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Chemical Geology 161 (1999) 215–224

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

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Effects of diagenesis on the isotopic record of late paleogene tropical sea surface temperatures

Daniel P. Schrag *

Laboratory for Geochemical Oceanography, Department of Earth and Planetary Sciences, Harvard University, 20 Oxford St., Cambridge, MA 02138, USA

Received 14 October 1997; accepted 27 November 1998

Abstract

Oxygen isotope records of planktonic foraminifera indicate that Late Eocene and Oligocene tropical sea surface temperatures were as much as 8°C lower than present at a time when high latitude sea surface temperatures were higher than present. Using a numerical model which describes oxygen isotope exchange during burial and recrystallization of deep sea carbonate, the effects of diagenesis on bulk carbonate $\delta^{18}O$ records for the Cenozoic are quantified for four tropical sites. Most of the observed variations in measured $\delta^{18}O$ values at all sites can be accounted for by diagenetic effects. There are no systematic trends that support substantial variations in tropical sea surface temperatures beyond diagenetic effects, with the possible exception of the Early Eocene for which the data are consistent with slightly higher sea surface temperatures. Reconstructions based on oxygen isotope records of planktonic foraminifera which indicate cooler tropical sea surface temperatures for the Eocene and Oligocene may be artifacts of diagenetic recrystallization as such records are particularly sensitive to diagenetic effects. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Diagenesis; Cenozoic; Late paleogene

1. Introduction

Sea surface temperature reconstructions based on oxygen isotope measurements of planktonic foraminifera indicate that high latitude surface oceans cooled by over 10°C from the Early Paleogene to the present (Shackleton and Kennett, 1975; Stott et al., 1989). The occurrence of fossil remains of warm dwelling plants and animals at high latitudes gives additional evidence for this dramatic Cenozoic climate change (Wolfe, 1980; Estes and Hutchison, 1980). However, oxygen isotope reconstructions of sea surface temperatures from low latitudes paint a very different picture of the evolution of Cenozoic climate. A reconstruction by Savin (1977) indicates that tropical oceans in the early Cenozoic were about as warm as modern tropical oceans, but then cooled by as much as 8°C through the Oligocene, followed by gradual warming in the Miocene. This interpretation is supported by isotopic studies of Early Eocene foraminifer (Shackleton and Boersma, 1981) and Late Eocene and Early Oligocene foraminifera (Keigwin and Corliss, 1986; Zachos et al., 1994, Zachos et al., this volume).

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* Tel.: +1-617-495-7676; fax: +1-617-495-8839; e-mail: schrag@eps.harvard.edu

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PII: S0009-2541(99)00088-1

Researchers have questioned whether oxygen isotope records for low latitude oceans accurately depict the history of tropical sea surface temperatures (Killingley, 1983; Schrag et al., 1995). The enigma arises from having lower tropical sea surface temperatures in the Eocene and Oligocene at the same time when high latitude sea surface temperatures and deep ocean temperatures were significantly higher than today. General circulation models predict that elevated atmospheric CO_2, which has been proposed as the cause of the Eocene warm climate at high latitudes (e.g., Berner et al., 1983), would result in higher tropical sea surface temperatures, not lower ones (Manabe and Bryan, 1985). Barron (1987) points out that if the isotopic paleotemperatures are correct, the globally averaged Eocene sea surface temperature was only a few degrees higher than today, and does not require an external forcing mechanism, such as increased concentrations of CO_2 in the atmosphere. Barron suggests that the distribution of Eocene sea surface temperatures could be accomplished by internal heat redistribution, such as increased poleward heat transport by the oceans. Others have argued that increased poleward heat transport by the oceans cannot account for the Eocene configuration of sea surface temperatures calculated from oxygen isotopes, specifically the lower temperatures at the equator. Crowley (1991) explores the possibility that production of warm saline bottom water (WSBW) in the subtropics could produce cooler temperatures at the equator, concluding that the required magnitude of WSBW production is on the outer limit of realistic values. Using an energy balance model, Horrell (1990) also concludes that increased poleward heat transport by the oceans cannot account for cool tropical sea surface temperatures. In a more recent discussion, Sloan et al. (1995) also argue that heat transport by the oceans is an unlikely explanation for Eocene climate. All of these studies, including that of Barron (1987), conclude that solving the problem requires reinterpretation of one of the major sources of information.

One explanation proposed by Zachos et al. (1994) is that the oxygen isotope data giving relatively low tropical sea surface temperatures are robust, but that data come from sites located in past upwelling zones. They point out that plate reconstructions place four of the five sites from which they have data in likely zones of upwelling. While their explanation is certainly plausible, this paper explores the possibility that the apparent paradox in Late Paleogene climate comes from a systematic bias in the isotopic paleotemperatures for low latitudes due to diagenesis of the carbonate microfossils. The oxygen isotopic composition of carbonate formed in warm tropical surface oceans is particularly sensitive to diagenetic modification because the original $\delta^{18}O$ value is several per mil lower than the $\delta^{18}O$ value of secondary calcite that precipitates during early diagenesis in equilibrium with cold pore fluids near the sediment–water interface. Recrystallization during early diagenesis will increase the $\delta^{18}O$ value, yielding a lower apparent temperature. This is not the case for calcite that formed in high latitude surface oceans or in the deep ocean because the original $\delta^{18}O$ values are in or close to isotopic equilibrium with cold bottom water.

The objective of this study is to determine whether diagenesis can explain the anomalously low tropical sea surface temperatures obtained for the Late Paleogene. I use numerical models to evaluate the contribution of diagenesis to the $\delta^{18}O$ record of bulk carbonate sediment from tropical sites, following the methods of Schrag et al. (1992, 1995). The approach is to test the null hypothesis that sea surface temperatures in the tropics were constant through time. For each site, a calculation is performed to determine the $\delta^{18}O$ of bulk carbonate following diagenetic recrystallization assuming that the original $\delta^{18}O$ values reflected constant sea surface temperatures. These model calculations are then compared with measured $\delta^{18}O$ values of bulk carbonate to evaluate how much of the observed variation can be explained by diagenesis. Systematic offsets from model-calculated compositions are likely to reflect true changes in sea surface temperature or isotopic composition.

Bulk carbonate is considered in these calculations rather than foraminiferal carbonate because recrystallization rates for bulk carbonate sediment can be determined independently from strontium exchange between bulk carbonate and pore fluids (Richter and DePaolo, 1987, 1988; Richter and Liang, 1993). This approach cannot be applied to foraminiferal oxygen isotope records directly because it is difficult to determine the recrystallization rate of foraminiferal calcite. While the vast majority of researchers since

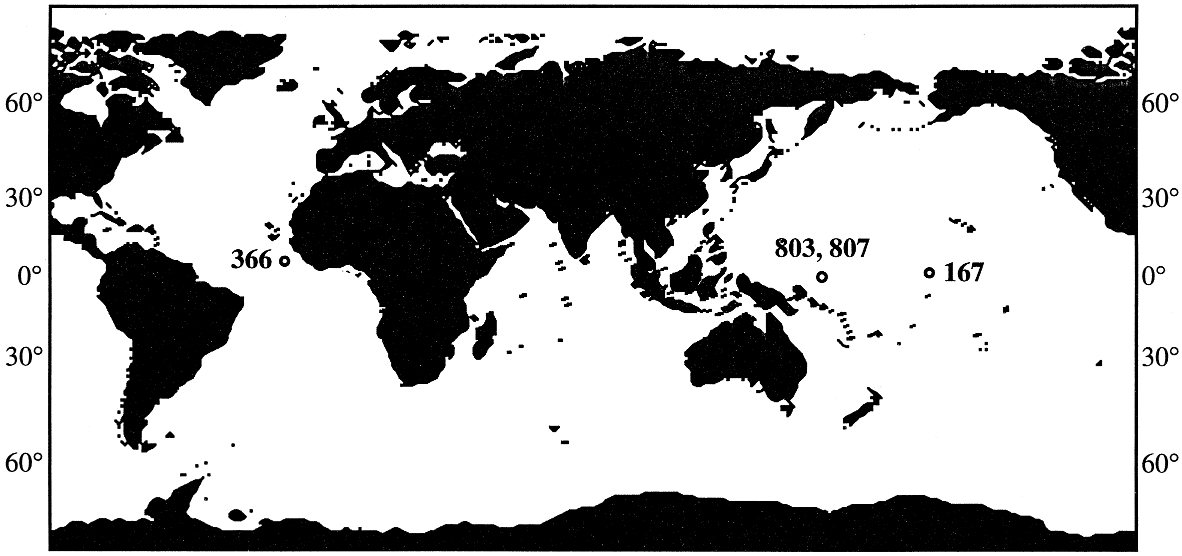

Fig. 1. Location map for DSDP and ODP Sites discussed in this study.

the work of Emiliani (1955) have relied exclusively on measurements of foraminifera tests for paleoceanographic analysis, several studies have shown that $\delta^{18}O$ values of coccoliths, which constitute most of the mass of bulk carbonate, vary with temperature in a manner similar to variations in $\delta^{18}O$ values of foraminiferal calcite (Dudley and Goodney, 1979; Goodney et al., 1980; Shackleton et al., 1993), although the absolute $\delta^{18}O$ value of bulk carbonate may be higher than that of planktonic foraminifera by 1–2‰, probably due to vital effects in the photosynthetic coccolithophorids. A major concern is that changes in the $\delta^{18}O$ of the bulk carbonate may be due to changes in composition of the bulk assemblage (i.e., the relative amounts of coccoliths and foraminifera) or changes in vital effects of the coccolithophorids, and not due to variations in sea surface temperature. This was examined by Schrag et al. (1995) by comparing bulk carbonate and planktonic foraminiferal $\delta^{18}O$ records for the Pleistocene (ODP Site 677A) and for the Paleogene (ODP Site 690) from sites where diagenetic effects were determined to be negligible. In both cases, the bulk carbonate records tracked the foraminiferal records, suggesting that if changes in vital effects of coccolithophorids or relative abundance of foraminifera and coccoliths do affect the bulk $\delta^{18}O$ records, they are of secondary importance, and that the bulk $\delta^{18}O$ records are adequate for estimating large scale changes in sea surface temperature, at least at sites with high carbonate content where coccolithophorids are much more abundant than foraminifera.

Schrag et al. (1995) compared results from diagenetic models with data from several Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) sites, including two tropical sites, 366 in the Eastern Atlantic, and 807 on the Ontong Java Plateau in the Western Pacific. In this paper, the data from Sites 366 and 807 are re-examined along with new data from Site 803 on the Ontong Java Plateau, and Site 167 in the Central Pacific where Douglas and Savin (1973) first produced a record of low latitude sea surface temperatures for the Cenozoic (see location map, Fig. 1). While the general approach is very similar to Schrag et al. (1995), the specific focus of this study is the mystery surrounding oxygen isotope records of cold tropics during warm climate episodes.

2. Methods

2.1. Analytical procedures

Isotopic data for bulk carbonates from DSDP Site 167 and ODP Site 803 were collected at the Berkeley Center for Isotope Geochemistry using a VG

Prism gas source mass spectrometer. For each sample, approximately 2 mg of bulk sediment was loaded into a stainless steel capsule and placed in a drying oven for 48 h at 50°C. Samples were then loaded into a VG Autocarb carousel with a common acid bath, and reacted in orthophosphoric acid at 90°C. The standard deviation (1σ) of measurements of standard calcite (Harvard University Carrara marble standard calibrated against NBS-19) spaced throughout each run averages 0.04‰ for $\delta^{18}O$. Reproducibility of bulk analyses given by the average difference between 25 pairs of replicate analyses is 0.06‰. Data are available from the author by request.

2.2. Numerical modeling

Model calculations described here simulate oxygen isotope exchange during deposition and compaction of sediment on the sea floor, and are identical to those described by Schrag et al. (1995). The critical parameters in the calculation for each site are sedimentation rate, porosity, recrystallization rate and temperature gradient. Sedimentation rates and porosities were taken from initial reports of the DSDP and ODP cruises. Following Richter and DePaolo (1987, 1988), recrystallization rate–age relationships are of the form $R = \alpha + \beta e^{-t/\gamma}$. Values of α, β and γ used for each site are listed in Table 1. For Sites 366, 803 and 807, β and γ were calculated from strontium concentration profiles of pore fluids (Couture et al., 1977; Kroenke et al., 1991), assuming that measured profiles are in steady state and transport is dominated by diffusion. This is a simplification of the approach taken by Richter and DePaolo (1987, 1988), but is accurate within their stated uncertainty of a factor of two. Because no strontium isotopic data of pore fluids are available for these sites, calculations use $\alpha = 0.005$, a value in the upper range of those calculated by Richter and Liang (1993). For Site 366, an identical calculation was performed for $\alpha = 0.01$. For Site 167, strontium data on pore fluids are not available so a recrystallization rate based on Site 366 was used. Vertical temperature gradients in the sediment column are estimated from global compilations of oceanic heat flow data (Louden, 1989). For Site 366, which sits on lower Paleocene ‘‘normal’’ oceanic crust, the temperature gradient is set initially at 60° km^{-1} and decreases linearly to 40° km^{-1} by the end of the run. For Site 167, which sits on Middle Cretaceous crust, the temperature gradient is set initially at 45° km^{-1} and decreases to 25° km^{-1} by the end of the run. For the Ontong Java sites, which sit on 120 Ma oceanic flood basalt, a lower gradient was applied, initially 35° km^{-1} decreasing to 25° km^{-1} by the end of the run.

Table 1
Recrystallization rate constants used in model calculations. The recrystallization rate (R) is of the form $R = \alpha + \beta e^{-t/\gamma}$ where t is time in millions of years, following on the formulation by Richter and Liang (1993)

Site	α	β	γ
167	0.005	0.06	6
366	0.005, 0.01	0.06	6
803	0.005	0.07	8
807	0.005	0.07	9

The model allows the $\delta^{18}O$ of seawater and the temperature of the deep ocean to change with time. These changes are calculated by partitioning the $\delta^{18}O$ curve for benthic foraminifera from Miller et al. (1987) into temperature and $\delta^{18}O_{seawater}$ components based on estimates of the impact of continental ice on seawater $\delta^{18}O$ by Shackleton and Kennett (1975), as described in (Schrag et al., 1995). The exact shape of the $\delta^{18}O_{seawater}$ curve is uncertain, but model runs using slightly different curves for $\delta^{18}O_{seawater}$ show that, within reasonable bounds, the choice does not affect significantly the calculations described here. As an input to the model, the isotopic composition of the carbonate sediment is set in equilibrium with the model $\delta^{18}O_{seawater}$ at constant temperature. Slight differences in $\delta^{18}O$ values of modern bulk carbonate between sites, which reflect true variability in sea surface temperature in the modern ocean, were accommodated in the initial composition by constant offsets. The outputs from the model calculations therefore simulate what the $\delta^{18}O$ values of diagenetically altered bulk carbonate would be if tropical sea surface temperature were constant through time. Deviations of the measured $\delta^{18}O$ values from those predicted by the model are then interpreted as possible variations in sea surface temperature.

3. Results

Measured $\delta^{18}O$ values plotted against depth and age are compared in Fig. 2. At all sites, $\delta^{18}O$ values increase initially, reaching maximum $\delta^{18}O$ values in sediment between 10 and 20 Ma. The $\delta^{18}O$ values of older, more deeply buried sediment decrease with age; steepest $\delta^{18}O$ gradients exist at Site 366 where $\delta^{18}O$ values reach −4.5‰ in 55 Ma old sediment at 800 m depth. At both Ontong Java Plateau sites (803 and 807) and Site 167, $\delta^{18}O$ values decrease slowly after the initial increase.

Model results are compared with measured $\delta^{18}O$ values in Fig. 3. For the Ontong Java Plateau sites (803, 807), the increase in $\delta^{18}O$ values during early recrystallization creates a shift of nearly 2‰ to higher $\delta^{18}O$ values in 10 to 20 Ma sediment. The relatively low geothermal gradient used in the calculations produces a slow decrease in $\delta^{18}O$ values with depth and age, matching the measured records. Measured values deviate, in general, less than 0.5‰ from the model-calculated curves, with the exception of sediment older than 50 Ma at Site 807 for which $\delta^{18}O$ values are consistently lower than the model-calculated curve.

At Site 366, where a higher temperature gradient was used, the increase during initial recrystallization is not as great — only 1.5‰ higher than the initial $\delta^{18}O$ value for 10 to 20 Ma sediment. As discussed by Schrag et al. (1995), one prominent feature of the measured record at Site 366 is perfectly reproduced by the model. In the measured record, a change in slope occurs in the $\delta^{18}O$ vs. age curve at 44 Ma. This change in slope also exists in both model curves despite the initial $\delta^{18}O$ value of carbonate used as an input to the model remaining constant through this age range. The source of this change in slope is a change in sedimentation rate, from 27 m/Ma before 44 Ma, to 9 m/Ma after 44 Ma. Sediment deposited before the change in sedimentation rate is buried rapidly so that recrystallization during early diagenesis occurs at a higher average temperature. Sediment

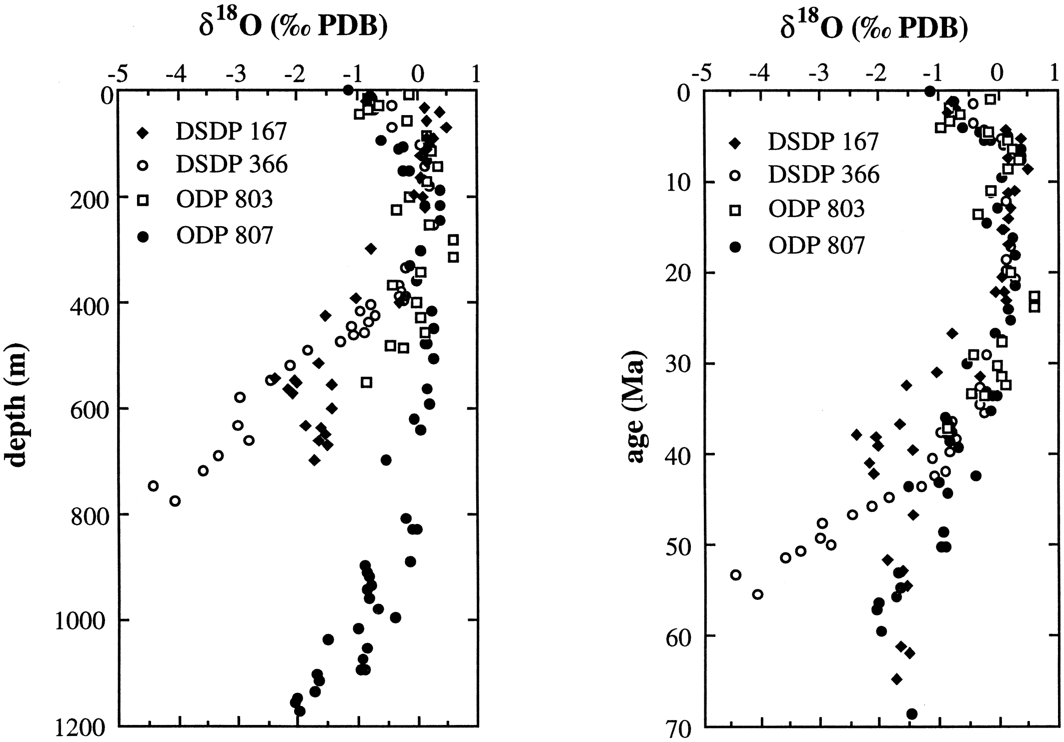

Fig. 2. Bulk carbonate oxygen isotope data for DSDP Site 366 and ODP Site 807 [data from Schrag et al., 1995] and DSDP Site 167 and ODP Site [this study], plotted against sediment age and burial depth.

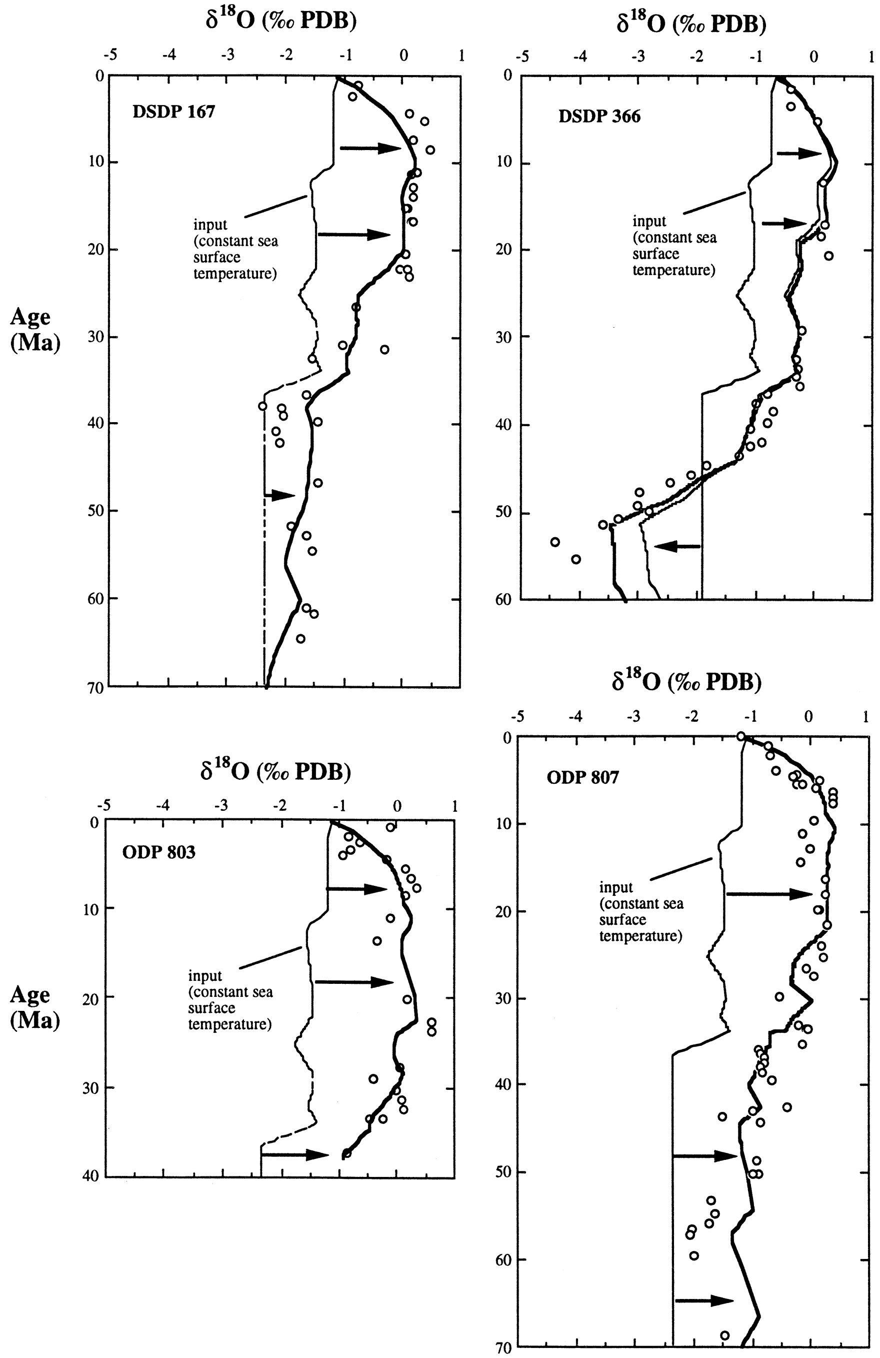

Fig. 3. Comparison of measured $\delta^{18}O$ values and model calculated values for sites 167, 366, 803 and 807 assuming that sea surface temperatures were constant through time. Two calculations are shown for site 366 using two different recrystallization rates (thin line: $\alpha = 0.005$; heavy line: $\alpha = 0.01$). Arrows indicate direction of diagenetic shifts.

deposited after the change is buried less rapidly so that early recrystallization takes place at lower temperatures resulting in more positive shifts in $\delta^{18}O$ values. The two recrystallization rates used in the model calculations ($\alpha = 0.005$, 0.01) give nearly identical results over most of the record; only in the oldest 10 Ma of the record do the two calculations diverge, with the higher rate yielding more negative $\delta^{18}O$ values. Measured $\delta^{18}O$ values are within 0.5‰ of the model-calculated curves, except for sediment older than 50 Ma where values are consistently lighter than both model-calculated curves.

At Site 167, the profile is similar to the Ontong Java sites. The effects of the slightly higher temperature gradient used in the calculations is offset by the lower sedimentation rate relative to Site 807. Again, the model curve does an excellent job of fitting the measured $\delta^{18}O$ values. Largest deviations at this site occur in sediment between 38 and 45 Ma, where measured $\delta^{18}O$ values are slightly lower than the model-calculated curve.

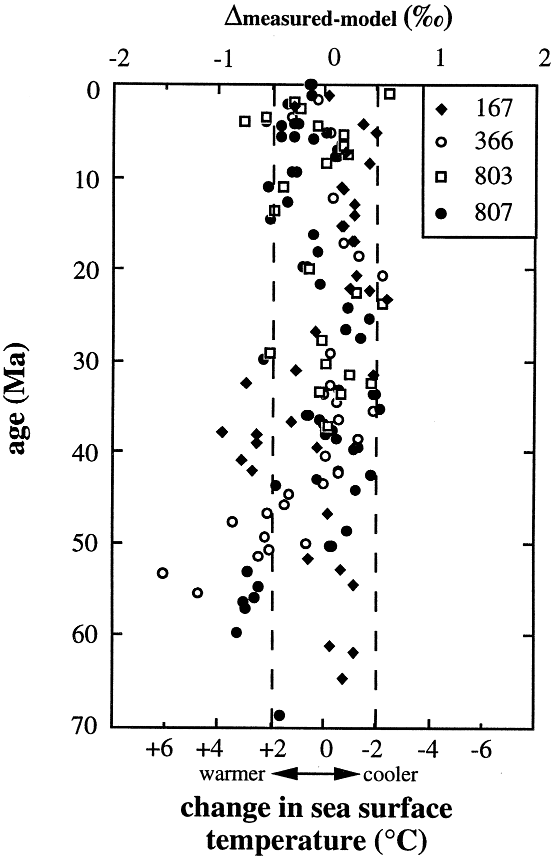

Fig. 4. Differences between measured $\delta^{18}O$ values of bulk carbonate and model-calculated $\delta^{18}O$ values for partially recrystallized carbonate assuming no change in sea surface temperature with time. The bottom scale assumes that differences are due to changes in sea surface temperature.

Fig. 4 shows the difference between measured $\delta^{18}O$ values and model-calculated values for all four sites, assuming constant sea surface temperature. Deviations likely reflect primary variability in the temperature and isotopic composition of the ocean; the scale on the bottom of Fig. 4 assumes that the deviations are due only to changes in temperature and not to differences from the model $\delta^{18}O_{seawater}$ curve. In general, the data scatter evenly between +0.5‰ and −0.5‰. This corresponds to less than ±2°C change in average tropical sea surface temperature through most of the Cenozoic. For Eocene sediment, measured $\delta^{18}O$ values are in general lighter than model-calculated ones, indicating that tropical sea surface temperatures were 2°–6°C higher than average during this time. No evidence from the bulk carbonate oxygen isotope records indicate that tropical sea surface temperatures were more than 2°C lower than today during anytime in the Cenozoic.

4. Discussion

4.1. Uncertainty in model calculations

The largest source of uncertainty in the model calculations is the recrystallization rate of the bulk carbonate. The approach employed here, to use the strontium concentration of pore fluid to obtain recrystallization rates as a function of age of bulk carbonate, describes how sediments are behaving today, and is probably accurate to within a factor of two (Richter and DePaolo, 1987, 1988; Richter and Liang, 1993). In addition, there is an implicit assumption that the recrystallization rate–age relationship measured today has not changed through time. Overall, this uncertainty results in an error in the calculated curves of approximately ±1‰. While this magnitude of error limits the ability to discriminate subtle changes in sea surface temperature by correcting the bulk carbonate records for diagenetic overprinting at any one site, the lack of any systematic deviation from the model calculated curves for all four sites with the exception of the Early Eocene (Fig. 4) is consistent with sea surface temperatures in the tropics being constant over most of the Cenozoic.

4.2. Comparison with results of previous studies

The lack of any apparent cooling in tropical sea surface temperature is inconsistent with the foraminiferal oxygen isotope records of the Eocene and Oligocene for which diagenetic effects remain undetermined (e.g., Zachos et al., 1994, Zachos et al., this volume). Note that this interpretation applies only to the long term evolution of sea surface temperatures in the Cenozoic, and is not relevant to debates concerning the magnitude of glacial to interglacial sea surface temperature fluctuations in the Pleistocene (Guilderson et al., 1994). The only evidence of systematic temperature change in the bulk carbonate records is in the Early Eocene. The warming of equatorial surface waters in the Early Eocene occurred when deep ocean and high latitude surface ocean temperatures reached maximum values for the Cenozoic (Miller et al., 1987; Stott et al., 1989). This result is consistent with the hypothesis that CO_2-induced greenhouse warming was the cause of warm Eocene climate (Freeman and Hayes, 1992; Berner et al., 1983), supported by GCM results predicting slightly higher sea surface temperatures near the equator at times when atmospheric CO_2 concentrations are high (Manabe and Bryan, 1985). If correct, this result eliminates the need to explain the warming in the Early Eocene with internal heat redistribution, as discussed by Barron (1987).

4.3. Do bulk carbonate records resolve the early paleogene climate enigma?

The modeling results emphasize the importance of diagenetic effects on δ^{18}O records from low latitude sites. At all sites studied, most of the variability in δ^{18}O values can be explained by diagenetic effects. For example, at Site 366, the total variation in the primary δ^{18}O record used as an input is less than 1.4‰, but model-simulated recrystallization produces variations of over 4‰. In particular, the initial increase in δ^{18}O values during early diagenesis is relevant to the apparent cold tropical sea surface temperatures for the Early Paleogene. If such shifts also apply to foraminiferal calcite, and were interpreted mistakenly as part of the primary signal, sea surface temperature reconstructions could be biased by as much as 8°C.

An important question is whether the results from bulk carbonate studies are relevant to isotope records produced from planktonic foraminifera. The crucial issue here is the recrystallization rate of foraminiferal calcite. If the recrystallization that occurs in the bulk carbonate affects similarly foraminifera tests either by overgrowth or by replacement of shell walls, the primary δ^{18}O value will also be affected. The resulting signal would be similar to the model curves described here (Fig. 3) which match the general shape of foraminiferal δ^{18}O records from low latitude sites with high δ^{18}O values in the Late Eocene through Early Miocene.

Most paleoceanographic studies that use foraminiferal isotope data select the best preserved foraminifera tests available. The claim is made that the selection process distinguishes primary from secondary calcite. However, this selection process usually involves inspection with a binocular microscope which may be inadequate to identify secondary calcite. Studies of test morphology using scanning electron microscopy illustrate how secondary calcite can precipitate on the insides of shells, or, even worse, can replace primary shell structures with little or no change in morphology (van der Lingen and Packham, 1975; Barrera et al., 1987). Some studies of foraminiferal oxygen isotope records seek to minimize the impact of diagenesis by selecting sites that are shallowly buried (Zachos et al., 1994). However, low latitude sites with low sedimentation rates may be equally susceptible to diagenetic effects causing oxygen isotope shifts which bias the temperature reconstructions toward lower apparent sea surface temperatures. Although the shallow burial depth may result in better preservation (i.e., lower recrystallization rate), the low sedimentation rate means that the δ^{18}O value of secondary calcite remains high relative to the primary value throughout the burial process. Without knowing the relative importance of these two effects, it is impossible to dismiss the possible impact of diagenesis on the planktonic foraminiferal isotope records.

One clue as to the relative rate of recrystallization of foraminiferal calcite comes from an investigation of how fossil preservation varies with latitude between sites on DSDP Leg 90. Nelson (1986) attributed the higher recrystallization observed at low latitude sites to the high abundance of discoasters and sphenoliths which provide ideal nucleation sites for calcite overgrowths. If this is correct, and secondary calcite precipitates preferentially on carbonate particles other than foraminifera tests, then the effective recrystallization rate of foraminiferal calcite should be slower than that for bulk carbonate, at least early in the diagenetic process when the difference between the $\delta^{18}O$ values of primary and secondary calcite are largest. However, even if the recrystallization rate is half of the rate for bulk carbonate, the effects of diagenesis on low latitude planktonic foraminifera will be significant. Because the potential for systematic bias is so large, accurate reconstruction of tropical sea surface temperatures of the Paleogene, whether from planktonic foraminiferal or from bulk carbonate oxygen isotope records, requires explicitly accounting for diagenetic effects.

5. Conclusions

The oxygen isotopic compositions of bulk carbonate from low latitude ODP and DSDP Sites show no systematic deviation from what would be expected if the calcite had formed at a constant sea surface temperature through the Cenozoic and then was altered during diagenesis, with the exception of sediment of Paleocene and Early Eocene age. Oxygen isotope values of bulk carbonate of this age are consistent with slightly higher sea surface temperatures than modern. While the uncertainty on these calculations is on the order of 1‰ (or 4°C), the model emphasizes the significance of diagenetic effects for all low latitude sites, biasing temperature reconstructions for surface waters in the Late Paleogene and early Neogene toward lower values. Such effects are one possible cause of the cold tropical sea surface temperatures during the Late Paleogene inferred from planktonic foraminiferal oxygen isotope records.

Acknowledgements

The author thanks Don DePaolo and Frank Richter for their advice and support. The paper was improved greatly by reviews from Jim Zachos and Isabel Montañez.

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