that tropical climate was relatively stable following the global cooling associated with the expansion of the East Antarctic Ice Sheet across the MMCT. These records from Sunbird-1 supports the robustness of contemporaneous alkenone based studies which exhibit similar absolute tropical SST estimates (*Herbert et al.*, 2016; *Huang et al.*, 2007; *Rousselle et al.*, 2013; *Seki et al.*, 2012; *Zhang et al.*, 2014) (Figure 8a). The U^{k}_{37} SST calibration fails to reconstruct SST>29ºC (*Müller et al.*, 1998) but these results using Mg/Ca paleo-thermometry suggest that this restriction does not apply to this time interval, unlike the preceding Miocene Climatic Optimum during which Mg/Ca temperature estimates are higher than those estimated with the U^{k}_{37} proxy (*Badger et al.*, 2013).



Age (Ma)
9
10
11
12
13
14
Sunbird-1 (unpooled)
Sunbird-1 (pooled)
ODP 722 (Huang 2007)
ODP 846 (Herbert 2016)
ODP 850 (Zhang 2014)
ODP 1241 (Seki 2012)
ODP 1338 (Rouselle 2013)
Upper Limit of $U^{k'}_{37}$
SST (°C)
30
28
26
24
22
A
Malta (Badger, 2013)
Tanzania (Stewart, 2004)
ODP 761 (Sosdian and Lear, this issue)
B

522

Figure 8: LA-ICP-MS derived SST at Sunbird-1 compared to and SST estimates at contemporaneous sites from (a) U^{k}_{37}, and (b) foraminiferal geochemistry. Estimates applying U^{k}_{37} are from ODP Site 722 (*Huang et al.*, 2007) in the Arabian Sea, and 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. Estimates applying the foraminiferal Mg/Ca proxy are from ODP Sites 761 (*Sosdian and Lear,* this issue) and terrestrial outcrops in Malta (*Badger et al.*, 2013). 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 U^{k}_{37} proxy (29ºC) is marked by the thick dashed black line. All previously published records used for comparison are kept on their original age models.

Although not a true tropical location, and only two data points, the *Badger et al.* (2013) Mg/Ca record from the Mediterranean estimates SST of ~27.5ºC at ~13 Ma, both within the Sunbird-1 SST uncertainty envelope (Figure 8b). Mg/Ca-SST records based on less well-preserved planktic foraminifera also suggest stable tropical SST of 27-29ºC between 13.8 and 11.4 Ma (*Sosdian and Lear*, this issue) (Figure 8b). This suggests that planktic foraminiferal Mg/Ca may be relatively robust to diagenetic recrystallization processes. Furthermore, well preserved planktic foraminifera from clay-rich sediments of coastal Tanzania yield Indian Ocean sea surface temperatures of 27ºC at 12.2 Ma and 29ºC at 11.55 Ma using the $\delta^{18}O$ paleo-thermometer (*Stewart et al.*, 2004), again in agreement with the Sunbird-1 temperature estimates (Figure 8b). Although sparse in number, previous absolute tropical SST estimates are in agreement with those reconstructed from Sunbird-1. It is worth noting that this study, as well as the tropical SST records of *Herbert et al.* (2016) and references therein, do not sample the warm pool of the Western Pacific, where we would expect SST to be greater than 29ºC, temperatures which unsaturated alkenones cannot reconstruct.

Although the improved estimates provided by the Sunbird-1 record suggest absolute tropical sea surface temperatures remained relatively stable through the mid-late Miocene some temporal variability does persist. Between 11.8 Ma and 11.7 Ma SST drops sharply by ~3ºC. Excluding one value of 28.6ºC at 11.62 Ma, this decrease in SST to ~24-25ºC persists for ~300 kyr before recovering to pre excursion values by 11.5 Ma. However, no transient decrease in sea surface temperature is recorded from contemporaneous alkenone based estimates of tropical SST utilizing the U^{k}_{37} proxy from the Arabian Sea (*Huang et al.*, 2007), and the Eastern Equatorial Pacific (*Herbert et al.*, 2016; *Rousselle et al.*, 2013; *Seki et al.*, 2012; *Zhang et al.*, 2014) (Figure 8a). This suggests that this observed transient ~3ºC SST decrease is not the result of a global driver, and supports a mechanism causing local ocean cooling of the surface waters at Sunbird-1. An alternative hypothesis is that an unaccounted increase in local salinity and/or pH, lowering foraminiferal Mg/Ca ratios, caused a bias to cooler temperatures between ~11.8 and 11.5 Ma. The planktic $\delta^{18}O$ record does not support a significant change in sea surface salinity at this time (Figure 7c). Despite incorporating varying pH from a globally distributed set of open ocean sites (*Sosdian et al.*, 2018), any localized changes in pH at Sunbird-1 cannot be accounted for. This may be particularly relevant considering the land-proximal, tectonically active nature of the study site. However, our preferred interpretation is for a local cooling between ~11.8 and 11.5 Ma. The lack of a marked increase in the planktic $\delta^{18}O$ record at this time implies that the cooling was associated with a freshening of surface waters (Figure 7c). Interestingly, this interval corresponds to a period of very high sedimentation rates (Figure S1), which might be consistent with enhanced precipitation and runoff, lowering regional surface salinity.

4.3 Implications for the global climate state during the mid-late Miocene

Previous studies, utilizing the U^{k}_{37} proxy suggest a substantial cooling of sea surface temperature at mid-to-high latitudes in both hemispheres between 10 and 5.5 Ma, whilst tropical sea surface temperatures show limited cooling in the late Miocene prior to ~7 Ma (*Herbert et al.*, 2016; *LaRiviere et al.*, 2012). The absolute tropical SST record reported in this study supports the finding that the latitudinal temperature gradient steepened in the late Miocene, as the climate system transitioned towards its modern-day state. Furthermore, support for the absolute temperatures reconstructed by the alkenone proxy suggests that the interval between 10 and 7.5 Ma was associated with enhanced polar amplification, significantly greater than that calculated for the greenhouse climate of the Eocene (*Cramwinckel et al.*, 2018). There is little evidence for a significant change in pCO_2 in this interval (*Sosdian et al.*, 2018; *Stoll et al.*, 2019). We speculate that the marked regional cooling between 10 and 7.5 Ma perhaps reflects processes internal to the climate system, involving for example ocean-atmospheric heat transport, sea ice extent, or changes in regional cloud cover. A combined data-modelling approach would help constrain possible factors and explore potential relationships between this highly heterogenous cooling and the CO_2 drawdown that was associated with the subsequent global late Miocene Cooling.

5 Conclusions

Our Sunbird-1 sea surface temperature estimates from LA-ICP-MS Mg/Ca analyses are in good agreement with those using the $\delta^{18}O$ paleo-thermometer on glassy foraminifera, supporting the use of LA-ICP-MS micro-analysis across multiple specimens for reconstructing paleotemperatures. This analytical technique has allowed the reconstruction of reliable Mg/Ca derived palaeotemperatures using foraminifera whose bulk trace element ratios demonstrate diagenetic contamination by authigenic coatings. This opens the potential for Mg/Ca paleothermometry on other challenging time intervals, and locations, where contaminant coatings have previously inhibited the geochemical analysis of primary foraminiferal calcite. We present new, absolute sea surface temperature records from planktic foraminiferal Mg/Ca for the south west Indian Ocean between 13.5 Ma and 9.5 Ma. Absolute estimates of 24-31ºC suggest that sea surface temperature was relatively constant through the interval, although our record also suggests two intervals of regional cooling and freshening of surface waters at 11.8 and 10.7 Ma. The late Miocene represented a key interval in the transition of Earth’s climate to its modern state, including the development of stronger latitudinal temperature gradients. Our new temperature record suggests different mechanisms may have been responsible for this cooling. The initial cooling from ~10 Ma at mid to high latitudes in both hemispheres was not associated with significant cooling at low latitudes. On the other hand, the late Miocene cooling between

~7.5 and 5.5 Ma was global in nature and associated with a drawdown in pCO_2. Further work should therefore explore the possibility of carbon cycle feedbacks in determining the full magnitude of the late Miocene Cooling.

Acknowledgments, Samples, and Data

This study uses samples from the Sunbird-1 core provided by BG-Group. Data can be found in Supplementary Tables S1 to S9 of the supporting information, and will be uploaded to the online database Pangaea. We thank Alexandra Nederbragt and Anabel Morte-Rodeñas for laboratory assistance. We thank the reviewers and editor for their insightful comments that improved the manuscript. This research was supported by NERC iCASE studentship BW/22003105 (M.G.N.), and NE/L009633/1grant to C.H.L.

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