

## Supplementary Material for Holbourn et al.

### CHRONOLOGY

The age model for the middle Miocene interval in ODP Site 1146 is based on a previously published astronomically-tuned chronology (Holbourn et al., 2005; 2007), except for one minor adjustment to account for a sediment gap of 39 cm (~20 k.y.) at the junction between Core 1146A-53X and -54X (501.24 mbsf). Relatively constant sedimentation rates (~ 2.5 cm/k.y.) allowed a minimal tuning approach that preserved original spectral characteristics evident in the depth domain.

### STABLE ISOTOPE ANALYSIS

We measured  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in the surface dwelling planktic foraminifers *Globigerinoides obliquus* or *Globigerinoides subquadratus*. Ten to 20 well-preserved tests from the size fraction 250-350  $\mu\text{m}$  in each sample were broken into large fragments, cleaned in alcohol in an ultrasonic bath, then dried at 40 °C before analysis. In rare samples, where species abundance was low, fewer specimens were analyzed. We also analyzed the shallow subsurface foraminifer *Globigerinoides trilobus* in the interval 501-513 mbsf corr. (14.72-14.30 Ma), where a fundamental change in surface hydrology occurs. For this, we used an aliquot from the homogenized, crushed samples intended for Mg/Ca analysis (~ 30-40 tests from the size fraction 250-350  $\mu\text{m}$ ).

Measurements were made with the Finnigan MAT 251 mass spectrometer at the Leibniz Laboratory, Kiel University (detailed methods in Holbourn et al., 2007). Standard external error is better than  $\pm 0.07\text{‰}$  and  $\pm 0.05\text{‰}$  for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , respectively. Replicate measurements on ~5 % of samples indicate mean reproducibility of  $\pm 0.12\text{‰}$  and  $\pm 0.11\text{‰}$  for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , respectively. Paired measurements in 51 samples indicate no significant offset in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  between *Gs. obliquus* and *Gs. subquadratus*.

### SPECTRAL ANALYSIS OF $\delta^{18}\text{O}$ TIME SERIES

Power spectra of planktic  $\delta^{18}\text{O}$  (Fig. 4A) were estimated using REDFIT (Schulz and Mudelsee, 2002). Analysis is based on a Welch-Overlapped-Segment-Averaging

method for unevenly spaced time series using 4 segments and a Hanning window. The resulting 6 dB bandwidth is 0.0017 cycles/k.y.

## MG/CA ANALYSIS

Up to 40 tests of *Gs. subquadratus* or *Gs. obliquus*, and *Gs. trilobus* from the 250–350  $\mu\text{m}$  size fraction were gently crushed and cleaned following methods outlined by Martin and Lea (2002), which include a reductive step with hydrazine to remove Mn-(hydr)oxides. Dissolved samples were analyzed on a Spectro Ciros CCD ICP OES at IFG, Kiel University, following a simultaneous intensity-ratio calibration method (de Villiers et al., 2002). Analytical precision is  $\sim 1.1\%$  (corresponding to  $\pm 0.02\text{ }^{\circ}\text{C}$ ), based on replicate measurements of an internal laboratory standard ( $n = 213$  during an analytical series of  $\sim 13$  months). Cleaning effectiveness was supported by uncorrelated Mg/Ca, Fe/Ca, and Mn/Ca.

To convert Mg/Ca measurements to temperature we use the multispecies calibration equation of Anand et al. (2003). Parallel measurements of *Gs. subquadratus* and *Gs. obliquus* reveal an average standard deviation of  $\sim 0.25$  mmol/mol ( $n = 38$ ), which corresponds to  $\pm 0.5\text{ }^{\circ}\text{C}$ . This is close to the average standard deviation for paired *Gs. subquadratus* ( $\sim 0.19$  mmol/mol;  $n = 24$ ), paired *Gs. obliquus* ( $\sim 0.22$  mmol/mol;  $n = 26$ ), and paired *Gs. trilobus* samples ( $\sim 0.18$  mmol/mol;  $n = 21$ ). The uncertainty of the paleotemperature estimate of  $\pm 1.2\text{ }^{\circ}\text{C}$  combines the standard deviation deduced from the calibration study ( $\pm 1.13\text{ }^{\circ}\text{C}$ ; Anand et al., 2003) and the analytical error of the Mg/Ca measurement. We applied no correction for the reductive step applied in our cleaning protocol, which generally results in a small decrease in Mg/Ca, leading to temperature underestimation of up to  $\sim 0.6\text{ }^{\circ}\text{C}$  (Rosenthal et al., 2004). A plot of surface Mg/Ca versus depth is shown in Supplementary Fig. 1.

Several lines of evidence support that dissolution does not significantly affect Mg/Ca values and that our data represent a primary signal: (1) Site 1146 was located in relatively shallow water depth during the middle Miocene ( $\sim 2000$  m or less); (2) Foraminifers are well-preserved, as the high clay content in sediment helped to reduce the corrosiveness of pore waters and to prevent post-depositional diagenesis; (3) Intervals of low benthic  $\delta^{13}\text{C}$  (poorer ventilation) and low benthic  $\delta^{18}\text{O}$  (warmer periods), when dissolution would be more likely, generally coincide with increases in

surface temperature; (4) Middle Miocene Mg/Ca values and temperature estimates are realistic, when compared to present day (Fig. 2, Supplementary Fig. 1).

## CENOZOIC EVOLUTION OF MG AND CA IN THE GLOBAL OCEAN

Secular changes in  $Mg/Ca_{sw}$  are caused by variations in continental weathering rates, hydrothermal alteration of basalts, carbonate deposition, and ion exchange reactions with clays. The long residence times of Mg (~13 Myr) and Ca (~1.1 Myr) in the ocean (Broecker and Peng, 1982) imply that changes in  $Mg/Ca_{sw}$  should be relatively slow and gradual, and thus beyond main orbital frequencies. However, the long-term evolution of  $Mg/Ca_{sw}$  remains poorly known and recent reconstructions based on modeling experiments and low-resolution analyses of evaporite fluid inclusions yielded vastly differing estimates (Sime et al., 2007). Although we initially explored two alternative approaches (outlined below) to evaluate potential offsets in our SST reconstructions, we opted to present uncorrected SST values, due to the limitations of current  $Mg/Ca_{sw}$  reconstructions. Our interpretations and conclusions are based on relatively short-term changes in planktic  $\delta^{18}O$  and SST, which occur on suborbital to orbital timescales and are beyond the temporal variability of  $Mg/Ca_{sw}$ .

(1) Several studies of past  $Mg/Ca_{sw}$  variability suggested a gradual increase through the Neogene to reach modern values of ~5.2 mol/mol (Wilkinson and Algeo, 1989; Stanley and Hardie, 1998; Lowenstein et al., 2001; Dickson, 2002; Horita et al., 2002).  $Mg/Ca_{sw}$  estimates of 4.2–2.7 mol/mol for the middle Miocene would therefore result in a systematic underestimation of paleotemperatures, assuming the fractionation of foraminiferal Mg/Ca from  $Mg/Ca_{sw}$  remains constant (0.059 mmol/mol calcite per 0.1 mol/mol seawater change following Brown, 1996). To evaluate the potential offset of our SST estimates, we modified the calibration equation of Anand et al. (2003) to adjust for the ratio of middle Miocene and modern  $Mg/Ca_{sw}$  following Lear et al. (2000):

$$T = (\ln Mg/Ca - \ln \frac{Mg/Ca_{sw-MM}}{Mg/Ca_{sw-AD}} - \ln 0.38) / 0.09$$

where T is the paleotemperature estimate in °C, Mg/Ca the measured foraminiferal Mg/Ca in mmol/mol,  $Mg/Ca_{sw-MM}$  the middle Miocene  $Mg/Ca_{sw}$  and  $Mg/Ca_{sw-AD}$  the modern  $Mg/Ca_{sw}$ . Results indicate that temperatures may be 2.4 to 7.3 °C warmer

than we initially estimated, depending on the selected middle Miocene Mg/Ca<sub>sw</sub> (Supplementary Fig. 1e-f). However, our original SST estimates (ranging from 26 to 30 °C) are close to present day values in the northern South China Sea (Fig. 3), implying any underestimation of SST should be relatively small (~2-3 °C).

(2) A recent geochemical modeling study by Fantle and DePaolo (2006) suggested that Mg/Ca<sub>sw</sub> did not change gradually but varied significantly over 2-4 Ma timecales during the last 20 Ma. Results indicated a marked decrease in Mg/Ca<sub>sw</sub> between ~14.7 Ma (~3.6 mol/mol) and ~13.2 Ma (~2.3 mol/mol), assuming variable  $\delta^{44}\text{Ca}$  weathering inputs to the ocean (see Fig. 12 in Fantle and DePaolo, 2006). To evaluate the potential influence of these Mg/Ca<sub>sw</sub> variations, we followed the method outlined in Medina-Elizalde et al. (2008), and re-calculated SST (Supplementary Fig. 1g.) Following this approach, SST shows a two-step increase from 31 to 37 °C between ~14.7 and ~13.6 Ma (508-484 m). Such a marked SST increase appears highly unlikely since (1) the planktic  $\delta^{18}\text{O}$  curve does not support a general warming trend after ~14 Ma; (2) warming > 5 °C in the subtropics following Antarctic ice expansion appears unrealistic; and (3) SST values of 33-37 °C are unreasonable for this subtropical location, where present-day seasonal range is 27 to 29 °C.

#### **CALCULATION OF $\delta^{18}\text{O}_{\text{SEAWATER}}$**

We initially calculated planktic  $\delta^{18}\text{O}_{\text{sw}}$  (Supplementary Fig. 1b) using the following equation from Bemis et al. (1998):

$$\delta^{18}\text{O}_{\text{sw}}(\text{V-SMOW}) = 0.27 + (T(^{\circ}\text{C}) - 16.5 + 4.8 \times \delta^{18}\text{O}_{\text{calcite}}(\text{V-PDB}))/4.8$$

We estimated ice volume contribution to  $\delta^{18}\text{O}_{\text{sw}}$  to be ~70% of benthic  $\delta^{18}\text{O}$  variability in accordance with middle Miocene estimates based on combined benthic Mg/Ca temperatures and  $\delta^{18}\text{O}$  measurements (Shevenell et al., 2008). To evaluate the component of  $\delta^{18}\text{O}_{\text{sw}}$  related to surface salinity (Fig. 2e), we corrected planktic  $\delta^{18}\text{O}_{\text{sw}}$  by subtracting 70% of a stacked high-resolution benthic foraminiferal record (from ODP Sites 1146 and 1237) after smoothing (20 pt moving average) and normalizing the stacked record to its highest values. Modern seasonal range of  $\delta^{18}\text{O}_{\text{sw}}$  at Site 1146 was calculated from sea surface salinity data (34.2 psu winter, 33.6 psu summer following Locarnini et al., 2006) using the tropical Pacific salinity/ $\delta^{18}\text{O}_{\text{sw}}$  relationship of Le Grande and Schmidt (2006). Estimates are 0.35 ‰ for winter and 0.19 ‰ for summer.

Data sets are archived at WDC-MARE (<http://www.pangaea.de>).

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**Supplementary Figure 1.** ODP Site 1146 benthic and planktic foraminiferal proxy data plotted against corrected mbsf. **a)** Benthic foraminiferal  $\delta^{18}\text{O}$  (Holbourn et al., 2005; 2007); **b)** planktic foraminiferal surface  $\delta^{18}\text{O}_{\text{sw}}$  uncorrected for ice volume; **c)** planktic foraminiferal surface Mg/Ca; **d)** Mg/Ca derived SST; **e-f)** Mg/Ca derived SST corrected for lowest/highest offset in middle Miocene Mg/Ca<sub>sw</sub> following Lear et al. (2000); **g)** Mg/Ca derived SST corrected for changing middle Miocene Mg/Ca<sub>sw</sub> following Medina-Elizalde (2008).

