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Implications of seawater Mg/Ca variability for Plio-Pleistocene tropical climate reconstruction

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ABSTRACT

Recent reconstructions of Mg and Ca concentrations of seawater indicate that seawater Mg/Ca changed significantly over the last 5 million years (Ma). Tropical sea surface temperature (SST) records for the last 5 Ma based on foraminiferal Mg/Ca paleothermometry assume constant seawater Mg/Ca. These SST records suggest that average equatorial Pacific SSTs remained thermally stable from 5 to 2 Ma, after which significant cooling occurred only in the eastern equatorial Pacific. This study examines the implications of adjusting available equatorial Pacific SST records based on Mg/Ca paleothermometry to account for the inferred past variations of seawater Mg/Ca. The results suggest that both the cold and the warm regions of the equatorial Pacific were much warmer during the early Pliocene (30–31 °C), and that both regions experienced a marked cooling from ~4 Ma to ~1 Ma. This new interpretation of foraminiferal Mg/Ca creates a discrepancy with alkenone unsaturation-based SST records from the eastern equatorial Pacific, which might be due to either overestimation of changes in past seawater Mg/Ca or to factors affecting the interpretation of the $U^{K'}_{37}$ index. The adjusted SST records are consistent with the hypothesis that higher levels of greenhouse gases maintained the warmth of the early Pliocene.

1. Introduction

Over the last 5 million years (Ma) global climate evolution is marked by two major transitions: the onset of the Northern Hemisphere glaciation (NHG) between 3 and 2 Ma and the mid-Pleistocene transition (MPT) at ~950 ka. A number of hypotheses have been proposed to explain the switch from early Pliocene global warmth (5–3.5 Ma) to the late Pliocene–Holocene "ice ages" (3 Ma to present) that invoke a gradual global cooling driven by decreasing atmospheric carbon dioxide concentrations (Saltzman and Maasch, 1991; Raymo et al., 1997; Mudelsee and Schulz, 1997; Paillard, 1998; Berger et al., 1999; Sigman et al., 2004; Huybers and Wunsch, 2005). A transition from a period of global warmth to cooler conditions is supported by sea surface temperature (SST) records from the eastern equatorial-upwelling regions based on foraminiferal Mg/Ca (Wara et al., 2005) and the $U^{K'}_{37}$ index (Liu and Herbert, 2004; Lawrence et al., 2006), and by foraminiferal $\delta^{18}O$ records of high-latitude climate (e.g. continental ice volume and bottom water temperatures) (Lisiecki and Raymo, 2005). A recent paleoclimate reconstruction based on Mg/Ca paleothermometry (Wara et al., 2005), however, appears to contradict global cooling because it indicates that the western equatorial Pacific (WEP) warm pool remained thermally stable over the last 5 Ma.

Medina-Elizalde and Lea (2005) pointed out that the western equatorial Pacific warm pool is ideal for addressing proposed forcing mechanisms of tropical climate variability because (i) warm pool thermal variability is linked throughout the tropics by convection (Sobel et al., 2002); (ii) the warm pool is less subject to regional oceanographic influences such as thermocline depth changes (Philander and Fedorov, 2003); and (iii) the warm pool is remote from the direct radiative influence of continental ice sheets and responds to radiative forcing by variable greenhouse gases concentrations in the atmosphere (Broccoli, 2000). The influence of radiative forcing by atmospheric greenhouse gases on the WEP warm pool is supported by the correspondence between the increase in the mean western equatorial Pacific sea surface temperature over the past 50 yr (+0.6 °C) (Hansen et al., 2006) and the increase in global surface temperatures over the same period attributed to increased greenhouse gas concentrations (Knutson and Manabe, 1998; Knutson et al., 1999; Hansen et al., 2006). Furthermore, evidence has been provided that the WEP warm pool not only responds to forcing by greenhouse gases on short time scales, but also responds on significantly longer time scales over the past 2 Ma (Lea, 2004; Medina-Elizalde and Lea, 2005).

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The stability of WEP warm pool SSTs, as reconstructed by Mg paleothermometry, rests on the assumption that the Mg/Ca ratio in seawater has remained constant over the time scale of investigation (10^5–10^6 yr time scales) (Visser et al., 2003; De Garidel-Thoron et al., 2005). Experimental studies have documented that the Mg/Ca ratio of an aqueous solution affects the Mg/Ca ratio of carbonate precipitated from solution (Katz, 1973; Mucci and Morse, 1983; Delaney et al., 1985; Oomori et al., 1987). The Mg/Ca ratio of a foraminiferal test precipitated in the surface ocean is therefore a function not only of temperature but of seawater composition as well.

Over time scales shorter than ~1 Ma, the assumption of invariable seawater Mg/Ca ratios (Mg/Ca_{sw}) is reasonable because both Mg and Ca have residence times in the ocean that are longer than 1 Ma (Mg ≈ 22 Ma, and Ca ≈ 1 Ma) (Fantle and DePaolo, 2005, 2006). Over time scales that are longer than 1 Ma, however, it is not certain that the Mg/Ca ratio of seawater is constant. While analyses of fluid inclusions in evaporites support the hypothesis that seawater Mg/Ca ratios have varied over time scales of tens of millions of years, these studies do not have the temporal resolution required to assess seawater evolution over the last 5 Ma (Lowenstein et al., 2001; Horita et al., 2002; Lowenstein et al., 2003). Recently, however, Fantle and DePaolo (2005, 2006) used numerical modeling techniques to constrain the Mg and Ca evolution of seawater with a resolution of ~500 kyr.

The purpose of this paper is to examine the effect of variable seawater Mg/Ca ratios on the interpretation of equatorial Pacific SST records. In turn, we explore the implications of adjustments to the existing SST records for tropical climate evolution over the last 5 Ma. Given the hypothesized response of the WEP warm pool to variations in global climate and climate forcing by atmospheric greenhouse gases, we focus on records from this region as well as from the eastern equatorial Pacific Ocean.

2. Methods

2.1. Constraining the Mg/Ca ratio of seawater

The Mg/Ca ratio of seawater over time is constrained by the analysis of fluid inclusions in evaporite minerals (Lowenstein et al., 2001; Horita et al., 2002; Lowenstein et al., 2003) and by modeling studies that examine seawater evolution over long time scales (Hardie, 1996; Berner, 2004). The fluid inclusion work, in particular, suffers from poor temporal resolution and large uncertainties in age assignments. As a result, it is difficult to relate with confidence climatic events in different proxy records with ocean chemical trends that are constrained by evaporite fluid inclusions. Thus, it is desirable to find analytical techniques that constrain Ca and Mg concentrations over time that not only have less age uncertainty, but are also unambiguous recorders of the marine environment.

Recently, Fantle and DePaolo (2005, 2006) used simple geochemical models of the Ca cycle to interpret the Ca isotopic composition of bulk nannofossil sediments in terms of Ca concentrations in the ocean. They found that marine Ca concentrations varied significantly over 2–4 Ma time scales and that this variability is a result of an imbalance between the major marine output flux (carbonate sedimentation) and the predominant input fluxes (weathering and hydrothermal) (Fantle and DePaolo, 2005; DePaolo, 2004). While variability of this sort has been observed in other Ca isotope proxies (Morris et al., 2005), it is important to point out that the interpretation of the Ca isotopic composition of marine carbonates in terms of seawater Ca concentrations is based on the assumption that relative Ca inputs and outputs control the isotopic composition of seawater and, thus, sediments that precipitate from it. This method of interpretation has been questioned by some and is currently an area of active research (Sime et al., 2007).

While the Ca isotope record can constrain marine Ca concentrations, recent reactive transport modeling suggests that Mg concentrations in the ocean have varied significantly over time scales that are less than the residence time of Mg (Fantle and DePaolo, 2006). Numerical models simulating diagenesis (diffusion, advection, and reaction) over tens of millions of years, in which reaction rates are constrained by measurements of pore fluid Sr concentration and isotopic composition, were used to estimate average seawater Mg concentrations over time. The models iteratively calculate how reaction between the solid and fluid acts to alter the Mg concentration of the initial seawater buried with the sediment (Fantle and DePaolo, 2006). This approach supposes that the partitioning of Mg in carbonate formed in the surface ocean is significantly different than the partitioning of Mg in carbonate-rich sedimentary sections, such as ODP Site 807A (Ontong Java Plateau, WEP). This hypothesis is supported to a degree by experimental investigations of Mg partitioning (Oomori et al., 1987). Yet the most critical factor in this approach to reconstructing Mg concentrations in seawater is that the diffusive reaction length scale (Ld) at 807A is large relative to the thickness of the section. Consideration of this length scale at ODP Site 807A suggests that Mg in the measured pore fluids is controlled to a large extent by upper boundary condition, i.e. the initial Mg derived from seawater. Diffusion and reaction therefore serve to modify, but not erase, the initial Mg concentration of the pore fluid.

Using previously published marine Ca concentration curves (Fantle and DePaolo, 2005) and a seawater Mg curve derived from modeling of ODP Site 807A, Fantle and DePaolo (2006) presented two Mg/Ca_{sw} curves for the past 20 Ma. The two seawater Mg/Ca curves were constructed by iteratively calculating a Mg curve using an empirical equilibrium partition coefficient for Mg in diagenetic carbonates (0.84; see Fantle and DePaolo, 2006 for details on the formulation used for the partition coefficient) and using two marine Ca curves, each of which assumes different behavior for the Ca isotopic composition of the weathering flux. In one case, it was assumed that the weathering flux had a constant isotopic composition over the past 20 Ma ($\delta^{44}Ca_W = \delta_W = -0.48‰$), whereas the second case assumed that the ocean is in steady state over some time scale longer than 4 Ma and calculated δ_W using a moving average.

It is important to note that, as with all investigations of the past, there is an inherent amount of uncertainty in the determination of seawater Mg/Ca over time. We do not quantify such uncertainty here. The largest source of uncertainty, however, is the partition coefficient for Mg. Both the diffusion coefficient and reaction rates are well constrained, the latter by Sr isotope and concentration data (Fantle and DePaolo, 2006). As Fantle and DePaolo (2006) illustrated, the variation of the partition coefficient across a fairly wide range ($K_{Mg} = 0.4$–0.84) does not change the basic behavior of seawater Mg over the past 15 Ma (Fig. 11a of that paper). Since seawater Mg concentrations dominate the Mg/Ca curve over this time, the basic conclusions of this study should be robust. The Ca record contributes less significant short-term oscillations to the Mg/Ca curve, and is therefore less critical to the current study.

The Mg/Ca_{sw} curves produced using the previously described techniques agree with lower resolution seawater Mg/Ca estimates based on measurements of fluid inclusions in marine evaporites (Lowenstein et al., 2001; Horita et al., 2002). The Mg/Ca_{sw} records derived from the DSDP 590B and the ODP 807A data show that Mg/Ca_{sw} reached a minimum of ~2.7 mol/mol during the early Pliocene at 4 Ma, almost a factor of two lower than modern Mg/Ca_{sw} levels (5.17 mol/mol). Between 4 Ma and the present, Mg/Ca_{sw} increased gradually from its minimum at 4 Ma to its present-day value (Fig. 1).

2.2. The Mg/Ca paleothermometry technique

One of the most utilized tools for the reconstruction of sea surface temperatures over the last 5 Ma is the Mg/Ca paleothermometry technique, which is based on the temperature dependence of the partition coefficient for Mg between the seawater and foraminiferal

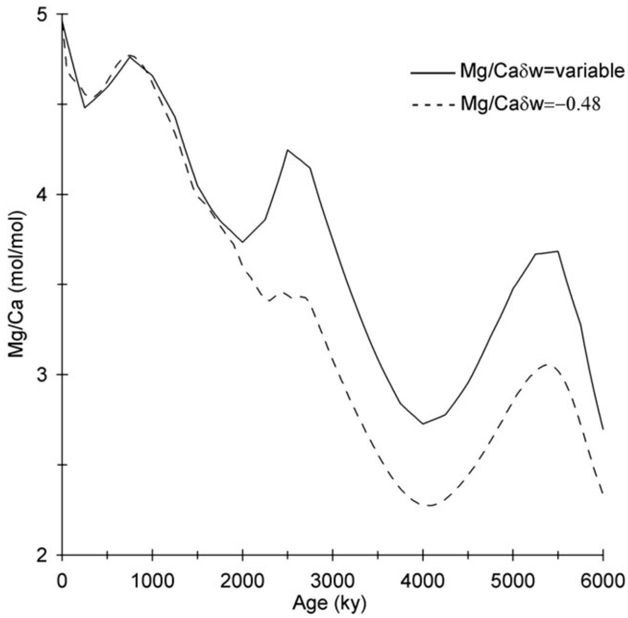

Fig. 1. Seawater Mg/Ca (Mg/Ca_{sw}) reconstructions by Fantle and DePaolo (2006) (FD06) (Fantle and DePaolo, 2006). These curves are based on two parameterizations of assumed δ^{44}Ca value for weathering inputs to the ocean (δ_W). In one case, it was assumed that the Ca isotopic composition of the weathering flux was constant (δ_W= −0.48‰) over the past 20 Ma, whereas in the other case, the Ca isotopic composition of the weathering flux was constrained assuming that the ocean is in steady state over some time scale longer than 4 Ma (δ_W=variable). The foraminiferal Mg/Ca-based SST records presented here were adjusted to account for past changes in seawater Mg/Ca using the curve that assumes variable δ^{44}Ca weathering inputs to the ocean.

calcite (Nürnberg et al., 1996). Core-top and culturing experiments suggest that this dependence is equivalent to a 9% exponential change in foraminiferal calcite Mg/Ca per degree Celsius temperature change in the water (Lea et al., 1999; Dekens et al., 2002; Anand et al., 2003; Barker et al., 2005):

$$(\mathrm{Mg/Ca})_{\mathrm{foram}} = b * e^{0.09*\mathrm{SST}}. \quad (1)$$

The "pre-exponential parameter" (b) is equivalent to the calcite Mg/Ca content at 0 °C under typical modern seawater Mg/Ca ratios of 5.17 mol/mol (Bruland, 1983).

We recalculated foraminiferal Mg/Ca-based SSTs using the Mg/Ca_{sw} curve that assumes variable δ^{44}Ca weathering inputs to the ocean (Fig. 1). This curve represents a more likely scenario with regard to the weathering input to the ocean and is also a more conservative estimate of past Mg/Ca_{sw} changes (Fig. 1). Using this Mg/Ca_{sw} curve, we reinterpret previously published equatorial Pacific Mg/Ca-based SST records that extend back to the early Pliocene. We adjusted Ocean Drilling Program (ODP) Hole 806B (0°N, 159°E, 2520-m water depth) Mg/Ca records from the western equatorial Pacific derived from the planktonic foraminifera *Globigerinoides ruber* and *Globigerinoides sacculifer* (Lea et al., 2000; Wara et al., 2005; Medina-Elizalde and Lea, 2005) which extend back to 1.3 and 5 Ma, respectively. We also adjusted the Mg/Ca record from ODP Hole 847 (0°N, 95°W, 3373-m water depth) from the eastern equatorial Pacific, which is based on the foraminifera *G. sacculifer* and which covers the 0 to 5 Ma time interval (Wara et al., 2005) (Fig. 2).

All foraminiferal Mg/Ca data were converted to SSTs using previously published relationships between measured calcite Mg/Ca and temperature (Dekens et al., 2002):

$$\textit{Globigerinoides ruber}: (\mathrm{Mg/Ca})_{\mathrm{foram}} = 0.38 \cdot \exp 0.09[\mathrm{SST} - 0.61(d) - 1.6\,°\mathrm{C}] \quad (2)$$

$$\textit{Globigerinoides sacculifer}: (\mathrm{Mg/Ca})_{\mathrm{foram}} = 0.37 \cdot \exp 0.09[\mathrm{SST} - 0.36(d) - 2.0\,°\mathrm{C}]. \quad (3)$$

Where sea surface temperature (SST) is in units of °C and d is the water depth of the surface sediment, in units of kilometers. The inclusion of a depth dependence accounts for the effect of dissolution on shell Mg/Ca.

To account for past Mg/Ca_{sw} variability, we adjusted the pre-exponential constants in Eqs. (2) and (3) by a percentage equal to that calculated from the difference between Mg/Ca_{sw} from a given age and a Mg/Ca_{sw} core-top value of 4.96 mol/mol, the assumed zero-age value in Fantle and DePaolo (2006). A second adjustment is required because Mg in calcite is also a function of the partition coefficient between calcite and seawater. Thermodynamic calculations (Busenberg and Plummer, 1989) and inorganic precipitation experiments (Mucci and Morse, 1983) indicate that the Mg partition coefficient in calcite increases as Mg/Ca decreases in seawater (Mucci and Morse, 1983). To account for this effect, we used the relationship derived from inorganic calcite precipitation (Mucci and Morse, 1983), which predicts a 12% exponential increase in the partition coefficient per molar

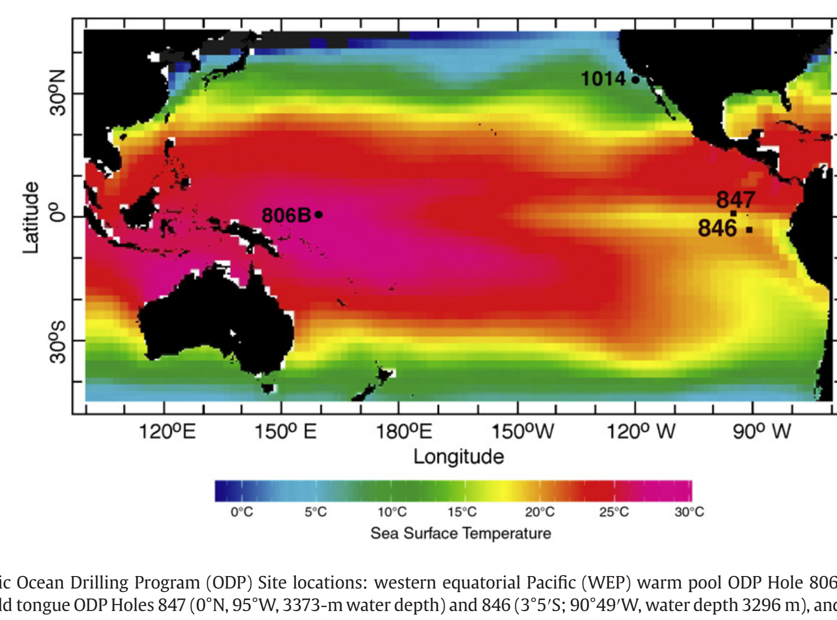

Fig. 2. Eastern and western Pacific Ocean Drilling Program (ODP) Site locations: western equatorial Pacific (WEP) warm pool ODP Hole 806B (0°N, 159°E, 2520-m water depth), eastern equatorial Pacific (EEP) cold tongue ODP Holes 847 (0°N, 95°W, 3373-m water depth) and 846 (3°5′S; 90°49′W, water depth 3296 m), and eastern Pacific ODP Hole 1014 (33°N, 120°W) (mean annual SSTs, accessed at URL: http://iridl.ldeo.columbia.edu/Sources/.NOAA/.NCDC/.ERSST/.version2/.SST).

Table 1
Eastern (Hole 847,846) and western equatorial Pacific (Hole 806B) average SSTs calculated for various time intervals (Wara et al., 2005; Dekens et al., 2007)

Time interval	ODP Hole 847 $U^{K'}_{37}$ SST adjusted	ODP Hole 847 $U^{K'}_{37}$ SST*	ODP Hole 846 $U^{K'}_{37}$ SST*	ODP Hole 847 Mg/Ca-unadjusted SST	ODP Hole 847 Mg/Ca-adjusted SST	ODP Hole 806B unadjusted SST	ODP Hole 806B adjusted SST
Quaternary (Last 1 Ma)	23.6	23.6	22.2	23.5	23.8	28.3	28.7
5–2 Ma B.P.	27.6	26.6	25.5	26.7	28.9	27.5	30.3
Early Pliocene (5–3.5 Ma B.P.)	28.3	27.0	26.3	26.8	29.8	27.6	31.3

ODP Hole 847 $U^{K'}_{37}$- SSTs adjusted, are based on using a non-linear calibration equation. In this case, values of $U^{K'}_{37}>0.88$ were converted to SSTs using the equation $U^{K'}_{37}=0.020$ SST+0.392 (Sonzogni et al., 1997), and values of $U^{K'}_{37}<0.88$ were converted to SST using the linear equation $U^{K'}_{37}=0.034$ SST+0.039 (Prahl et al., 1988). *Average ODP Hole 846 and 847 SSTs are based on the $U^{K'}_{37}$ index using the linear calibration by Prahl et al., (1988) only.

drop in Mg/Ca_{sw}. Some marine taxa appear to follow this functionality (Ries, 2004, 2006), and there is limited culturing data suggesting that this relationship applies to foraminifera (Delaney et al., 1985). Future culturing studies, however, are needed to establish how the foraminiferal partition coefficient changes for varying seawater Mg/Ca.

To place the adjusted Mg/Ca-SST records in context, we first compare the originally published Mg/Ca records with independent high resolution temperature records based on the $U^{K'}_{37}$ index from ODP Hole 846 (3°5′S; 90°49′W) (Liu and Herbert, 2004; Lawrence et al., 2006) and ODP Hole 847 (0°N, 95°W, 3373-m water depth) (Dekens et al., 2007). We then compare these records to the SST records adjusted for changing Mg/Ca_{sw} over the last 5 Ma.

Because the oxygen isotopic composition of foraminiferal calcite is a function of both the oxygen isotopic composition of the water from which it formed and the temperature-dependent fractionation factor, the adjusted SST estimates and $\delta^{18}O$ values also yield an adjusted value for the $\delta^{18}O$ composition of seawater ($\delta^{18}O_{sw}$). We use the following low light paleotemperature equation to calculate the seawater $\delta^{18}O$ record from the $\delta^{18}O$ of *Orbulina universa* (Bemis et al., 1998):

$$\delta^{18}O_{sw} = (SST - 16.5 + 4.8*\delta^{18}O_{calcite})/4.8 + 0.27.$$

We then examine the salinity changes implied by these records in the context of independent evidence of hydrological variability of the equatorial Pacific during the Pliocene.

3. Results

3.1. The eastern equatorial Pacific (EEP) cold tongue

The ODP Hole 847 and 846 $U^{K'}_{37}$-derived SST records (Liu and Herbert, 2004; Lawrence et al., 2006; Dekens et al., 2007) suggest that the EEP cold tongue had an SST of ~26.5 °C during the early Pliocene (from 3.5 to 5 Ma), and ~22.5 °C during the last 1 Ma (Table 1). The ODP Hole 847 SST record calculated assuming constant Mg/Ca_{sw} (Wara et al., 2005) had an SST of ~26.8 °C during the early Pliocene and ~23.5 °C during the last 1 Ma in close agreement with the $U^{K'}_{27}$ proxy (Table 1). These two proxy records differ, however, in the details of surface temperature evolution over the last 5 Ma. First, the $U^{K'}_{37}$-derived SST records suggest that the EEP cold tongue experienced a 1.3 °C (Hole 847) (Dekens et al., 2007) to 2.6 °C (Hole 846) (Lawrence et al., 2006)cooling during the Pliocene, between 5 and 2 Ma (Fig. 3). The unadjusted SST record based on foraminiferal Mg/Ca, however, suggests no cooling during this time interval (Fig. 3). Second, the $U^{K'}_{37}$-based SST records indicate a fairly uniform 3 to 4 °C cooling between 4.3 Ma and 1 Ma, whereas the unadjusted Mg/Ca proxy suggests a cooling of 3.3 °C primarily occurring after 2 Ma (Fig. 3). Finally, the foraminiferal Mg/Ca-SST record indicates a glacial to interglacial (GI) SST range of 5.4 °C (±2SD, data detrended) whereas a more modest GI SST range of 3.8 °C (±2SD, data detrended) is suggested by the $U^{K'}_{37}$ record from Hole 847 (Dekens et al., 2007) (Fig. 3).

The adjusted Mg/Ca-SST record suggests that the eastern equatorial Pacific cold tongue was 6 °C warmer during the early Pliocene than the last 1 Ma, compared to the 3.3 °C difference suggested by the unadjusted SST record (Figs. 3, 4, Table 1). The higher mid-Pliocene EEP SSTs suggested by the adjusted SST record arise from the inferred Mg/Ca_{sw} minimum of 2.7 at ~4 Ma in Fantle and DePaolo (2006) (Fig. 4B). Lower seawater Mg/Ca ratios, when applied to a measured foraminiferal Mg/Ca record, result in higher inferred SSTs. Whereas there is no observable cooling between 5 and 2 Ma when assuming constant seawater Mg/Ca, including the effect of variable Mg/Ca_{sw} alters the interpretation to suggest a 2.6 °C cooling. This 2.6 °C cooling is twice as pronounced as the cooling implied by the $U^{K'}_{37}$ record from Hole 847 (1.3 °C), but similar to $U^{K'}_{37}$ record from Hole 846 (2.8 °C) (Figs. 3, 4C).

Whereas the agreement in cooling trends between the adjusted Mg/Ca-SST record and the alkenone-SST record is improved between 5 and 2 Ma, particularly when compared to the Hole 846 SST record, the

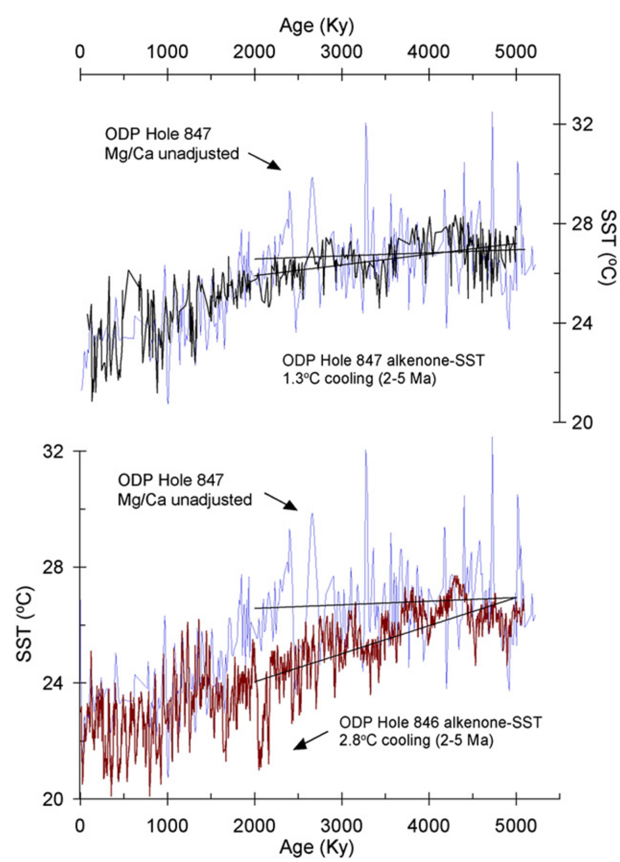

Fig. 3. Eastern equatorial Pacific ODP Hole 847 Mg/Ca-SST record based on the planktonic foraminifer *Globigerinoides sacculifer* and assuming constant seawater Mg/Ca (Wara et al., 2005) (blue). ODP Hole 847 SST record (Dekens et al., 2007) (black, top) and ODP Hole 846 SST record (Liu and Herbert, 2004; Lawrence et al., 2006) (dark red, bottom) based on the $U^{K'}_{37}$ index. No cooling between 5 and 2 Ma is suggested by Mg/Ca-SSTs when assuming constant seawater Mg/Ca. The $U^{K'}_{37}$-derived SST records from ODP Holes 847 and 846 suggest a cooling of 1.3 °C and 2.8 °C between 5 and 2 Ma, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

assumption of variable Mg/Ca_{sw} creates disagreement between the two proxies when considering the absolute magnitude of cooling over the entire 5 Ma time period. Specifically, the adjusted Mg/Ca record supports a cooling of ~6 °C since 5 Ma, larger than the ~4 °C cooling suggested by the $U^{K'}_{37}$ index-based records (Lawrence et al., 2006; Dekens et al., 2007) (Fig. 4C, Table 1). In addition, the adjusted Mg/Ca record suggests mean absolute early Pliocene SSTs of ~30 °C, higher than the 27 °C implied by the $U^{K'}_{37}$ index. Lawrence et al. (2006) and Dekens et al. (2007) applied a linear calibration that relates $U^{K'}_{37}$ index to alkenone production temperature, based on culturing experiments at temperatures between 8 and 25 °C (Prahl et al., 1988). Recent field-based calibration studies, however, show that the relationship between surface water $U^{K'}_{37}$ index and alkenone production temperature is best described by a non-linear regression (Conte et al., 2006). Using an equation with a slope that is sensitive to high SSTs >24 °C (i.e. 0.020) (Sonzogni et al., 1997), confirmed recently in a warm pool study (De Garidel-Thoron et al., 2007) and in a global $U^{K'}_{37}$ calibration study

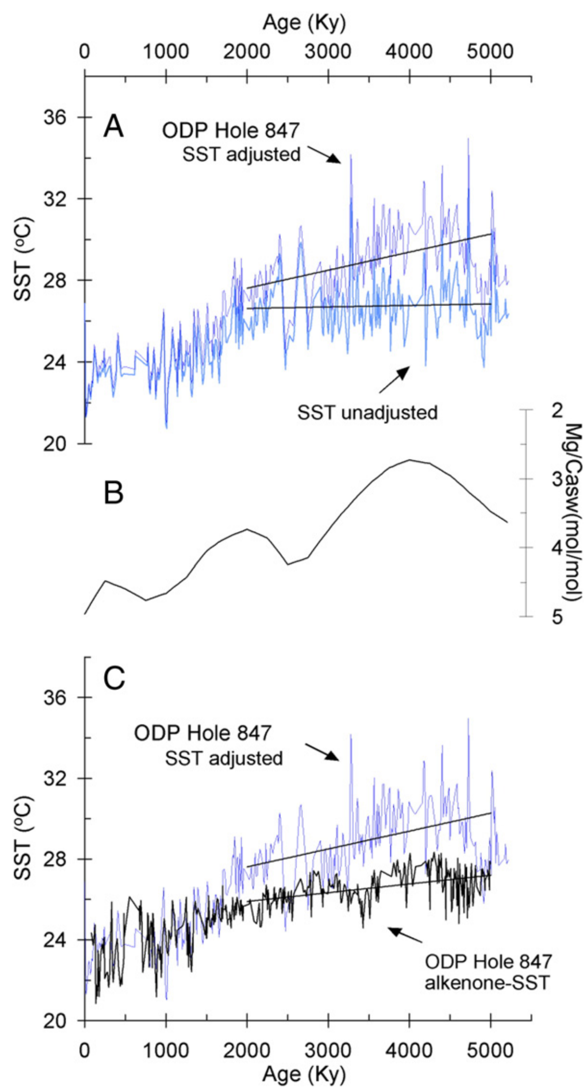

Fig. 4. Eastern equatorial Pacific SST records for the last 5 Ma. (A) ODP 847 unadjusted and adjusted SST records based on the foraminifer *G. sacculifer* (Wara et al., 2005). (B) FD06 seawater Mg/Ca curve (axis inverted). (C) ODP Hole 847 adjusted SST record (Wara et al., 2005) and ODP Hole 847 SST record based on the alkenone unsaturation index (Dekens et al., 2007). Lines are linear regressions from 5 to 2 Ma. The adjusted SST record and the $U^{K'}_{37}$-SST record suggest that the EEP cooled by 2.6 °C and 1.3 °C, respectively, from 5 to 2 Ma. The unadjusted SST record implies, however, no cooling during this time. The adjusted SST record suggests that average SSTs were ~30 °C at 4 Ma whereas the alkenone index suggests they were ~28 °C.

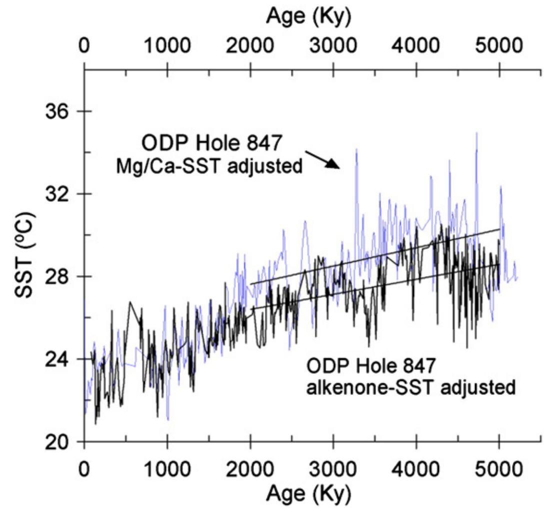

Fig. 5. ODP Hole 847 eastern equatorial Pacific SST records based on adjusted foraminiferal Mg/Ca (Wara et al., 2005) and on the $U^{K'}_{37}$ index (Dekens et al., 2007). Hole 847 $U^{K'}_{37}$ values were converted to SSTs by using the equation $U^{K'}_{37}$=0.020 SST+0.392 (Sonzogni et al., 1997) at values of $U^{K'}_{37}$ >0.88, and by using the linear relationship $U^{K'}_{37}$=0.034 SST+0.039 at values of $U^{K'}_{37}$ <0.88 (Prahl et al., 1988). Alkenone-SSTs suggest a cooling of ~5 °C since 5 Ma, closer to the 6 °C cooling suggested by Mg/Ca-based SSTs based on variable seawater Mg/Ca, and also a glacial to interglacial (GI) SST range of 5 °C (±2SD, data detrended), in closer agreement with the GI suggested by Mg/Ca-derived SSTs of 5.4 °C (±2SD, data detrended).

(Conte et al., 2006), we recalculate alkenone-based SSTs from ODP Hole 847 (Fig. 5). The revised alkenone-SSTs suggest a cooling of ~5 °C since 5 Ma, closer to the 6 °C cooling suggested by Mg/Ca-based SSTs based on variable seawater Mg/Ca (Table 1). In addition, consideration of non-linearity in the alkenone index at SSTs >24 °C (Sonzogni et al., 1997) indicates a GI SST range of 5 °C (±2SD, data detrended), in closer agreement with the GI suggested by Mg/Ca-derived SSTs of 5.4 °C (Figs. 4, 5).

The $U^{K'}_{37}$-based SST records (Holes 846 and 847) and the Mg/Ca-based SST record, have one key similarity that emerges only after the correction for changing Mg/Ca_{sw}: a long-term cooling from 5 to 2 Ma of ~2.6 °C (Table 1, Figs. 3, 4). The Pliocene cooling in the EEP cold tongue is evident only in the adjusted record; in particular, this cooling trend is related to the gradual increase in Mg/Ca_{sw} from a minimum of 2.7 at 4 Ma to 3.8 at ~2 Ma (Fantle and DePaolo, 2006).

3.2. The western equatorial Pacific (WEP) warm pool

ODP Hole 806B SST records based on the Mg/Ca ratios of planktonic foraminifera *G. ruber* (Medina-Elizalde and Lea, 2005) and *G. sacculifer* (Wara et al., 2005) and the assumption of constant seawater Mg/Ca indicate that, between 5 Ma and the present, the WEP warm pool remained relatively stable with average SSTs of 27.8±1 °C (Wara et al., 2005) (Fig. 6, Table 1). SSTs adjusted to account for variable Mg/Ca_{sw} over this time interval indicate, in contrast, that the WEP warm pool was on average ~31 °C during the early Pliocene (from 3.5 to 5 Ma) and ~29 °C during the Late Pleistocene (Fig. 6, Table 1). A significant ~3.5 °C cooling emerges between 4.3 and 2 Ma, which was previously absent from the unadjusted record (Fig. 6). The cooling observed in the ODP Hole 806B record is less pronounced than the 6 °C cooling implied for the EEP cold tongue by the adjusted ODP Hole 847 Mg/Ca-based SST record between 4.3 and 0.8 Ma (Fig. 7). Finally, the adjusted record from the western equatorial Pacific (Medina-Elizalde and Lea, 2005) suggests a distinct cooling trend from 1.3 Ma to present that is similar to that in the eastern equatorial Pacific inferred from $U^{K'}_{37}$ records (Liu and Herbert, 2004) (Fig. 8).

Consideration of variable seawater Mg/Ca ratios over the past 5 Ma changes the interpretation of temperature and climate evolution in

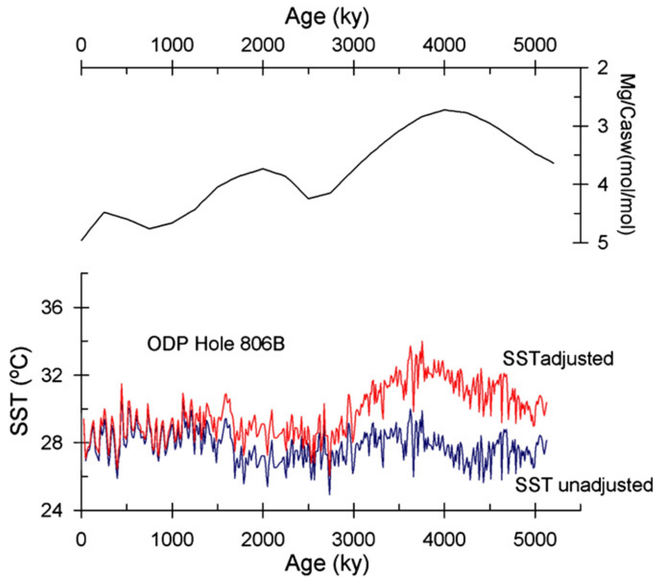

Fig. 6. ODP Hole 806B western equatorial Pacific (WEP) warm pool adjusted and unadjusted SST records spanning the last 5 Ma, based on the planktonic foraminifer *Globigerinoides sacculifer* (Wara et al., 2005). Early Pliocene SSTs suggested by the adjusted and unadjusted records are ~32 °C and ~28 °C, respectively. The adjusted SST record indicates that the WEP cooled by ~3 °C from 5 to 1 Ma. The unadjusted SST record, however, implies that SSTs of the WEP warm pool remained relatively constant (28±1 °C) during this time. FD06 seawater Mg/Ca curve is shown (top) (axis inverted).

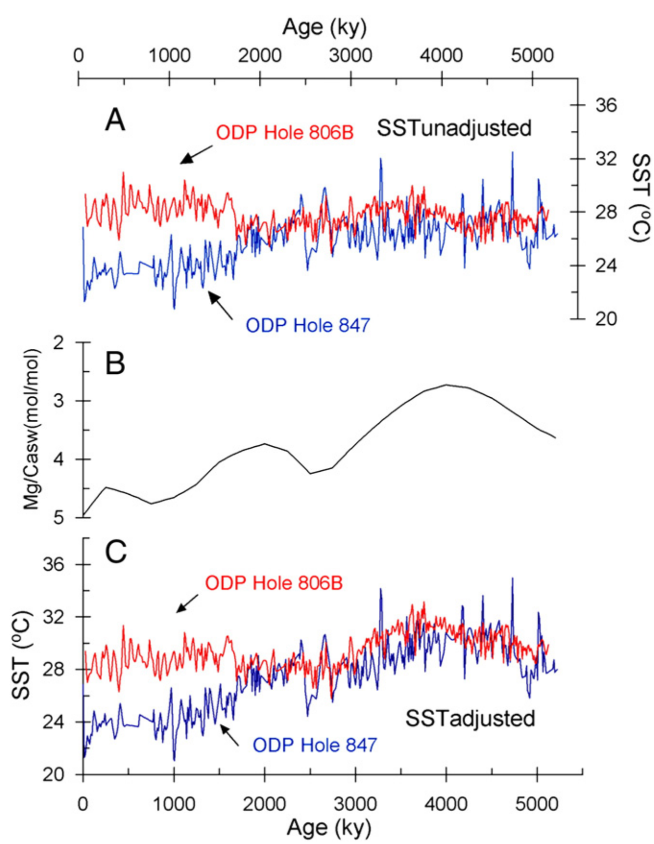

Fig. 7. (A) ODP Hole 847 EEP cold tongue (blue) and ODP Hole 806B WEP warm pool unadjusted Mg/Ca-SST records (red) based on the planktonic foraminifer *G. sacculifer* (Wara et al., 2005). (B) FD06 seawater Mg/Ca reconstruction (axis inverted). (C) ODP Hole 847 EEP cold tongue (blue) and ODP Hole 806B WEP warm pool adjusted Mg/Ca-SST records (red) based on the planktonic foraminifer *G. sacculifer* (Wara et al., 2005). Significant cooling is suggested by the adjusted SST records from 4 to 2 Ma.

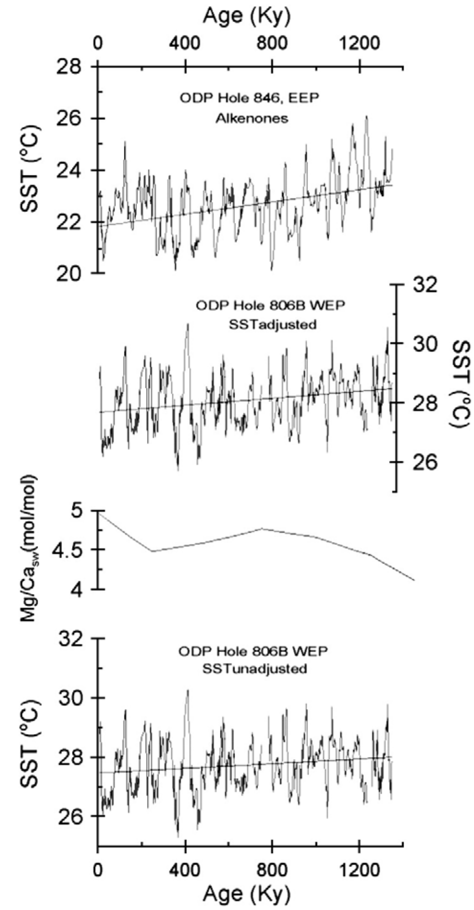

Fig. 8. EEP cold tongue and WEP warm pool SST records for the last 1.3 Ma. (A) ODP Hole 846 alkenone-based SST record (Liu and Herbert, 2004). (B) ODP Hole 806B WEP warm pool adjusted SST record based on Mg/Ca from the planktonic foraminifer *Globigerinoides ruber* (Medina-Elizalde and Lea, 2005). (C) FD06 seawater Mg/Ca reconstruction. (D) ODP Hole 806B unadjusted WEP warm pool SST record based on the planktonic foraminifer *G. ruber* (Medina-Elizalde and Lea, 2005). The adjusted WEP warm pool SST record suggests a cooling of ~1 °C similar to that implied for the EEP cold tongue by the ODP Hole 846 alkenone-SST record.

the eastern and western Pacific Ocean. Whereas the unadjusted record (constant Mg/Ca_{sw}) implies late Pliocene (after ~2.2 Ma) cooling only in the eastern equatorial Pacific, the adjusted record (variable Mg/Ca_{sw}) suggests that cooling began in the early Pliocene (~4 Ma) in both the eastern and western equatorial Pacific (Fig. 7A) (Wara et al., 2005). Another striking difference between the unadjusted and adjusted records is the overall range of temperatures observed. In the unadjusted case, temperatures in the equatorial Pacific varied between ~22 and 29 °C; in the adjusted case, temperatures ranged between ~22 and 31 °C. Maximum SSTs during the early Pliocene (~31 °C) occur at ~4 Ma in both the eastern and western equatorial Pacific, coincident with the reconstructed minimum in Mg/Ca_{sw} at this time.

3.3. Seawater $\delta^{18}O$ ($\delta^{18}O_{sw}$) variability

The use of a variable Mg/Ca_{sw} curve significantly alters the interpreted SST records of the eastern (ODP Hole 847) and western (ODP Hole 806B) equatorial Pacific. When these adjusted SST records are utilized to determine the oxygen isotopic composition of seawater ($\delta^{18}O_{sw}$) over the last 5 Ma, some noteworthy differences arise. For instance, if we assume constant Mg/Ca_{sw}, $\delta^{18}O_{sw}$ in the WEP (Wara et al., 2005) increased by 0.4‰ between 5 Ma and present, while in the EEP $\delta^{18}O_{sw}$ decreased by 0.2‰ (Fig. 9A, B). In contrast, if we assume

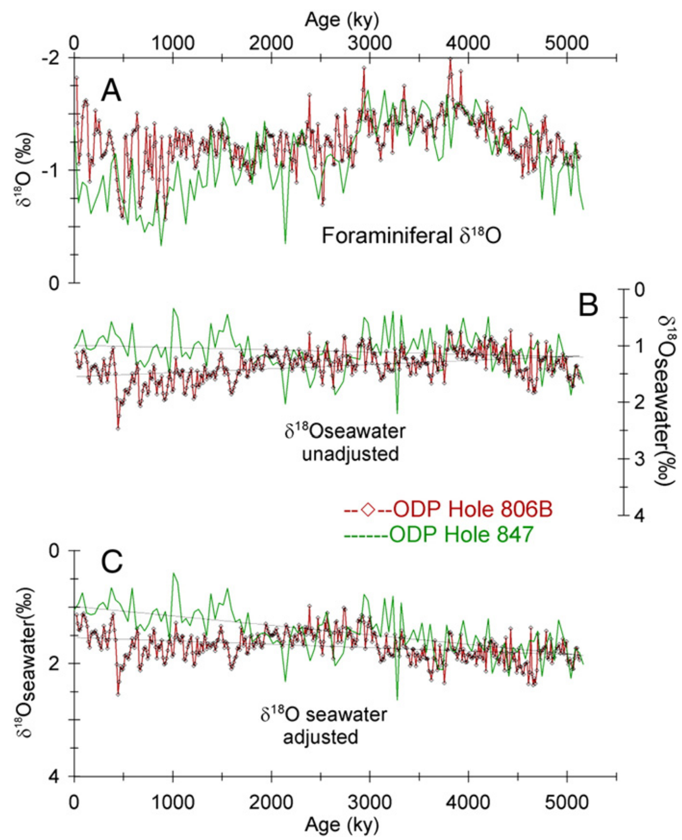

Fig. 9. (A) ODP Hole 806B WEP (red) and ODP Hole 847 EEP (green) *G. sacculifer* $\delta^{18}O$ records (Wara et al., 2005). (B) ODP Hole 806B WEP (red) and ODP Hole 847 EEP (green) seawater $\delta^{18}O$ ($\delta^{18}O_{sw}$) records based on unadjusted Mg/Ca-SSTs. (C) ODP Hole 806B WEP (red) and ODP Hole 847 EEP (green) seawater $\delta^{18}O$ ($\delta^{18}O_{sw}$) records based on adjusted Mg/Ca-SSTs. The assumption of constant Mg/Ca_{sw} suggests $\delta^{18}O_{sw}$ in the WEP increased by 0.4‰ between 5 Ma and present, while in the eastern equatorial Pacific $\delta^{18}O_{sw}$ decreased by 0.2‰. Variable seawater Mg/Ca, $\delta^{18}O_{sw}$ in the western and eastern equatorial Pacific decreased by 0.3‰ and 0.8‰, respectively, over the same time interval. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

variable seawater Mg/Ca (Wara et al., 2005), $\delta^{18}O_{sw}$ in the western and eastern equatorial Pacific decreased by 0.3‰ and 0.8‰, respectively, over the same time interval (Fig. 9C).

4. Discussion

The proposed Mg/Ca curve for seawater requires justification in order to be considered a viable alternative to the case that assumes constant Mg/Ca_{sw}. Because the overall trend of the seawater Mg/Ca curve over the past 5 Ma is dominated by changes in the Mg concentration in the ocean, it is worth focusing on this component of the changing Mg/Ca ratio. As pointed out in Fantle and DePaolo (2006), there is evidence over the past 5 Ma or so for a substantial increase in the accumulation rates of terrestrial sediments (Molnar, 2004). This increase in sedimentation is evident on a global scale, from the eastern and western Alps and the Amazon and Mississippi deltas to the Yellow River and East China Sea, and this sedimentation increase implies that erosion rates have increased globally since 5 Ma. Predicting the impact of higher erosion rates on the Mg concentration of seawater is not straightforward. It is reasonable, however, to argue that, assuming Mg removal via hydrothermal alteration occurs on a longer time scale than Mg input via weathering, the Mg/Ca ratio of seawater would be affected by a change in Mg flux to the ocean. Of course, Ca is also added via weathering, but this rationale assumes that Ca removal processes operate on time scales that are similar to, and not significantly longer than, the time scale of weathering.

What are the implications of variable seawater Mg/Ca ratios on previously-interpreted foraminiferal Mg/Ca records, when considered over the past 5 Ma? The results of our analysis indicate that: (1) the range of equatorial Pacific sea surface temperatures over the past 5 Ma may have been significantly larger (3–6 °C) than previously thought (4 °C) (Fig. 7, Table 1); (2) both the cold and the warm regions of the equatorial Pacific were warmer during the early Pliocene with SSTs of ~31 °C (Fig. 7, Table 1); (3) substantial cooling of both the eastern and western equatorial Pacific began in the early Pliocene at ~4 Ma and continued until the Late Pleistocene (Figs. 7, 8 and Table 1); (4) over the past 5 Ma, the inferred changes in the oxygen isotopic composition of the equatorial Pacific are significantly different than previously thought (Fig. 9). The previous interpretation of foraminiferal Mg/Ca suggests a thermally stable western equatorial Pacific during the Pliocene, whereas our revised interpretation indicates that a substantial cooling occurred between ~4 and 2 Ma. Which of these interpretations is correct?

First, there is some evidence that the Pliocene SST records derived from unadjusted Mg/Ca and $U^{K'}_{37}$ proxies require some degree of correction. Because ODP Sites 847 and 846 have similar mean annual SSTs (23.9 °C) and seasonal ranges of SSTs (2.4 °C) at present (Smith and Reynolds, 2004), they should record similar oceanographic conditions and temperature histories over the past 5 Ma. The temperature trends in the alkenone-SST records (Hole 847 and 846) and the unadjusted foraminiferal Mg/Ca-SST record (Hole 847), however, do not agree in detail over the Pliocene (Fig. 3). Assuming that the cooling trend (if not the actual magnitude of the cooling) indicated by the alkenone record is accurate, then it is logical to conclude that the lack of cooling in the Mg/Ca-SST record is related to some variable, such as seawater Mg/Ca, that is unaccounted for in the SST determination. In an indirect way, this argument justifies our examination of the effects of variable Mg/Ca_{sw} on interpreted SSTs. Additional support for previously unaccounted for Mg/Ca_{sw} changes in Mg/Ca-SST estimations is provided by a Pliocene North Atlantic deepwater temperature record based on the Mg/Ca content of fossil ostracodes (Dwyer et al., 1995). In contrast to the Late Pliocene long-term cooling suggested by foraminiferal $\delta^{18}O$ records of high-latitude climate, the ostracod-based North Atlantic deepwater temperature record implies no cooling at this time (Dwyer et al., 1995).

Second, the absolute SSTs determined by accounting for variable Mg/Ca_{sw} exceed the $U^{K'}_{37}$-based upper limit of SSTs by a maximum of 2 °C. If it were certain that the alkenone record was accurately recording SST, this discrepancy could be attributed to an overestimation of seawater Mg/Ca change. An alternative hypothesis is that the $U^{K'}_{37}$ index is a non-linear function of SSTs above 24 °C, as indicated by culturing, water column, and core-top field studies (Sonzogni et al., 1997; Conte et al., 1998, 2006). Plio-Pleistocene Hole 847 SSTs that account for this non-linearity in the alkenone calibration curve at high temperatures agree with the adjusted foraminiferal Mg/Ca-SSTs to within ~1 °C (Fig. 5). This ~1 °C difference can be explained by the estimated uncertainty in proxy SSTs associated with the $U^{K'}_{37}$ index and Mg/Ca paleothermometry. The potential error in $U^{K'}_{37}$-based SST estimates related to aspects of the ecology, genetics and physiology of alkenone producers and attributable to inter-laboratory differences in the data sets used in the calibration studies is ±1.3 °C (standard error) (Lawrence et al., 2007). Similarly, the uncertainty of foraminiferal Mg/Ca-based SST estimations suggested by core-top studies is ±1.2 °C (standard error) (Dekens et al., 2002).

Support for a large Pliocene to present EEP temperature range of ~6 °C is provided by SST records from higher latitude sites with modern temperatures of less than 18 °C, below the saturation temperature for the $U^{K'}_{37}$ index (Lawrence et al., 2007). $U^{K'}_{37}$-SST records from ODP Holes 1014 (California Margin, 33°N, 120°W) and 1084 (SE Atlantic margin, 26°S, 13°E), which have average annual temperatures of 15.8 °C and 16.5 °C, respectively, suggest that surface temperatures at these sites were ~8 °C warmer during the early Pliocene (Ravelo et al., 2004; Haywood et al., 2005). A desirable data set to test the hypothesis that seawater Mg/Ca ratios were much lower during the Pliocene and that, at the same time, Pliocene temperatures were globally 3 to 6 °C warmer than the present, would consist of combined Mg/Ca and $U^{K'}_{37}$-SSTs from mid-latitude sites like ODP Sites 1014 and 1084. We would predict that the SST change recorded by unadjusted Mg/Ca-based SSTs would be smaller than those recorded by the $U^{K'}_{37}$ index.

4.1. Implications of adjusted SST on the mid-Pleistocene transition (MPT)

Evidence for cooling during the mid-Pleistocene transition, as the length and intensity of the glacial cycles increased, is provided by Mg/Ca and alkenone-SST records from cold equatorial-upwelling regions (Liu and Herbert, 2004; Wara et al., 2005), and by foraminiferal $\delta^{18}O$ records reflecting high-latitude climatic processes (e.g. ice volume and bottom water temperatures) (Lisiecki and Raymo, 2005). To date, however, there has not been any evidence of cooling at low latitudes, such as in the WEP warm pool (Wara et al., 2005; Medina-Elizalde and Lea, 2005; De Garidel-Thoron et al., 2005) using paleothermometry techniques such as Mg/Ca. Previous studies of the WEP warm pool, however, did not take into account variability in seawater Mg/Ca ratios. The adjusted Mg/Ca-based SST record presented here shows a previously-unobserved and fairly pronounced cooling of ~1 °C over the MPT between 1.3 and 0.8 Ma, in agreement with previously published Pleistocene climate records (Wara et al., 2005; Liu and Herbert, 2004) (Fig. 8).

The presence of cooling in the WEP during the mid-Pleistocene transition has significant implications for the mechanisms controlling climate during this time. A variety of mechanisms proposed to explain the MPT invoke high-latitude processes (i.e. sea ice dynamics) triggered by gradual global cooling (Saltzman and Maasch, 1991; Raymo et al., 1997; Mudelsee and Schulz, 1997; Paillard, 1998; Berger et al., 1999; Huybers and Wunsch, 2005; Sigman et al., 2004) associated with a decrease in atmospheric CO_2 concentrations (Raymo et al., 1997; Mudelsee and Schulz, 1997; Paillard, 1998; Berger et al., 1999). The low latitude cooling (~1 °C) trend observed in the adjusted Mg/Ca record supports models that invoke a long-term global cooling to explain the switch in the length and intensity of the glacial cycles during the MPT (Saltzman and Maasch, 1991; Raymo et al., 1997; Mudelsee and Schulz, 1997; Paillard, 1998; Berger et al., 1999; Huybers and Wunsch, 2005). Furthermore, the synchronous and similar degree of cooling in the western and eastern equatorial Pacific over the last ~1.3 Ma supports the hypothesis that global cooling was the result of a decrease in atmospheric greenhouse forcing. If this cooling was driven by falling atmospheric CO_2, we predict that pre-MPT pCO_2 levels, were in the range 317–360 ppm (see next section for methods).

4.2. Implications of variable seawater Mg/Ca on Pliocene climate evolution

The equatorial Pacific Mg/Ca-SST records that incorporate variable seawater Mg/Ca present a new picture of low latitude Pliocene temperature evolution. The adjusted records suggest that equatorial Pacific SSTs were ~31 °C at ~4 Ma and cooled by 3.5 to 6 °C thereafter. After 1.8 Ma, the temperatures of the eastern and the western equatorial Pacific start to diverge as a result of a more rapid cooling of the eastern equatorial Pacific (Fig. 7C).

Today, seasonal variations in sea surface temperatures in the eastern and western equatorial Pacific are decoupled. The primary explanation for this decoupling is that seasonal changes in the depth of the thermocline control eastern equatorial Pacific SSTs whereas the thermocline is too deep to affect SSTs in the western equatorial Pacific (Philander and Fedorov, 2003). It has been suggested that the long-term cooling in eastern equatorial-upwelling regions from the early Pliocene to ~1 Ma was a consequence of Cenozoic global cooling (Lear et al., 2000) and a progressive shoaling of the thermocline (Philander and Fedorov, 2003). This hypothesis assumes thermal stability of the WEP warm pool over the last 5 Ma, as suggested by the unadjusted Mg/Ca-SST warm pool record (Wara et al., 2005) (Fig. 5). This mechanism, which invokes a progressive shoaling of the thermocline, is inconsistent with a simultaneous and similar degree of cooling from 5 to 2 Ma, as indicated by the equatorial Pacific records that account for variable Mg/Ca_{sw} (i.e., Fig. 8). Furthermore, equatorial Pacific cooling implied by these records occurred at a time when poleward heat transport by the Kuroshio current weakened due to the closure of the Panamanian Seaway (Motoi et al., 2005). Because the weakening of the Kuroshio current should have decreased the heat transport from the equatorial Pacific, the Pliocene cooling in the adjusted records could reflect cooling processes strong enough to overwhelm the circulation change. A likely mechanism for this cooling is a gradual reduction in radiative forcing by atmospheric greenhouse gases (Raymo et al., 1996; Haywood et al., 2005).

An interesting exercise is to use the adjusted warm pool record to calculate the level of greenhouse forcing, expressed as atmospheric CO_2 concentration, required to explain Pliocene SSTs. Modern warm pool SST at the site of Hole 806B is 29.2 °C, whereas peak reconstructed Pliocene SSTs were 32 °C. We use the following equation to relate this 3 °C temperature difference to atmospheric carbon dioxide levels:

$$[CO_2] = 280\exp(\Delta T/5.3*1/\lambda);$$

where ΔT is the temperature change relative to pre-anthropogenic conditions (°C), λ is the climate sensitivity factor (°C per W/m^2), 280 is the pre-anthropogenic concentration of atmospheric CO_2 (ppm) and 5.3 is the radiative forcing term (Hansen et al., 2005). In our calculations, we consider a range of climate sensitivity factors (λ=0.75, 1.3 and 1.5 °C per W/m^2) (Lea, 2004; Hansen et al., 2005) that reflect the range from fast climate feedbacks only (the so-called Charney sensitivity (Hansen et al., 2007)) to those that include slow geological feedbacks such as ice sheet and surface albedo changes. For λ=0.75, 1.3 and °C per W/m^2, we estimate Pliocene atmospheric CO_2 concentrations to have been 595, 432 and 408 ppm, respectively (Fig. 10). For comparison, current estimates of Pliocene pCO_2 vary between ~250 ppm (Pearson and Palmer, 2000) and 420 ppm (Van Der Burgh et al., 1993; Raymo et al.,

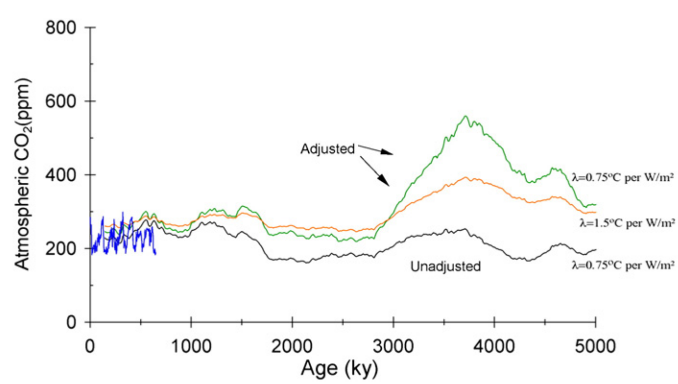

Fig. 10. Atmospheric CO_2 reconstructions back to 5 Ma based on western equatorial Pacific ODP 806B adjusted and unadjusted Mg/Ca-SST records (Wara et al., 2005) and on climate sensitivity factors that reflect fast climate feedbacks (λ=0.75 °C per W/m^2) and slow geological feedbacks (λ=1.5 °C per W/m^2) (Lea, 2004; Hansen et al., 2005). These records were calculated using running average mean SSTs with a window of ~250 ky. Western equatorial Pacific SSTs are assumed to be at equilibrium with mean global air surface temperatures. Estimated atmospheric CO_2 concentrations at 4 Ma based on adjusted SSTs and λ of 0.75 (green curve) and 1.5 °C per W/m^2 (orange), are 595 and 408 ppm, respectively. Estimated atmospheric CO_2 based on unadjusted SSTs and λ of 1.5 °C per W/m^2 is ~247 ppm (black curve). Antarctic Epica Dome Concordia and Vostok atmospheric CO_2 record back to 650 ky is shown for comparison (blue) (Siegenthaler et al., 2005). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

1996). The highest calculated value, based on fast feedbacks only, may be somewhat unrealistic because it does not include the long time scale geological feedbacks that would amplify the Plio-Pleistocene cooling driven by a reduction in greenhouse gas forcing. The two lower values, however, overlap with previously published estimates of Pliocene pCO_2. The critical point of this analysis is that the temperature range that we calculate using a variable seawater Mg/Ca curve is not unrealistic, when considered in the context of Pliocene pCO_2 estimates.

4.3. Equatorial Pacific hydrological changes suggested by adjusted Mg/Ca-SSTs

The seawater $\delta^{18}O$ ($\delta^{18}O_{sw}$) records of the last 5 Ma, based on adjusted SSTs from ODP Sites 806B and 847, become progressively more negative by 0.55–1‰ over the Plio-Pleistocene (Fig. 9). This change takes into account a positive shift of ~0.25‰ caused by the expansion of the northern hemisphere ice sheets (Fairbanks, 1989; Miller et al., 2005). On the basis of modern $\delta^{18}O$-salinity relationships (LeGrande and Schmidt, 2006), the 0.55 to 1.0‰ decrease in equatorial Pacific $\delta^{18}O_{sw}$, reflects an estimated surface salinity reduction of ~2–4 salinity units (p.s.u) from the early Pliocene to present. Is there any independent evidence that supports a progressive freshening of the equatorial Pacific during the Pliocene?

Using foraminiferal $\delta^{18}O$ records from the Atlantic/Caribbean and the east Pacific regions, Steph et al. (2006) inferred that the progressive closure of the Panamanian Gateway restricted surface water exchange between the Caribbean and the east Pacific Ocean. As a result, the input of low-salinity Pacific water masses into the Caribbean was reduced, potentially causing a decrease in surface salinity in the Pacific with respect to the Caribbean. The resulting salinity gradient between these two regions would be enhanced by the net atmospheric transport of water vapor from the Atlantic/Caribbean into the Pacific, which increased surface salinities in the Caribbean and decreased surface salinity in the tropical east Pacific (Broecker and Denton, 1989). These two mechanisms, which contributed to the modern salinity contrast between the Atlantic/Caribbean and the east Pacific, could also explain the Pliocene freshening of the equatorial Pacific as implied by the adjusted $\delta^{18}O_{sw}$ records. It is uncertain, however, whether such changes could account for the magnitude of freshening suggested by the reinterpreted $\delta^{18}O_{sw}$ record.

4.4. The Pliocene paradox

The alkenone-SST and unadjusted foraminiferal Mg/Ca-SST records indicate that the east–west equatorial Pacific SST gradient was reduced during the early Pliocene, resembling a permanent El Niño (Ravelo et al., 2004; Wara et al., 2005) (Fig. 8). This permanent El Niño could have contributed to Pliocene warmth by eliminating stratus clouds, subsequently reducing albedo and increasing atmospheric water vapor (Fedorov et al., 2006). The minimal equatorial Pacific zonal SST gradient suggested by these records, however, cannot explain Pliocene warmth at high latitudes, as indicated by atmospheric and general circulation models (GCM) (Winton, 2003; Haywood and Valdes, 2004; Haywood et al., 2007). The minimal early Pliocene zonal SST gradient is primarily due to warmer SSTs in the eastern equatorial Pacific and very similar to present SSTs in the western equatorial Pacific, as recorded by the unadjusted records. To maintain early Pliocene warmth at high latitudes with significantly warmer SSTs in the EEP, as suggested by the alkenone unsaturation index, climate models require the WEP warm pool SSTs exceed 30 °C. But an increase in WEP SST >30 °C would eliminate the permanent El Niño (Fedorov et al., 2006). Given this paradox, how do we explain early Pliocene warmth at both high and low latitudes?

The SST records calculated using variable Mg/Ca_{sw} imply that the entire equatorial Pacific was warmer than 30 °C during the early Pliocene (Fig. 7C). Elevated atmospheric greenhouse gases and their associated feedbacks (Hansen et al., 1984; Soden and Held, 2006) could have maintained both low and high-latitude warmth, with a reduced east–west equatorial SST gradient. Recent modeling experiments for the mid-Pliocene using the HadCM3 GCM with specified pCO_2 at 400 and 560 ppmv suggest that WEP SSTs could have been 31–33 °C and EEP SSTs could have been 29–31 °C, in good agreement with the adjusted Mg/Ca-SST records (A. Haywood, Univ. of Leeds, UK, 2007, pers. comm.). In addition to greenhouse forcing, climate feedbacks related to a permanent El Niño may have also played an important role in the warmth of the early Pliocene (Fedorov et al., 2006).

5. Conclusions

Available paleoclimate SST records based on foraminiferal Mg/Ca assume that seawater Mg/Ca ratios have remained unchanged. Recent investigations have shown that Ca and Mg concentrations in the ocean may vary significantly over million-year time scales (Fantle and DePaolo, 2006). We used previously published high resolution records of Mg and Ca concentrations in the ocean (Fantle and DePaolo, 2006) to reinterpret available equatorial Pacific foraminiferal Mg/Ca-SST records of the last 5 Ma.

Equatorial Pacific Sea surface temperature records based on foraminiferal Mg/Ca and assuming constant seawater Mg/Ca ratios suggest that Pliocene western equatorial Pacific warm pool SSTs were similar to today and that eastern equatorial Pacific cold tongue SSTs were significantly warmer. When these records are reinterpreted assuming variable seawater Mg/Ca ratios (Fantle and DePaolo, 2006), a different picture emerges: both the cold and the warm regions of the equatorial Pacific were warmer during the early Pliocene (30–31 °C), and both regions experienced a marked cooling from the Pliocene to present. The new interpretation of foraminiferal Mg/Ca creates a discrepancy with alkenone-based SST records from the eastern equatorial Pacific which can be resolved by utilizing a shallow response curve for alkenone unsaturation in warm tropical waters.

The adjusted SST records are consistent with the hypothesis that higher levels of greenhouse gases, in combination with El Niño feedbacks, maintained the warmth of the early Pliocene. Consequently, these records imply that the Pliocene cooling was at least partly driven by a drop in the atmospheric concentration of greenhouse gases. Given how these adjustments affect interpretation of Plio-Pleistocene climate evolution, it is imperative that the Fantle and DePaolo (2006) results for seawater Mg/Ca evolution be independently reproduced in other sites and/or verified using alternative approaches. A seawater Mg/Ca curve with improved time resolution is also an important target. Lastly, it is essential to better constrain the influence of solution Mg/Ca on the partition coefficient of foraminiferal Mg/Ca.

Acknowledgments

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