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A 5 million year comparison of Mg/Ca and alkenone paleothermometers

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[1] Geochemical sea surface temperature (SST) proxies such as the magnesium to calcium ratio (Mg/Ca) in foraminifera and the alkenone unsaturation index ($U_{37}^{K'}$) are becoming widely used in pre-Pleistocene climate records. This study quantitatively compares previously published Mg/Ca and $U_{37}^{K'}$ data from Ocean Drilling Program (ODP) site 847 in the eastern equatorial Pacific to assess the utility of these proxies to reconstruct tropical SST over the last 5 Ma. Foraminiferal Mg/Ca–SST calibrations that include a dissolution correction are most appropriate at this location because they provide SST estimates for the youngest sample that are close to modern mean annual SST. The long-term trends in the two records are remarkably similar and confirm a ~3.5°C cooling trend from the early Pliocene warm period to the late Pleistocene noted in previous work. Absolute temperature estimates are similar for both proxies when errors in the dissolution correction used to estimate SST from Mg/Ca are taken into account. Comparing the two SST records at ODP site 847 to other records in the region shows that the eastern equatorial Pacific was 2–4°C warmer during the early Pliocene compared to today.

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1. Introduction

[2] The early Pliocene (3–4.6 Ma) is the most recent period in Earth history when the average global temperature was higher than today for a sustained period of time. While Pliocene CO_2 concentrations were similar to today (estimated to be ~370 ppm) [*Raymo et al.*, 1996; *Van der Burgh et al.*, 1993], global temperature was ~3°C higher than today according to computer modeling [*Haywood et al.*, 2000; *Sloan et al.*, 1996], implying climate sensitivity to atmospheric CO_2 changes greater than predicted by climate models [*Intergovernmental Panel on Climate Change*, 2007]. Although the early Pliocene is not a perfect analog for anthropogenic climate change, it has been the focus of much research on climate feedbacks that warm the Earth [e.g., *Barreiro et*

al., 2006; *Crowley*, 1996; *Haywood et al.*, 2007; *Huybers and Molnar*, 2007].

[3] As a critical component of data-model comparison studies, the Pliocene Research Interpretation and Synoptic Mapping (PRISM) reconstructed a spatial map of the early Pliocene (2.97–3.29 Ma) sea surface temperature (SST) using planktonic foraminifera, diatom, and ostracode assemblage data [*Dowsett et al.*, 1996, 1999]. This reconstruction suggests higher SST compared to today at high latitudes but very little change at low latitudes. However, geochemical estimates of past SST are needed since there is uncertainty in fossil assemblage data due to the assumption that extinct species have the same ecological preferences as their descendants.

[4] Given the importance of tropical climate dynamics in the modern climate system, some researchers have hypothesized that changes in the tropical oceans could have contributed to the transition from global warmth of the early Pliocene to the ice age climate of the late Pliocene and Pleistocene [*Billups et al.*, 1999; *Fedorov et al.*, 2006; *Philander and Fedorov*, 2003; *Ravelo et al.*, 2004]. The potential global influence of tropical oceans during this climate transition has led to an increased effort to reconstruct tropical SST through the Pliocene using geochemical proxies.

[5] Two geochemical SST proxies now being widely applied in subtropical and tropical regions over the last several million years are the Mg/Ca ratio of planktonic foraminifera and the saturation state of alkenones produced by coccolithophorids, or the alkenone unsaturation index ($U_{37}^{K'}$). $U_{37}^{K'}$ is most applicable in areas with relatively high organic carbon preservation in the sediments and where SST are <29°C [*Muller et al.*, 1998; *Pelejero and Calvo*, 2003], while Mg/Ca is limited to areas with good calcite preservation [*Brown and Elderfield*, 1996]. The potential biases for these two proxies are different because they are related to the growth of different organisms and are preserved in different sediment fractions.

[6] Studies of glacial to interglacial climate change demonstrate that Mg/Ca of foraminifera and $U_{37}^{K'}$ often record similar amplitude SST changes in low and middle latitudes [*Bard*, 2001; *Gagan et al.*, 2004; *Henderiks and Bollmann*, 2004; *Leduc et al.*, 2007; *Nurnberg et al.*, 2000], although some discrepancies between the two proxies have also been noted [*De Garidel-Thoron et al.*, 2007; *Horikawa et al.*, 2006; *Weldeab et al.*, 2007]. Although these studies have been insightful, the application of foraminiferal Mg/Ca and $U_{37}^{K'}$ paleothermometry to pre-Pleistocene sediments introduces an additional set of potential biases. This study is the first to take a detailed quantitative approach to comparing the Mg/Ca and $U_{37}^{K'}$ SST proxies in pre-Pleistocene records.

[7] In the eastern equatorial Pacific (EEP), Ocean Drilling Program (ODP) site 847 (0°N, 95°W, 3346 m water depth) (Figure 1) is located in a depositional and oceanographic setting where both proxies can be applied. The relatively high organic carbon content of the sediment, along with SST that do not exceed the upper limit of this proxy (saturation is reached at ~29°C [*Muller et al.*, 1998; *Prahl and Wakeham*, 1987]), make ODP site 847 an excellent site for $U_{37}^{K'}$ analysis. Planktonic foraminifera are well preserved during the Pleistocene, although poorer preservation exists during the Pliocene [*Mayer et al.*, 1992], indicating that dissolution affects on the Mg/Ca proxy will need to be considered. ODP site 847 is the only location to date where both Mg/Ca and $U_{37}^{K'}$ SST records exist through the last 5 Ma and therefore presents an opportunity to improve the confidence in the applicability of both proxies on pre-Pleistocene timescales. To this end, this study quantitatively compares the previously published Mg/Ca based SST record [*Wara et al.*, 2005] (Figure 2a) and the $U_{37}^{K'}$ based SST record [*Dekens et al.*, 2007] (Figure 2b) at ODP site 847 in terms of the long-term trends, the absolute temperature estimates, and the variability within each record.

2. Proxy Background

[8] $U_{37}^{K'}$ ($U_{37}^{K'}$ = [$C_{37:2}$]/[$C_{37:2}$ + $C_{37:3}$]) is a widely applied SST proxy. Although some work indicates potential biases, global core top studies demonstrate that $U_{37}^{K'}$ correlates best with mean annual temperatures [*Conte et al.*, 2006; *Muller et al.*, 1998]. Species differences in the $U_{37}^{K'}$-temperature relationship implied by culturing work [*Conte et al.*, 1998; *Herbert*, 2001; *Prahl et al.*, 1988] would clearly be a concern for paleoceanographic reconstructions, but studies have generally not shown changes in $U_{37}^{K'}$ coincident with shifts in haptophyte algae species [*McClymont et al.*, 2005; *Villanueva et al.*, 2002]. Although no detailed census counts of coccoliths have been done at ODP site 847, biostratographic data indicate that the appearances or disappearances of particular species of nannofossils [*Mayer et al.*, 1992] are not associated with shifts in $U_{37}^{K'}$. Ecological preferences for subsurface

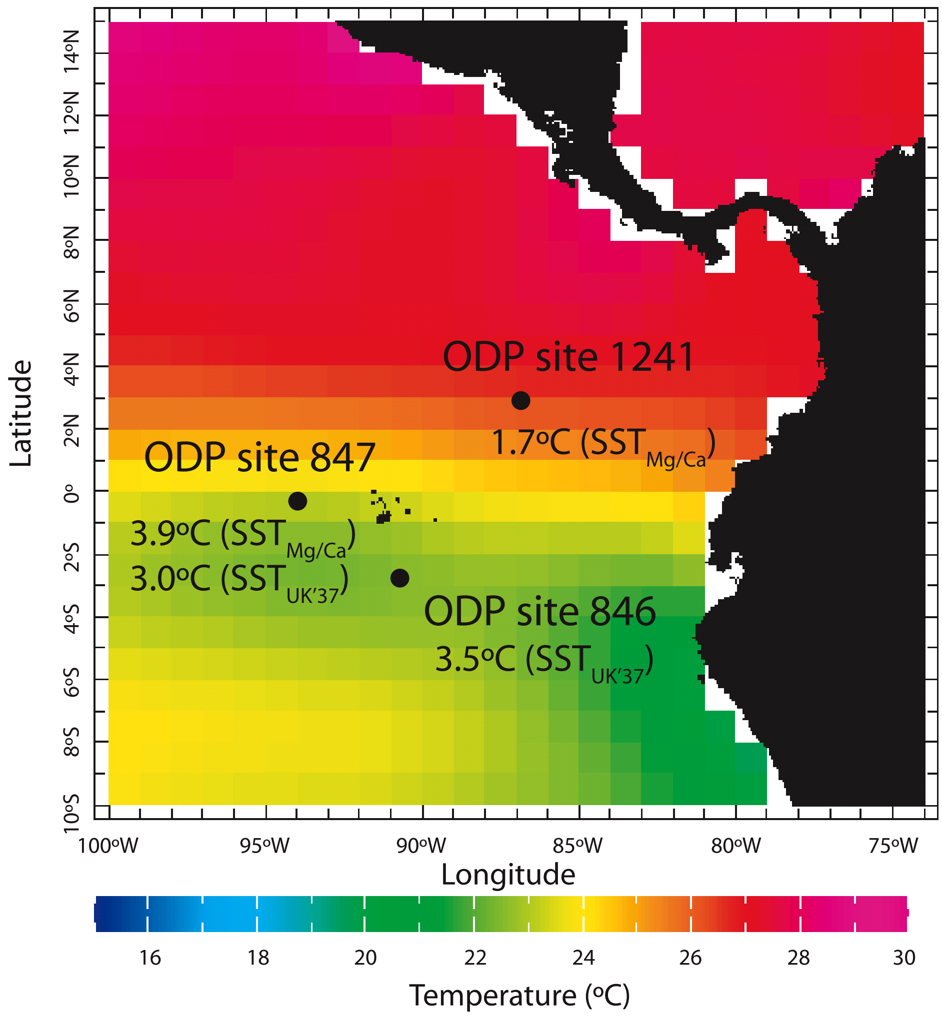

Figure 1. The colored map shows modern mean annual sea surface temperature (SST) [*Levitus and Boyer*, 1994]. The modern locations of Ocean Drilling Program (ODP) site 847 (0°N, 95°19′W, 3346 m water depth), ODP site 1241 (5°50′N, 86°26′W, 2027 m water depth), and ODP site 846 (3°S, 90°50′W) are shown. ODP site 1241 has tectonically moved northeast and its location 5 Ma was 3°N, 87.7°W. ODP sites 847 and 846 both moved east at the same latitude and were located at 98°W and 93.5°W, respectively. Superimposed is the difference between Pliocene (3–4.6 Ma) and modern mean annual SST at each site. Note that only ODP site 1241 has a different mean annual SST for its modern and paleolocation. We therefore calculated the difference between the Pliocene and modern relative to its paleolocation.

[*Bentaleb et al.*, 1999] and seasonal [*Volkman*, 2000] growth could also introduce biases. However, global core top studies demonstrate that $U^{K'}_{37}$ correlates best with mean annual temperatures at 0–10 m, suggesting that slow sedimentary processes may average out the variability introduced by these ecological factors [*Herbert*, 2001; *Lawrence et al.*, 2007]. Although there is significant degradation of alkenones within the sediments [*Gong and Hollander*, 1999; *Hoefs et al.*, 1998; *Prahl et al.*, 1989], most studies demonstrate that $U^{K'}_{37}$ is not affected and the temperature signal is preserved [*Grimalt et al.*, 2000].

[9] The Mg/Ca ratio of planktonic foraminifera is a SST proxy that has been widely applied to generate Pleistocene climate records. The main concern regarding this proxy is that preferential dissolution of the Mg rich portions of the shell lowers the Mg/Ca ratio [*Brown and Elderfield*, 1996; *Hastings et al.*, 1998; *Lorens et al.*, 1977; *Rosenthal and Boyle*, 1993; *Rosenthal et al.*, 2000], thereby lowering the temperature estimate. This bias is minimized by selecting sites with well preserved calcite, and progress has been made in incorporating a dissolution correction in

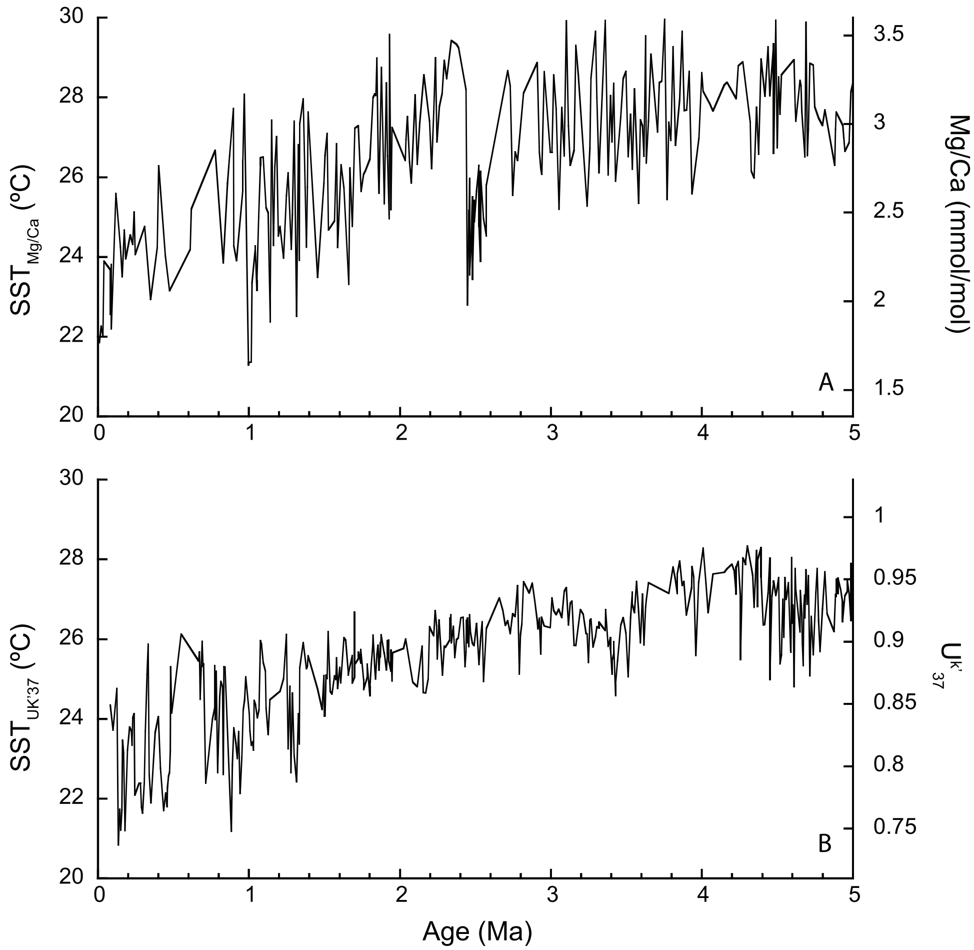

Figure 2. Pliocene-Pleistocene climate records, showing (a) *G. sacculifer* (without sac-like final chamber) Mg/Ca at ODP site 847 [*Wara et al.*, 2005]. Mg/Ca was converted to temperature using the ΔCO_3^{2-} corrected calibration of *Dekens et al.* [2002] and a ΔCO_3^{2-} value of -10.3 μmol/Kg. (b) $U_{37}^{K'}$ record from ODP site 847 [*Dekens et al.*, 2007] and converted to SST using the global calibration of *Muller et al.* [1998].

calibrations [*Dekens et al.*, 2002; *Rosenthal and Lohmann*, 2002]. Other diagenetic biases could result from recrystallization resulting in high Mg (and manganese, Mn) calcite overcoatings [*Barker et al.*, 2003; *Boyle*, 1983].

[10] One assumption underlying Mg/Ca paleothermometry in sediments of Pliocene and Pleistocene age is that the Mg/Ca of seawater has not changed significantly. Changes in the Mg/Ca of seawater have likely occurred over the last 100 Ma [*Berner*, 2004; *Horita et al.*, 2002; *Lowenstein et al.*, 2001; *Steuber and Rauch*, 2005]. However, because of the long residence times of Mg and Ca in the ocean, changes in the Mg/Ca of seawater were likely gradual with no substantial changes in Mg/Ca of seawater since the Pliocene. This assumption is being tested, but there are still many unconstrained factors that limit the accurate deconvolution of changes in the concentrations of Mg [*Fantle and DePaolo*, 2006] and Ca [*Sime et al.*, 2007] in seawater from measurements of sediment and pore water chemistry. The assumption that Mg/Ca of seawater did not change significantly since the Pliocene is indirectly supported in this study by comparing SST changes estimated from Mg/Ca of planktonic foraminifera with those estimated from $U_{37}^{K'}$, an independent proxy.

3. SST Based on Mg/Ca of *G. sacculifer*

[11] Calibration approaches for this proxy include using laboratory culturing studies [*Mashiotta et al.*, 1999; *Nurnberg et al.*, 1996], sediment traps material [*Anand and Elderfield*, 2003], and core top sediments [*Dekens et al.*, 2002; *Elderfield and Ganssen*, 2000; *Rosenthal and Lohmann*, 2002]

Table 1. Mg/Ca Calibrations[a]

Model	Source	Mg/Ca = A exp(B × T): A	Mg/Ca = A exp(B × T): B	Predicted T: 10 ka	Predicted T: 0–500 ka	Reference
A	core tops (North Atlantic) eight species of planktonic foraminifera	0.52 ± 0.085	0.10	12.7°C	14.4°C	[*Elderfield and Ganssen*, 2000]
B	sediment traps multiple planktonic species	0.38 ± 0.02	0.090 ± 0.003	17.7°C	19.2°C	[*Anand and Elderfield*, 2003]
C	culturing *G. sacculifer*	0.491	0.076	17.6°C	19.7°C	[*Nürnberg et al.*, 2000]
D	core tops *G. sacculifer* (355–425 μm)	(0.181 + 0.0032 × wt)	0.095	NA	NA	[*Rosenthal and Lohmann*, 2002]
E	core tops (water depth correction) *G. sacculifer*	0.31/exp(0.032 × WD)	0.09 ± 0.013	21.2°C	23.0°C	[*Dekens et al.*, 2002]
F	core tops (ΔCO_3^{2-} correction) *G. sacculifer*	$0.31 \times \exp(0.0040 \times \Delta CO_3^{2-})$	0.084 ± 0.014	21.9°C	23.8°C	[*Dekens et al.*, 2002]

[a] Values for A and B are given with 95% confidence intervals where provided in the original reference. Note that the form of equations by *Dekens et al.* [2002] is different from the original study (though they are mathematically the same) in that the dissolution correction has been incorporated in A rather than in B. This was done to allow easier comparison between the calibrations. The predicted temperature for the youngest available sample (Ocean Drilling Program site 847B, 1H1 45 cm, 10 ka) are based on a Mg/Ca measurement of 1.865 mmol/mol.

(Table 1). In all studies, the relationship between Mg/Ca and temperature is exponential:

$$\text{Mg/Ca} = \text{A} \times e^{(\text{BT})} \quad (1)$$

where T is temperature. Published calibration studies derive B values of 0.09 ± 0.01, indicating that Mg/Ca increases by ~9% per degree Celsius, and A values ranging from 0.31 to 0.52 (Table 1).

[12] Mg/Ca ratios of *G. sacculifer* at ODP Site 847 were converted to SST using six calibration equations (Figure 3; Table 1). Owing to the similarity in parameter B (values range by ~11%), all calibrations indicate a similar ~3.5°C cooling trend from the early Pliocene to today. The greater disagreement in parameter A (values range by ~25%) results in a range of absolute temperature estimates. For example, SST estimates for the youngest sediment sample range from 12.8°C to 21.9°C (Table 1). Because parameter A is higher in the calibration of *Elderfield and Ganssen* [2000] (Model A in Table 1, Figure 3) compared to other calibrations, the resulting temperature estimates are offset from the other five calibrations. This calibration includes only nine samples of *G. sacculifer* and does not include tropical sites with similar SST to ODP Site 847. Because of these limitations, we conclude that this calibration is not appropriate for our study.

3.1. Core Top Versus Culturing and Sediment Trap Calibrations

[13] The remaining five calibrations cluster into two groups (Figure 3). Calibrations based on sediment trap (Model B) [*Anand and Elderfield*, 2003] and culturing work (Model C) [*Nurnberg et al.*, 2000] produce lower SST estimates than calibrations based on core top samples (Models D–F) [*Dekens et al.*, 2002; *Rosenthal and Lohmann*, 2002]. The two groups of calibrations mainly differ in the way they implicitly and explicitly account for postdepositional dissolution effects on the Mg/Ca of foraminifera shells.

[14] Partial dissolution of foraminiferal calcite lowers the Mg/Ca ratio and results in a low-temperature bias [*Brown and Elderfield*, 1996]. Dissolution occurs when ΔCO_3^{2-} is less than zero, where ΔCO_3^{2-} is the difference between the saturation and in situ concentration of CO_3^{2-} ($\Delta CO_3^{2-} = [CO_3^{2-}]_{saturation} - [CO_3^{2-}]_{in\ situ}$). The core top calibrations attempt to correct for this postdepositional process by incorporating a dissolution correction into parameter A, which effectively

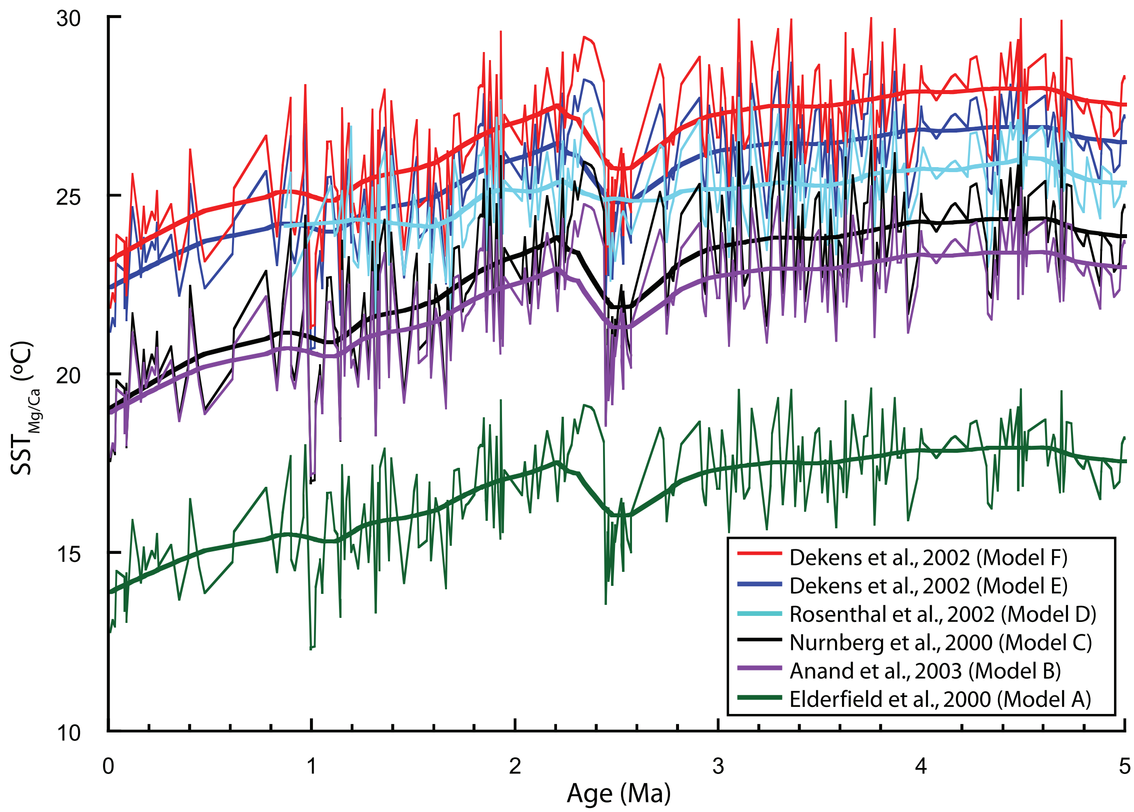

Figure 3. Mg/Ca calibrations, showing ODP site 847 Mg/Ca (*G. sacculifer*, without sac-like final chamber) data converted to SST using six different calibrations (Table 1). Modern mean annual SST at this location is 23.8°C while the temperature at 20 m is 21.4°C. In each record the thin line connects the individual data points while the thick line is a locally weighted least squares smoothing of the data.

increases the SST estimate to offset the dissolution bias (Models D–F) [*Dekens et al.*, 2002; *Rosenthal and Lohmann*, 2002].

[15] Since dissolution of foraminifera lowers foraminiferal shell mass, *Rosenthal and Lohmann* [2002] used the average shell mass of *G. sacculifer* as an indicator of dissolution, such that $A = 0.181 + 0.0032 \times wt$, where wt is the average weight of shell (Model D). The study by *Dekens et al.* [2002] approached the dissolution correction in two ways. First, because pressure has a large effect on $[CO_3^{2-}]_{saturation}$, ΔCO_3^{2-} decreases with increasing water depth, and model E includes a dissolution correction based on water depth (WD) such that $A = 0.31/\exp(0.032 \times WD)$. Second, *Dekens et al.* [2002] also used ΔCO_3^{2-} as a correction for dissolution such that $A = 0.31 \times \exp(0.0040 \times \Delta CO_3^{2-})$ (Model F).

[16] Because dissolution is a postdepositional process, removing the dissolution correction from the core top calibrations should yield similar temperature estimates compared to those calculated using culturing and sediment trap calibrations. To remove the dissolution correction from Model E (water depth corrected calibration) [*Dekens et al.*, 2002], the water depth is set to 0 m, resulting in a value for A of 0.37, similar to the culturing and sediment trap calibrations of *Anand and Elderfield* [2003] and *Nurnberg et al.* [2000] (A = 0.49 and 0.38, respectively). In model F (ΔCO_3^{2-} corrected calibration [*Dekens et al.*, 2002]) a ΔCO_3^{2-} of 0 μmol/kg (i.e., calcite saturation at the lysocline) results in a value of 0.31 for A, which is lower than other calibrations. This is not surprising because dissolution of Mg-rich calcite occurs even above the lysocline [*Dekens et al.*, 2002]. To achieve a value for A of 0.37, ΔCO_3^{2-} must be 40 μmol/kg, which is the value at ~200 m (World Ocean Circulation Experiment, WOCE, P19, #373).

[17] Removing the dissolution correction from the shell weight-corrected calibration (Model D) [*Rosenthal and Lohmann*, 2002] requires an estimate of the predissolved mass of *G. sacculifer*.

Because shell mass was not reported in the culturing [*Nurnberg et al.*, 2000] and sediment trap studies [*Anand and Elderfield*, 2003], we used the largest observed average shell weight of *G. sacculifer* (42 μg) in our ODP site 847 record to calculate a value of 0.32 for A. Although this value for A is low relative to those obtained in culturing and sediment trap studies (Models B and C), it is most likely an underestimate; given that ODP site 847 is at 3346 m, even the largest sample has been exposed to some dissolution. In all, after removing the dissolution correction from core top calibrations and recalculating A, there is better agreement in its value among all the calibrations (0.38 ± 0.07 compared to 0.40 ± 0.10 before removing the dissolution corrections), indicating they all account similarly for the temperature effect on foraminiferal Mg/Ca.

[18] ODP site 847 is located at a water depth of 3346 m, where ΔCO_3^{2-} is -10.3 μmol/kg (estimated using total carbon and pCO_2 data from WOCE cruise P19 #373 and the Program Developed for CO_2 System Calculations) [*Lewis and Wallace*, 1998]. Consequently, while this site is above the carbonate compensation depth (CCD), it is not above the saturation horizon, and the foraminifera shells have undergone some dissolution. It is therefore important to use a calibration that includes a correction for dissolution. Applying the dissolution corrected equations to Mg/Ca analyses of shells from core top samples yields SST estimates similar to the modern temperatures at 0 and 20 m (23.1°C and 21.4°C, respectively) at this site, but the culturing and sediment trap based calibrations yield SST estimates (17.6°C and 17.7°C, respectively) that are not consistent with modern temperature observations (Table 1). It is important to keep in mind that the dissolution correction in the calibration remains constant throughout the record, and therefore any changes in preservation could still lead to a temperature bias.

3.2. Comparing Dissolution-Corrected Core Top Calibrations

[19] The calibration by *Rosenthal and Lohmann* [2002] assumes that the initial weight of a *G. sacculifer* test is constant and therefore the final weight is used to estimate dissolution. However, in cultures the initial mass is related to the $[CO_3^{2-}]_{in\ situ}$ during calcification [*Bemis et al.*, 1998], and in core top samples shell density is related to calcification temperature [*Elderfield*, 2001], potentially leading to errors of $\sim$1°C in the temperature estimates [*Rosenthal and Lohmann*, 2002]. Furthermore, proper application of the *Rosenthal and Lohmann* [2002] calibration requires that the 350–425 μm size fraction be used to generate the down core record. Unfortunately, owing to scarcity of *G. sacculifer* in ODP site 847, some portions of the record was generated using the 250–350 μm size fraction; combined with concerns regarding the initial test weight, we have selected not to apply the *Rosenthal and Lohmann* [2002] calibration to our Mg/Ca data from ODP site 847.

[20] The two calibrations which appear to be the most appropriate for this data set are those based on tropical Atlantic and Pacific core tops [*Dekens et al.*, 2002]. One calibration (Model E) uses water depth to correct for dissolution because ΔCO_3^{2-} decreases, and dissolution increases, with water depth. The other calibration (Model F) uses the value of ΔCO_3^{2-} at the core site as a dissolution correction [*Dekens et al.*, 2002], but estimates for ΔCO_3^{2-} are often sparse. Both calibrations assume that the dissolution correction (either water depth or ΔCO_3^{2-}) remains the same throughout the record. Despite the differences in these calibrations, they result in similar temperature estimates for the youngest sample at ODP site 847 (21.2°C and 21.9°C using the water depth and ΔCO_3^{2-} corrections, respectively).

[21] In sum, the most appropriate calibration for converting Mg/Ca data to SST at ODP site 847 (and at all other deep sea sediment core locations where dissolution might be a factor) is a one that includes a dissolution correction, although possible changes in ΔCO_3^{2-} need to be examined independently. While culturing and sediment trap work has quantified the effect of calcification temperature on foramininferal Mg/Ca, it does not account for postdepositional processes.

4. SST Based on $U_{37}^{K'}$

[22] The $U_{37}^{K'}$ SST proxy has been calibrated using laboratory culturing, sediment trap, and core top studies. Discrepancies in culturing calibrations imply different relationships between $U_{37}^{K'}$ and SST for different species of haptophyte algae [*Herbert*, 2001]. There is considerably more agreement in the sediment trap-based calibrations, although these have demonstrated the potential importance of haptophyte ecology in recording the $U_{37}^{K'}$ signal

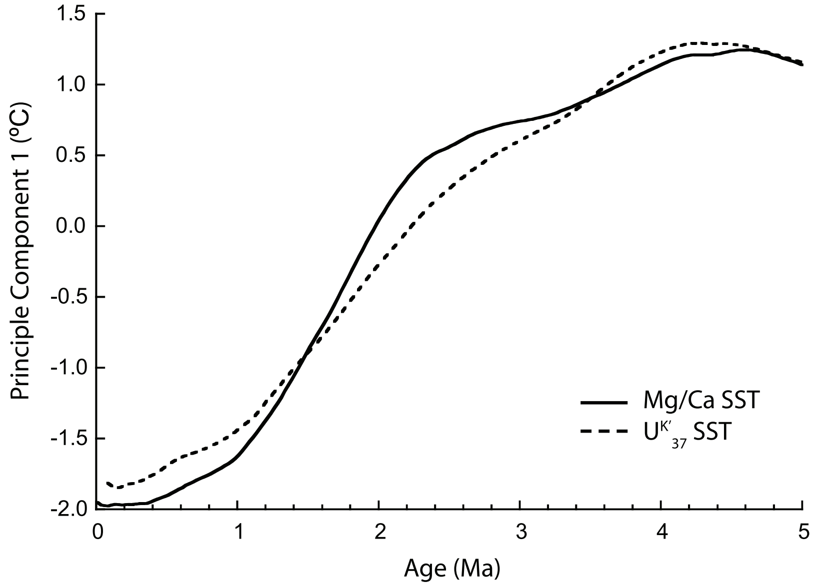

Figure 4. Long-term trends. To compare the long-term trends in the $SST_{Mg/Ca}$ and $SST_{UK'37}$ records we performed a single spectral analysis on each record independently. The first principal components shows that the long-term trends of $SST_{Mg/Ca}$ and $SST_{UK'37}$ record a cooling of approximately 3.5°C through the last 5 Ma at ODP site 847.

[*Conte and Eglington*, 1993; *Goni et al.*, 2001; *Herbert*, 2001; *Lawrence et al.*, 2007; *Sikes and Volkman*, 1993].

[23] Despite the differences in the culturing and sediment trap calibrations, there is wide agreement among $U^{K'}_{37}$–SST calibrations based on core top sediment samples. There are regional calibrations from the Atlantic Ocean [*Rosell-Mele et al.*, 1995], Indian Ocean [*Sonzogni et al.*, 1997], California margin [*Herbert and Schuffert*, 1998], western Pacific Ocean [*Bentaleb et al.*, 2002], eastern south Atlantic Ocean [*Muller et al.*, 1998], and Southern Ocean [*Sikes et al.*, 1997]. These calibrations, as well as the two extensive global core top calibrations [*Conte et al.*, 2006; *Muller et al.*, 1998], demonstrate a robust linear relationship between $U^{K'}_{37}$ and the mean annual SST of the overlying surface waters. All the core top calibrations are statistically the same as the original calibration derived from a culturing experiment of *E. huxlei* [*Prahl and Wakeham*, 1987] (see *Lawrence et al.* [2007] for review). Therefore, unlike the Mg/Ca SST proxy, there is little controversy regarding the calibration choice for the $U^{K'}_{37}$ temperature proxy, although biases need to be considered in the interpretation of temperature changes. In this study, we apply the calibration of *Muller et al.* [1998], a global core top calibration, and assess the potential influence of ecological factors and diagenetic processes in the interpretation of the temperature estimates.

5. Comparing the Alkenone and Mg/Ca SST Records at ODP Site 847

5.1. Long-Term Trends

[24] To compare the long-term trends of the SST record based on the Mg/Ca of foraminifera ($SST_{Mg/Ca}$) to the SST record based on $U^{K'}_{37}$ ($SST_{UK'37}$), we performed a single spectral analysis (SSA) on each record independently. This method determines the empirical orthogonal functions in the time domain and effectively filters out noise from the primary signal, which reflects the main physical phenomena [*Vautard and Ghil*, 1989]. The first principal components of the records are similar (Figure 4) and show that the long-term trends record ~3.5°C cooling through the last 5 Ma at ODP site 847. This is strong evidence that any potential biases in the proxy records are not changing with time. For example, the assumption that changes in the Mg/Ca of seawater are relatively small is confirmed; if it were changing, then the amplitude of the long-term trend in the $SST_{Mg/Ca}$ record and the $SST_{UK'37}$ would not be expected to be the same. Although there have been changes in the Mg/Ca of seawater over the last 100 Ma [*Steuber and Rauch*, 2005], the results of our study

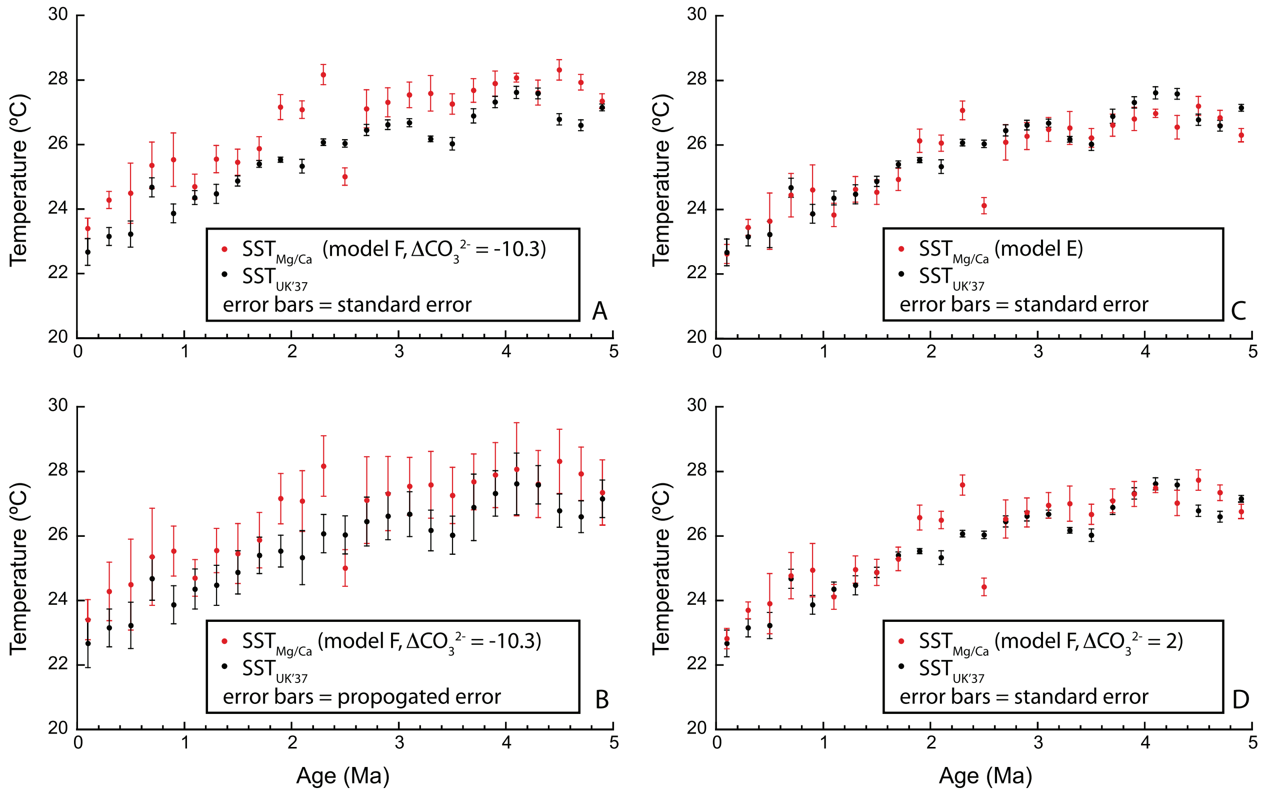

Figure 5. ODP site 847 $SST_{Mg/Ca}$ and $SST_{UK'37}$, with the data separated into 200 ka bins and the mean plotted. $U^{K'}_{37}$ is converted to SST using the global core top calibration of [*Muller et al.*, 1998]. (a) Mg/Ca converted to SST using the ΔCO_3^{2-} corrected calibration [*Dekens et al.*, 2002] and a ΔCO_3^{2-} value of -10.3 μmol/Kg. The error bars show the standard error of the mean, which is calculated as the standard deviation of the data divided by the square root of the number of data points in the bin ($\sigma/\sqrt{n}$). (b) Same as Figure 5a, but the error bars are the propagated errors of the calibration (see section 4.2). (c) Mg/Ca converted to SST using the water depth corrected calibration [*Dekens et al.*, 2002], and the error bars show the standard error of the mean. (d) Mg/Ca converted to SST using the ΔCO_3^{2-} corrected calibration [*Dekens et al.*, 2002] and a ΔCO_3^{2-} value of 2. The error bars show the standard error of the mean.

contradict estimates of significant changes in the Pliocene [*Fantle and DePaolo*, 2006] and are instead consistent with the idea that Mg/Ca of seawater changes were relatively small and do not have a large impact on $SST_{Mg/Ca}$ records over the Plio-Pleistocene. The excellent agreement in the long term trends of both proxy records also supports the idea that although alkenones are degraded within the sediments, the primary temperature signal is preserved.

[25] One feature evident in the primary data, but not in the SSA, is the dip in $SST_{Mg/Ca}$ at ~2.5 Ma, a feature that is not observed in the $SST_{UK'37}$ record (Figure 2). The fact that this feature is not seen in the first principal component of the SSA (Figure 4) indicates that it is not a significant deviation from the long-term trend. The low Mg/Ca feature was recorded in two size fractions (350–450 and 250–350 um) of *G. sacculifer*, but is not coincident with any changes in Mn/Ca or shell mass, indicating that it is unlikely to result of postdepositional overgrowths or dissolution. It is possible that this feature reflects a local dissolution event (the same feature is not seen in a Mg/Ca of *G. sacculifer* record at ODP site 806 in the western Pacific warm pool) [*Wara et al.*, 2005]. The Mg/Ca record at ODP site 1241 includes a steep decrease in values from 3 to 2.5 Ma [*Groeneveld et al.*, 2006], but no data exist younger than 2.5 Ma, making it difficult to assess whether the record contains the same feature as recorded at ODP site 847.

5.2. Absolute Temperature Estimates

[26] There is a clear offset between the $SST_{Mg/Ca}$ and $SST_{UK'37}$ records at ODP site 847, with Mg/Ca consistently yielding warmer SST estimates (by ~1°C) compared to $U^{K'}_{37}$. Because Mg/Ca and $U^{K'}_{37}$ were not measured in the exact same samples, we

compare absolute values of $SST_{Mg/Ca}$ and $SST_{UK'37}$ by dividing the data in each record into bins of 200 ka (Figure 5), a time interval sufficiently long to provide good statistics but not so long that any one bin includes a large portion of the long-term trend. We initially examine $SST_{Mg/Ca}$ estimates derived using model F (Table 1), the ΔCO_3^{2-} dissolution corrected core top calibration [*Dekens et al.*, 2002] using a value of -10.3 μmol/kg for ΔCO_3^{2-} (as in initial publication of the data) [*Wara et al.*, 2005]. We calculated the mean and standard error of the mean ($\sigma_{\bar{x}} = \sigma_x/\sqrt{n}$; where σ indicates the standard error and $\bar{x}$ is the mean of the data x) for each bin (Figure 5a).

[27] Most of the $SST_{Mg/Ca}$ and $SST_{UK'37}$ bin means are not within one standard error of each other. A two-tailed student's t-test found that 40% of the bins had a p value <0.05, indicating the means were statistically different from one another at the 5% confidence level. However, both the calculation of the standard error of the mean and the student's t-test assume there is no uncertainty in individual data points. Although analytical errors of the primary measurements are essentially negligible (analytical reproducibility for a liquid standard for Mg/Ca was 0.051 mmol/mol and for $U_{37}^{K'}$ was 0.005, equivalent to ±0.3°C and ±0.14°C, respectively [*Dekens et al.*, 2007; *Wara et al.*, 2005]), the calibrations used to calculate SST from the primary data introduces uncertainty for each data point. Therefore, as both the standard error of the mean and the student's t-test do not account for the calibration error, they overestimate the certainty in the mean of the binned data.

[28] To quantify the calibration uncertainties we propagated the errors of each of the calibrations. We estimate the errors in the $U_{37}^{K'}$ SST estimates by first rearranging the linear calibration ($U_{37}^{K'}$ = a + b(SST)):

$$SST_{UK'37} = (1/b)U_{37}^{K'} - (1/b)a \qquad (2)$$

The uncertainty (σ_{SST}) in the SST estimate, neglecting covariance in the parameters, can be calculated using the uncertainties in parameters a and b and standard error propagation methods [*Taylor*, 1997]. Uncertainty in a (σ_a) and b (σ_b) are reported in the calibration study [*Muller et al.*, 1998].

$$\sigma_{SST}^2 = \sigma_a^2(\partial SST/\partial a)^2 + \sigma_b^2(\partial SST/\partial b)^2 + \sigma_{UK'37}^2(\partial SST/\partial U_{37}^{K'})^2 \qquad (3)$$

where ∂SST/∂a is the partial derivative of equation (2) with respect to a, ∂SST/∂b is the partial derivative of the equation (2) with respect to b, etc. Errors were propagation for each data point, and the average uncertainty (σ_{SST}) is 1.6°C for $SST_{UK'37}$ at ODP site 847. The same process was undertaken for the core top calibration of Mg/Ca that uses ΔCO_3^{2-} as a dissolution correction (Model F).

$$SST_{Mg/Ca} = a + b[\ln(Mg/Ca)] + c \times \Delta CO_3^{2-} \qquad (4)$$

The uncertainty (σ_{SST}) in the SST estimate, neglecting covariance in the parameters, is given by:

$$\sigma_{SST}^2 = \sigma_a^2(\partial SST/\partial a)^2 + \sigma_b^2(\partial SST/\partial b)^2 + \sigma_c^2(\partial SST/\partial c)^2 \qquad (5)$$

The average uncertainty (σ_{SST}) is 1.7°C for $SST_{Mg/Ca}$ at ODP site 847.

[29] The error bars in Figure 5b represent estimates of the error of the means, given the propagated errors described above, calculated as follows:

$$\sigma_{mean\ SST}^2 = \sigma_{SST}/\sqrt{N} \qquad (6)$$

Accounting for calibration uncertainties (Figure 5b) leads to larger errors than the standard error of the mean (Figure 5a), and the binned data overlap within error in all but two of the bins. However, there is a consistent offset, and $SST_{Mg/Ca}$ is higher (by ~1°C) than $SST_{UK'37}$ in all but one of the bins, suggesting a systematic bias in at least one of the proxies. This bias could reflect ecological differences in how the proxies are recorded, or it could stem from systematic errors in the calibrations.

[30] *G. sacculifer* does not show strong seasonal preferences in the tropics [*Bé and Hutson*, 1977; *Fairbanks et al.*, 1982; *Ravelo and Fairbanks*, 1992], and the addition of gametogenic calcite at depth [*Bé*, 1980; *Fairbanks et al.*, 1982] would yield colder SST estimates and therefore cannot explain the observed offset. Although coccolithophorids have been observed to live in the subsurface in oligotrophic gyres and have shown some seasonal bias in middle and high latitudes [e.g., *Prahl et al.*, 1993, 2001], global core top studies have consistently shown that the best correlation exists between $U_{37}^{K'}$ and mean annual temperatures of the top 10 m of the water column [*Conte et al.*, 2006; *Muller et al.*, 1998]. In addition, the pattern of the $SST_{UK'37}$ record at ODP 847 is not consis-

Table 2. World Ocean Circulation Experiment Sites[a]

WOCE Cruise	WOCE Station	Latitude	Longitude	ΔCO_3^{2-} (μmol/kg)
P19C	346	10.5°S	85.8°W	−1.6
P19C	351	8.0°S	85.8°W	−3.3
P19C	355	6.0°S	85.8°W	−1.6
P19C	359	4.0°S	85.8°W	−2.5
P19C	361	3.0°S	85.8°W	−2.5
P19C	373	0.0°N	85.8°W	−10.3
P19C	379	1.0°N	85.8°W	−8.9
P19C	385	3.0°N	85.8°W	−9.0
P19C	395	6.7°N	88.8°W	−6.6
P19C	413	13.0°N	91.8°W	−9.8
P18N	121	9.2°S	104.1°W	−2.5
P18N	124	8.1°S	105.8°W	−0.8
P18N	129	6.2°S	108.6°W	−0.8
P18N	133	4.5°S	110.3°W	2.5
P18N	137	2.7°S	110.3°W	0.8
P18N	141	1.3°S	110.3°W	2.5
P18N	145	0.0°N	110.3°W	2.5
P18N	151	2.0°N	110.3°W	0.8
P18N	155	3.5°N	110.3°W	0.8
P18N	159	5.5°N	110.3°W	−1.6
P18N	163	7.5°N	110.3°W	−2.5
P18N	168	10.0°N	110.0°W	−4.1

[a] Temperature, salinity, silicate concentration, phosphate concentration, total carbon, and pCO_2 data were used from the given World Ocean Circulation Experiment (WOCE) [*Schlitzer*, 2000] sites to calculate ΔCO_3^{2-} at 3346 m depth using the program developed for CO_2 system calculations [*Lewis and Wallace*, 1998].

tent with records of subsurface temperature changes in the region [*Cannariato and Ravelo*, 1997; *Wara et al.*, 2005]. Because there is no clear ecological explanation for the $SST_{Mg/Ca}$ and $SST_{UK'37}$ offset we turn our attention to the Mg/Ca proxy calibrations.

[31] Although we propagated the errors in the calibrations, the Mg/Ca calibration also has uncertainty in the estimate of ΔCO_3^{2-}, and the propagation of errors should include an additional term [*Taylor*, 1997]:

$$\sigma_{SST}^2 = \sigma_a^2(\partial SST/\partial a)^2 + \sigma_b^2(\partial SST/\partial b)^2 + \sigma_c^2(\partial SST/\partial c)^2 + \sigma_{\Delta CO32-}{}^2(\partial SST/\partial \Delta CO_3^{2-})^2 \quad (7)$$

Unfortunately, the data required to constrain ΔCO_3^{2-} are sparse. For example, the average distance between cores in the calibration study and the WOCE site from which data was used to calculate ΔCO_3^{2-} is 1° latitude and 5° longitude [*Dekens et al.*, 2002]. Using all available WOCE sites in the EEP at the depth of ODP site 847, we found the average ΔCO_3^{2-} in the region is -2.6 ± 4.0 μmol/kg and varies between −10 and 2 μmol/kg (Table 2).

[32] When ΔCO_3^{2-} is −10.3 μmol/kg, $SST_{Mg/Ca}$ is ~1°C warmer than $SST_{UK'37}$ (Figure 5b). However, when a ΔCO_3^{2-} value of 2 μmol/kg is used, the difference decreases to 0.6°C and the offset of the $SST_{Mg/Ca}$ relative to $SST_{UK'37}$ is no longer systematic ($SST_{Mg/Ca}$ are higher by more than the standard error in only 28% of the bins) (Figure 5d). Using the water depth dissolution correction (Model E; Figure 5c) yields lower SST estimates compared to the ΔCO_3^{2-} calibration, and therefore it also reduces the offset between $SST_{Mg/Ca}$ and $SST_{UK'37}$.The fact that uncertainty in the dissolution correction produces a range of possible absolute temperature estimates is not surprising given the complexity of parameterizing dissolution. Future research that applies the Mg/Ca SST proxy should report a range of possible temperatures that results from the estimated error of the dissolution correction, particularly when comparing temperature records from different sites and/or different proxies.

5.3. Variability Differences

[33] To compare the variability of the $SST_{Mg/Ca}$ and $SST_{UK'37}$ records, we calculated the averages and standard deviations for the late Pleistocene (0–0.5 Ma) and early Pliocene (3–4.6 Ma). The $SST_{Mg/Ca}$ and $SST_{UK'37}$ standard deviations for the late Pleistocene are the same (1.2°C). During the early Pliocene $SST_{UK'37}$ has a lower standard deviation (0.9°C) compared to the Pleistocene, while $SST_{Mg/Ca}$ has the same standard deviation (1.2°C) as in the Pleistocene.

[34] Because the $SST_{Mg/Ca}$ and $SST_{UK'37}$ records are from the same site and should therefore reflect the same climate variability, the different standard deviations of the two proxies during the Pliocene indicates that one proxy, and possibly both, is not accurately reflecting climate variability at this location. In order to address this, we compare the SST records at ODP site 847 to two published high-resolution records in the region. The $SST_{UK'37}$ record at ODP site 846 (located southeast of ODP site 847; Figure 1) and the $SST_{Mg/Ca}$ record at ODP site 1241 (northeast of ODP site 847) have a resolution of ~3 ka and ~4 ka, respectively [*Groeneveld et al.*, 2006; *Lawrence et al.*, 2006], and record glacial-interglacial variability (Figure 6a). The standard deviations for the Pleistocene are similar at the three sites with available data (1.2°C, 1.2°C, and 1.0°C for ODP site 847 $SST_{Mg/Ca}$, ODP site 847 $SST_{UK'37}$, and ODP site 846 $SST_{UK'37}$, respectively; Table 3). The similarity in the standard deviation demonstrates that although the resolutions of the records at ODP site 847 are low (10–20 ka), they are likely capturing the true ampli-

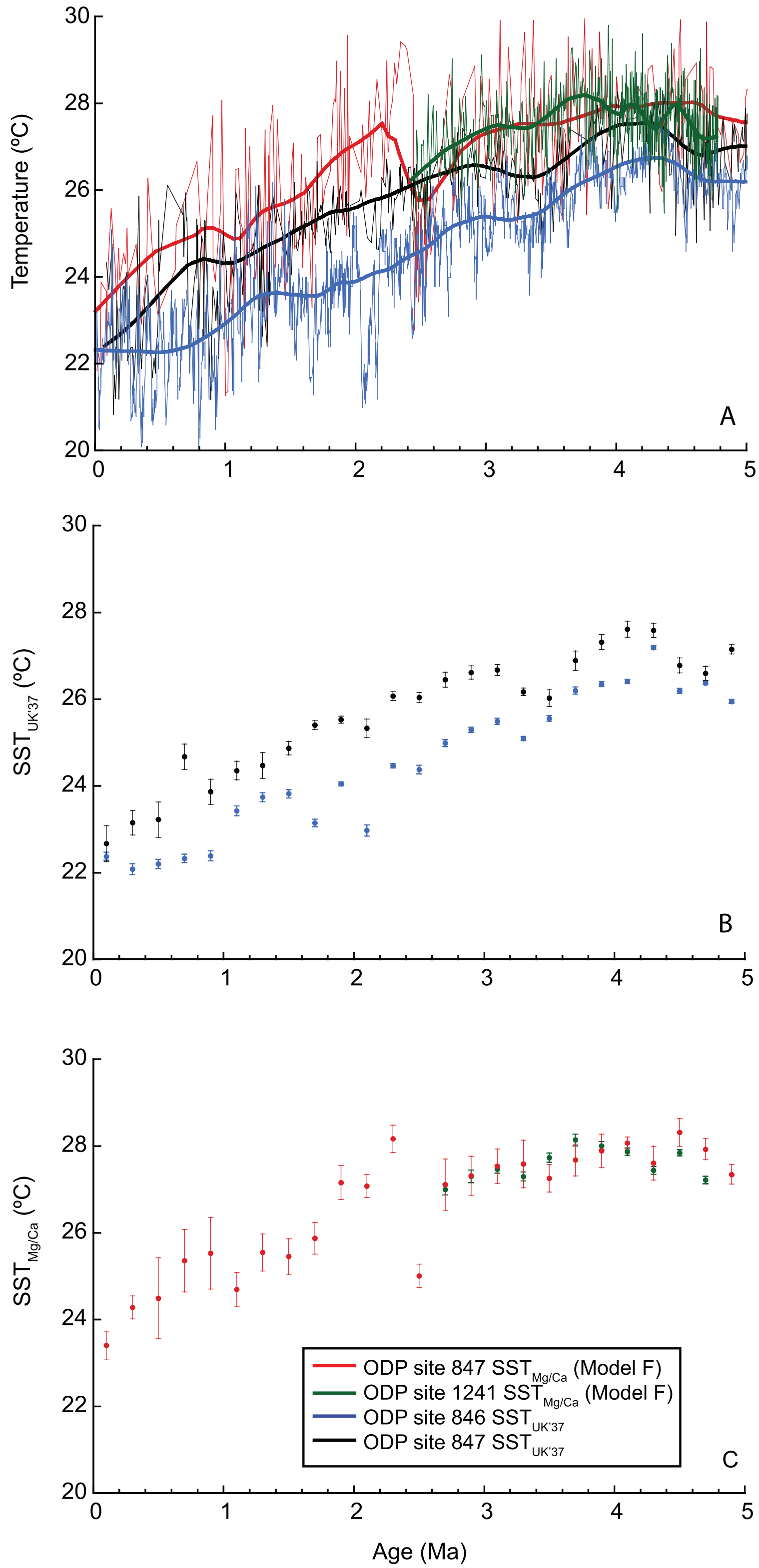

Figure 6. Regional SST records, showing (a) Mg/Ca SST records from ODP site 847 [*Wara et al.*, 2005] and ODP site 1241 [*Groeneveld et al.*, 2006] converted to SST using the ΔCO_3^{2-} corrected calibration [*Dekens et al.*, 2002], and $U_{37}^{K'}$ SST records from ODP site 847 [*Dekens et al.*, 2007] and ODP site 846 [*Lawrence et al.*, 2006]. For each record the thin line connects the individual data points and the thick line is a locally weighted least squares smoothing. (b) The mean and standard error of 200 ka binned $U_{37}^{K'}$ SST data from ODP sites 847 and 846. (c) The mean and standard error of 200 ka binned Mg/Ca SST from ODP sites 847 and 1241.

Table 3. Regional SST Records[a]

Record	Modern Mean Annual	Late Pleistocene (0–0.5 Ma) Average	Late Pleistocene (0–0.5 Ma) Standard Deviation	Early Pliocene (3–4.6 Ma) Average	Early Pliocene (3–4.6 Ma) Standard Deviation	Difference Pliocene-Pleistocene	Difference Pliocene-Modern
ODP site 847 $U^{K'}_{37}$ [*Dekens et al.*, 2007]	23.8°C 24.0°C*	23.0°C	1.2°C	26.8°C	0.9°C	3.8°C	3.0°C
ODP site 847 Mg/Ca [*Wara et al.*, 2005]	23.8°C 24.0°C*	23.8°C	1.2°C	27.7°C	1.2°C	3.9°C	3.9°C
ODP site 846 $U^{K'}_{37}$ [*Lawrence et al.*, 2006]	22.5°C 22.5°C*	22.2°C	1.0°C	26.0°C	0.8°C	3.8°C	3.5°C
ODP site 1241 Mg/Ca [*Groeneveld et al.*, 2006]	27.4°C 26.0°C*	NA	NA	27.7°C	0.7°C	NA	1.7°C

[a] Modern sea surface temperature (SST) for the sites modern location and its location 5 Ma. Asterisk indicates *Levitus and Boyer* [1994]. The mean and standard error were calculated for all data in the late Pleistocene and the early Pliocene. Also shown are the differences between the early Pliocene and the late Pleistocene and the difference between the Pliocene and the modern temperature. Note that only Ocean Drilling Program (ODP) site 1241 has a different mean annual SST for its modern and paleolocation. We therefore calculated the difference between the Pliocene and modern relative to its paleolocation.

tude of the glacial-interglacial cycles as recorded by the higher-resolution SST record at ODP site 846.

[35] During the Pliocene the standard deviation of the $SST_{Mg/Ca}$ record at ODP site 847 (1.2°C) is higher than that of the other three records (0.9°C, 0.7°C, and 0.8°C for ODP site 847 $SST_{UK'37}$, ODP site 1241 $SST_{Mg/Ca}$, and ODP site 846 $SST_{UK'37}$, respectively). We suspect that the relatively high variability in our $SST_{Mg/Ca}$ record at ODP site 847 results from postdepositional processes associated with the proxy. *G. sacculifer* tests were not abundant; ~50% of the data points in the record result from measurements of 10 shells or fewer. The standard deviation of Pliocene SST estimates made on samples with <10 shells (1.2°C) is not different from that of measurements of samples with >10 shells (1.4°C), indicating that biases due to subsampling of the foramininfera population cannot explain the high variability of the record.

[36] Another possibility is that generally poor preservation imparts "noise" on the $SST_{Mg/Ca}$ record. For example, increased productivity throughout the Pliocene could have lead to increased organic carbon content in the sediment and the respiration of carbon leads to lower $[CO_3^{2-}]_{in\ situ}$ in the pore waters. However, productivity in the eastern equatorial Pacific through the last 5 Ma was highest between 1.5 and 3 Ma [*Dekens et al.*, 2007; *Lawrence et al.*, 2006]. Because a change in the variance of the $SST_{Mg/Ca}$ record does not coincide with this time period we conclude that changes in preservation due to changes in productivity cannot explain the high variance of the $SST_{Mg/Ca}$ record at ODP site 847.

[37] Finally, the relatively high variance in the Pliocene $SST_{Mg/Ca}$ data at ODP site 847 could be related to postdepositional recrystallization as indicated by relatively high Mn/Ca found in *G. sacculifer*. Previous work in the EEP has shown high Mn/Ca (>0.1 mmol/mol) indicating the possible presence of Mn rich carbonate coatings [*Boyle*, 1983]. Although preparation of ODP site 847 foraminifera samples included a reductive cleaning step to remove oxy-hydroxide coatings [*Wara et al.*, 2005], the mean Mn/Ca in the record is 1.45 ± 0.31 mmol/mol, higher than the recommended limit of 0.6 mmol/mol [*Boyle*, 1983]. Even so, the Mg/Mn ratio in the overcoatings is thought to be ~0.1 [*Barker et al.*, 2003], which would contribute at most 0.2 mmol/mol to the observed Mg/Ca ratios. The observed Mn/Ca range during the early Pliocene (0.71 to 2.24 mmol/mol) could therefore introduce a temperature bias between 0.3°C and 1°C. While the excellent agreement between the $SST_{Mg/Ca}$ and $SST_{UK'37}$ records indicate that overcoatings do not affect the long-term trend in the Mg/Ca SST record, they could be responsible for the relatively high variance of the $SST_{Mg/Ca}$ record.

6. Comparing SST Records at ODP Site 847 to Other Records in the Region

[38] The warmer than modern SST during the Pliocene recorded by the Mg/Ca and $U^{K'}_{37}$ SST proxies at ODP site 847, together with other evidence in the EEP and the western equatorial Pacific, have previously been interpreted to reflect that the mean state of the tropical Pacific had an El

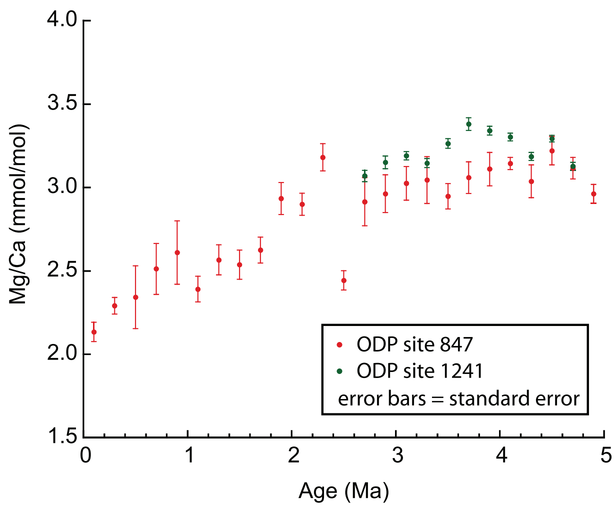

Figure 7. Mg/Ca for *G. sacculifer* from ODP site 847 [*Wara et al.*, 2005] and ODP site 1241 [*Groeneveld et al.*, 2006]. Data were separated into 200 ka bins and the mean is plotted. The error bars show the standard error of the mean, which is calculated as the standard deviation of the data divided by the square root of the number of data points in the bin ($\sigma/\sqrt{n}$).

Niño-like pattern of SST [*Ravelo et al.*, 2006, and references therein].

[39] The Mg/Ca record at ODP site 1241, just north of the equatorial cold tongue (Figure 1), was initially interpreted to reflect temperatures similar to today, suggesting that the early Pliocene did not have an El Niño-like SST pattern [*Groeneveld et al.*, 2006]. However, *Groeneveld et al.* [2006] used a Mg/Ca calibration derived from cultured *G. sacculifer* (model C) [*Nurnberg et al.*, 2000], which, as previously discussed, does not account for the dissolution effects, and therefore consistently yields lower SST estimates when applied to sediments. We eliminate Mg/Ca-SST calibration issues by directly comparing Mg/Ca data at ODP sites 1241 and 847, in 200 ka bins. The standard error bars are smaller for ODP site 1241 data because of its higher resolution compared to ODP site 847 data (Figure 7). More importantly, Mg/Ca values are similar for both records, although ODP site 1241 has slightly higher values due to better preservation (water depths are 2027 m and 3346 m for ODP site 1241 and 847, respectively).

[40] To calculate SST from Mg/Ca data, it makes most sense to use the same calibration at both sites. We utilize the core top calibration of *Dekens et al.* [2002] (Model F), which yields the most realistic SST for the youngest sample at ODP sites 847 (no Pleistocene data are available at ODP site 1241). Using the closest carbon chemistry data available, we calculate ΔCO_3^{2-} values for ODP site 1241 at the modern location (WOCE P19C #385, 3°N, 85.8°W) and at the Pliocene paleolocation (WOCE P19C #395, 6.7°N, 88.8°W) (5.1 μmol/kg and 5.8 μmol/kg, respectively). Because most ODP site 1241 data is from the warm Pliocene, we used a ΔCO_3^{2-} value of 5.8 μmol/kg in the calibration equation. For ODP site 847 we used the closest available WOCE site (WOCE P19C #373, 0°N, 85.8°W) to estimate ΔCO_3^{2-}. After converting Mg/Ca to SST the binned data at ODP sites 847 and 1241 reveal that SST estimates overlap within the standard error for most of the bins during the early Pliocene (Figure 6c). This result demonstrates that the small offset in Mg/Ca is a result of preservational differences, as a dissolution corrected calibration eliminates the offset. It further confirms that both ODP sites 847 and 1241 support the idea that the east equatorial Pacific SSTs were warmer than present by several degrees in the early Pliocene warm period.

7. Summary

[41] The Mg/Ca and $U^{K'}_{37}$ SST proxies have in recent years been applied to address Pliocene climate questions [*Dekens et al.*, 2007; *deMenocal et al.*, 2006; *Groeneveld et al.*, 2006; *Lawrence et al.*, 2006, 2007; *Wara et al.*, 2005]. Although much work has been done to compare these two proxies in Pleistocene glacial/interglacial records, and $SST_{Mg/Ca}$ and $SST_{UK'37}$ records at ODP site 847 have been previously published [*Dekens et al.*, 2007; *Wara et al.*, 2005], this study is the first to quantitatively compare the two proxies on pre-Pleistocene timescales.

[42] Earlier multiproxy studies show similar glacial-interglacial $SST_{UK'37}$ and $SST_{Mg/Ca}$ variability in most tropical regions [*Bard*, 2001; *Gagan et al.*, 2004; *Henderiks and Bollmann*, 2004; *Leduc et al.*, 2007; *Nurnberg et al.*, 2000]. One notable exception is in the western tropical Pacific, where glacial-interglacial $SST_{UK'37}$ changes were smaller than $SST_{Mg/Ca}$, which was hypothesized to be due to subsurface growth of coccolithophorids [*De Garidel-Thoron et al.*, 2007]. Given the excellent agreement between the $SST_{UK'37}$ and $SST_{Mg/Ca}$ records at ODP site 847 and the dissimilarity between the $SST_{UK'37}$ record and isotopic records of *G. tumida* (a foraminifera which inhabits the base of the photic zone) at the same and nearby sites [*Cannariato and Ravelo*, 1997; *Wara et al.*, 2005], we conclude that $U^{K'}_{37}$ is recording near surface temperatures at this location. In the eastern

equatorial Atlantic $SST_{UK'37}$ and $SST_{Mg/Ca}$ are inconsistent for the early Holocene due to strong seasonal changes in hydrography [*Weldeab et al.*, 2007]. The agreement of long-term trends of $SST_{UK'37}$ and $SST_{Mg/Ca}$ at ODP site 847 indicates that both proxies record mean annual SST, which is consistent with large-scale calibrations for both proxies [*Conte et al.*, 2006; *Dekens et al.*, 2002; *Muller et al.*, 1998; *Rosenthal and Lohmann*, 2002]. Although the possible influence of seasonality and subsurface growth must be considered at any location, the remarkable similarity of the long-term trends of $SST_{Mg/Ca}$ and $SST_{UK'37}$ records at ODP site 847 indicates that these are not a concern in these Plio-Pleistocene records.

[43] One concern with the application of the Mg/Ca SST proxy is that preferential dissolution of the Mg-rich parts of the foraminiferal shell leads to a cold temperature bias [*Brown and Elderfield*, 1996]. We find that a core top based foramininferal Mg/Ca−SST calibration that applies a dissolution correction [*Dekens et al.*, 2002] provides a core top temperature estimate close to the modern SST. Comparing Mg/Ca records at ODP sites 847 and 1241 highlights the importance of considering dissolution when interpreting Mg/Ca records. The primary Mg/Ca data of the two records overlap, and the application of the same dissolution corrected calibration demonstrates that the Pliocene SST estimates for these two sites are the same, indicating that the eastern equatorial Pacific was 2−4°C warmer during the early Pliocene compared to today.

[44] Although the application of a dissolution corrected calibration should be applied to Mg/Ca data, it is important to keep in mind that preservational changes through time are not accounted for, as the correction parameter is constant throughout the record and is based on modern conditions. In addition, there is uncertainty in ΔCO_3^{2-} at most locations, and at ODP site 847 this led to an apparent offset between $SST_{Mg/Ca}$ and $SST_{UK'37}$. There is, in fact, a range of possible $SST_{Mg/Ca}$ depending on how dissolution is corrected for, and this range overlaps with $SST_{UK'37}$.

[45] Secondary calcite overgrowth is another possible diagenetic affect on Mg/Ca. Although it is likely that oxy-hydroxide overcoatings, as indicated by relatively high Mn/Ca content of the shells, appear to add variance to the $SST_{Mg/Ca}$ record at ODP site 847, the overall agreement between the two proxy records indicates that the Mg paleothermometer is accurately recording long-term changes in SST at ODP site 847.

[46] The long-term trends of $SST_{Mg/Ca}$ and $SST_{UK'37}$ at ODP site 847 are remarkably similar, strong evidence that the $U_{37}^{K'}$−SST relationship is unchanged through time and that degradation of alkenones does not alter the primary temperature signal. It is also a strong indication that changes in the Mg/Ca of seawater are relatively small, as any large changes would change the amplitude of the temperature change through time.

[47] The excellent agreement between $SST_{Mg/Ca}$ and $SST_{UK'37}$ at ODP site 847, both in the long-term trends and the absolute temperature estimates, dramatically increases our confidence in the Pliocene SST estimates at this location and indicates that both Mg/Ca in planktonic foraminifera and $U_{37}^{K'}$ recorded by coccolithophorids can be reliable SST proxies on pre-Pleistocene records.

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