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Reconstructing past sea surface temperatures: Correcting for diagenesis of bulk marine carbonate

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Abstract—A numerical model which describes oxygen isotope exchange during burial and recrystallization of deep-sea carbonate is used to obtain information on how sea surface temperatures have varied in the past by correcting measured $\delta^{18}O$ values of bulk carbonate for diagenetic overprinting. Comparison of bulk carbonate and planktonic foraminiferal $\delta^{18}O$ records from ODP site 677A indicates that the oxygen isotopic composition of bulk carbonate does reflect changes in sea surface temperature and $\delta^{18}O$. At ODP Site 690, we calculate that diagenetic effects are small, and that both bulk carbonate and planktonic foraminiferal $\delta^{18}O$ records accurately reflect Paleogene warming of high latitude surface oceans, biased from diagenesis by no more than 1°C. The same is likely to be true for other high latitude sites where sedimentation rates are low. At DSDP sites 516 and 525, the effects of diagenesis are more significant. Measured $\delta^{18}O$ values of Eocene bulk carbonates are more than 2‰ lower at deeply buried site 516 than at site 525, consistent with the model prediction that the effects of diagenesis should be proportional to sedimentation rate. Model-corrections reconcile the differences in the data between the two sites; the resulting paleotemperature reconstruction indicates a 4°C cooling of mid-latitude surface oceans since the Eocene. At low latitudes, the contrast in temperature between the ocean surface and bottom makes the carbonate $\delta^{18}O$ values particularly sensitive to diagenetic effects; most of the observed variations in measured $\delta^{18}O$ values are accounted for by diagenetic effects rather than by sea surface temperature variations. We show that the data are consistent with constant equatorial sea surface temperatures through most of the Cenozoic, with the possible exception of the early Eocene, when slightly higher temperatures are indicated. We suggest that the lower equatorial sea surface temperatures for the Eocene and Oligocene reported in other oxygen isotope studies are artifacts of diagenetic recrystallization, and that it is impossible to reconstruct accurately equatorial sea surface temperatures without explicitly accounting for diagenetic overprinting.

INTRODUCTION

The oxygen isotopic compositions of carbonate fossils in deep-sea sediments record how the temperature and oxygen isotopic composition of seawater have changed through time. The temperature component of the record results from temperature-dependent fractionation of oxygen isotopes between water and calcite. Changes in the isotopic composition of seawater primarily reflect changes in the volume of low-$\delta^{18}O$ continental ice sheets. Because both these factors are sensitive indicators of global climate, oxygen isotope records provide information about the history of Earth's climate system.

Paleoclimate reconstructions derived from the oxygen isotopic composition of deep-sea carbonate rely on the assumption that postdepositional diagenetic recrystallization has not changed the carbonate's original isotopic composition. There has been long-standing concern that diagenesis has modified the primary isotopic signal (Urey et al., 1951; Killingley, 1983), yet the extent of this degradation is not well determined. In a previous paper (Schrag et al., 1992), we used a numerical model to simulate oxygen isotope exchange between solids (basalt and carbonate) and fluids in the oceanic crust. We proposed that the effects of diagenesis on oxygen

isotope records from marine carbonates could be quantified by combining such a model of oxygen isotope transport and reaction with measured $\delta^{18}O$ values of deep-sea carbonate. Using this approach, it is possible to determine those sites where the effects of diagenesis are likely to be significant. In addition, the models allow oxygen isotope records to be corrected for diagenetic overprinting; the resulting paleotemperatures are reliable to the extent that parameters used in the model (e.g., sedimentation rate, porosity, recrystallization rate) can be determined. Application of the model-correction strategy is probably limited to $\delta^{18}O$ records for bulk carbonate sediment (rather than foraminifera) because independent methods of estimating recrystallization rates exist only for bulk carbonate (Richter and DePaolo, 1987, 1988; Richter and Liang, 1993). However, the magnitude of the corrections determined for bulk carbonate can be used to assess how sensitive foraminiferal $\delta^{18}O$ records are to the effects of diagenesis. For sites where diagenetic effects are large, correcting bulk carbonate $\delta^{18}O$ records using our modeling approach may provide the best means for extracting reliable paleoclimate information.

In this paper, we compare results of numerical models similar to the one described by Schrag et al. (1992) with measured $\delta^{18}O$ values of bulk carbonates from Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) cores at high, mid, and low latitude sites. By evaluating the magni-

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tude of diagenetic effects, we reconstruct the evolution of Cenozoic sea surface temperatures from bulk carbonate $\delta^{18}O$ records. In doing this, we demonstrate the utility of the model-correction strategy both in identifying those situations in which diagenetic effects can be ignored and in extracting paleotemperature information from heavily altered samples where diagenetic effects are significant.

How does Diagenesis Affect the Oxygen Isotopic Composition of Carbonate Sediment?

The oxygen isotopic composition of primary biogenic calcite deposited on the ocean floor is determined by the composition and temperature of the water in which the calcite was formed. During diagenesis, this primary calcite dissolves and is replaced by secondary calcite that precipitates in isotopic equilibrium with pore fluids in the sediment column. In general, the equilibrium $\delta^{18}O$ value of secondary calcite decreases with increasing burial depth because temperature increases and $\delta^{18}O$ of pore fluid typically decreases with depth in the sediment; the latter being due to extended low temperature alteration of the underlying basaltic basement (McDuff and Gieskes, 1976; Lawrence and Gieskes, 1981). In this context, it is possible to predict qualitatively how recrystallization of carbonate during diagenesis will modify primary $\delta^{18}O$ values (Lawrence et al., 1975; Lawrence, 1988; Fig. 1). Recrystallization causes $\delta^{18}O$ values of carbonate formed in cold water (i.e., high-latitude planktonic assemblages and all benthic assemblages) to decrease. Recrystallization causes $\delta^{18}O$ values of carbonate formed in warm water (i.e., low-latitude planktonic assemblages) to increase initially because primary $\delta^{18}O$ values are lower than the value in equilibrium with cold pore fluids near the sediment-water interface. Only as temperature increases with deeper burial does recrystallization lower the $\delta^{18}O$ value of the assemblage. To move beyond this qualitative description requires a model that takes into account the sedimentation rate, the slope of the equilibrium calcite line (set by the vertical temperature gradient and the $\delta^{18}O$-depth gradient in the pore fluid; Fig. 1), and the recrystallization rate of the carbonate. Then, by examining model calculations and data from sites where differences exist in the parameters used in the model, we can evaluate the accuracy of the model in quantifying and correcting for diagenetic overprinting.

Pore Fluid Strontium as a Monitor of Recrystallization Rates for Bulk Carbonate

In order to model how diagenesis changes the oxygen isotopic composition of marine carbonate, we need to know the recrystallization rate of deep-sea carbonate. Recrystallization rates for bulk carbonate can be determined by modeling strontium exchange and transport in deep-sea sediments and pore fluids (Baker et al., 1985; Richter and DePaolo, 1987, 1988; Richter and Liang, 1993). Strontium is particularly useful, because both the concentration and the isotopic composition of strontium in the pore fluid are sensitive to carbonate recrystallization, whereas for oxygen, carbonate recrystallization has relatively minor effects on $\delta^{18}O$ values of pore fluid (Schrag et al., 1992).
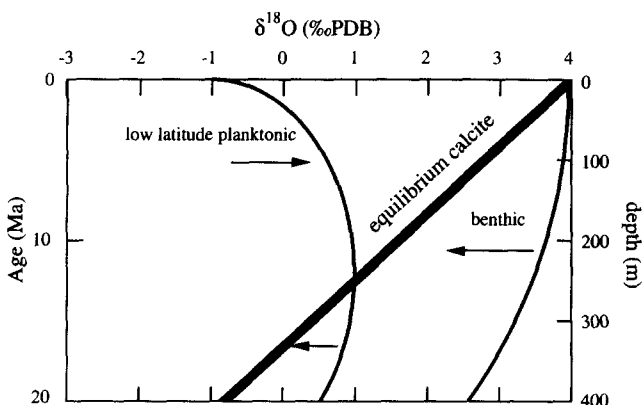

FIG. 1. Schematic diagram showing how $\delta^{18}O$ values of marine carbonate are affected by diagenetic recrystallization. The heavy line indicates the $\delta^{18}O$ value of secondary calcite in equilibrium with pore fluid for a vertical temperature gradient of $-50°$ km^{-1}, or a temperature gradient of $-40°$ km^{-1} and a $\delta^{18}O$ gradient in the pore fluid of $-2.5‰$ km^{-1}. The thin lines show schematically how the $\delta^{18}O$ values of bulk carbonate evolve during burial accompanied by recrystallization. Recrystallization results in negative shifts in $\delta^{18}O$ values of carbonate formed in cold water (benthic), and first positive and then negative shifts in carbonate formed in warm water (low latitude planktonic).

Because of biological effects, carbonate deposited on the ocean floor is enriched in strontium relative to calcite in equilibrium with seawater. Dissolution and reprecipitation of carbonate increases the strontium concentration of coexisting pore fluid, establishing a diffusive flux of strontium out the top of the sediment column. In the diffusive boundary layer near the top of the sediment column, the recrystallization rate is determined from the gradient of the strontium concentration of the pore fluid. Beneath the diffusive boundary layer, which typically ranges from 100 to 300 meters in thickness, the strontium concentration of the pore fluid is nearly in equilibrium with the solid, so no information about recrystallization rates deeper in the sediment column can be retrieved from the pore fluid strontium concentration. Information about recrystallization rates below the diffusive boundary layer comes from strontium isotopic disequilibrium between solid and fluid. Where the $^{87}Sr/^{86}Sr$ ratio of the solid changes rapidly with depth, diffusion smoothes the $^{87}Sr/^{86}Sr$ ratio in the fluid while recrystallization tends to pull the fluid back toward local isotopic equilibrium with the solid. By modeling the competing effects of diffusion and recrystallization, the recrystallization rate of older, more deeply buried sediment can be determined.

The approach used by Richter and DePaolo (1987, 1988) and Richter and Liang (1993) is to assume that recrystallization rate as a function of sediment age has the form $R = \alpha + \beta e^{-t/\gamma}$ where t is time in millions of years and α, β, and γ are constants. Using a numerical model, values of α, β, and γ are determined by fitting the model to observed strontium concentration and isotope ratio profiles from DSDP and ODP cores. The recrystallization rate immediately after burial is set mainly by β which varies from 0.01 to 0.1 m.y.$^{-1}$ among the sites studied by Richter and Liang (1993). The value of γ describes how quickly the recrystallization rate decreases with age, and varies from 2.5 to 12.5 m.y. Values for β and γ are

determined primarily from porewater strontium concentration data, whereas values for α, which reflect the recrystallization rate of older sediment and vary from 0.001 to 0.0055 m.y.$^{-1}$, must be obtained from isotopic data. Recrystallization rates appear to be faster at low latitudes than at high latitudes, consistent with the observation by Nelson (1986) that microfossil preservation is better and the ooze-to-chalk transition occurs deeper at high latitude sites.

We point out that, because strontium in the pore fluid is affected by the net exchange of all fractions of the solid, calculated recrystallization rates are valid only for bulk carbonate and do not necessarily apply to individual fractions such as foraminifera tests. Determination of recrystallization rates that apply to foraminiferal carbonate is far more difficult and uncertain. Visual estimation of the amount of secondary calcite yields only a qualitative result (van der Lingen and Packham, 1975; Barrera et al., 1987) because secondary calcite can precipitate on the insides of shells, or, even worse, can replace primary shell structures with only minor changes in morphology. Chemical methods are not viable because primary biogenic calcite and secondary calcite can be chemically similar and physically inseparable.

Site Selection

We examine bulk carbonate oxygen isotope records from five DSDP and ODP sites (Fig. 2). At high latitudes, where our model predicts that the effects of diagenesis on the $\delta^{18}O$ values of bulk carbonate should be small as long as sedimentation rate is low, we examine oxygen isotope data from Shackleton and Hall (1989) for ODP site 690 located at 60°S in the Weddell Sea. At site 690, nearly continuous carbonate deposition proceeded through the Paleogene, but at a slow sedimentation rate, the depth of the Cretaceous-Tertiary boundary at site 690 is only 210 meters. At mid-latitudes, we compare two sites located near 30°S in the South Atlantic. Site 516, located in the Brazil Basin, has a relatively high sedimentation rate; carbonate deposition over the last 85 million years has produced over 1200 meters of sediment. Site 525, located on the Walvis Ridge, has a much lower sedi-

Table 1. Oxygen isotope data for bulk carbonate from DSDP Site 366.

depth (m)	Age (Ma)	$\delta^{18}O$ (‰ PDB)
30.60	1.5	-0.41
69.05	3.5	-0.42
103.77	5.2	0.06
143.52	12.2	0.14
179.62	17.1	0.20
216.57	18.5	0.14
254.77	20.6	0.26
335.90	29.2	-0.21
368.40	32.6	-0.30
377.57	33.5	-0.28
387.76	34.6	-0.31
396.60	35.5	-0.22
405.96	36.5	-0.79
415.59	37.5	-0.98
424.04	38.4	-0.70
436.00	39.7	-0.81
443.80	40.5	-1.10
457.85	42.0	-0.89
461.52	42.4	-1.08
471.98	43.5	-1.29
489.50	44.6	-1.85
519.94	45.7	-2.11
548.83	46.7	-2.46
577.63	47.7	-2.97
633.17 ·	49.3	-3.00
662.33	50.0	-2.82
691.54	50.7	-3.33
719.62	51.3	-3.60
748.29	53.4	-4.42
776.92	55.4	-4.05

mentation rate; carbonate deposition since the Maastrichtian has produced 470 meters of sediment including a discontinuity from the Eocene to the Late Oligocene. For site 516, we use $\delta^{18}O$ values of bulk carbonate from this study (Table 2) as well as data from Renard (1984). For site 525, we use data from Shackleton and Hall (1984). At low latitudes where our model predicts that diagenesis should have the largest
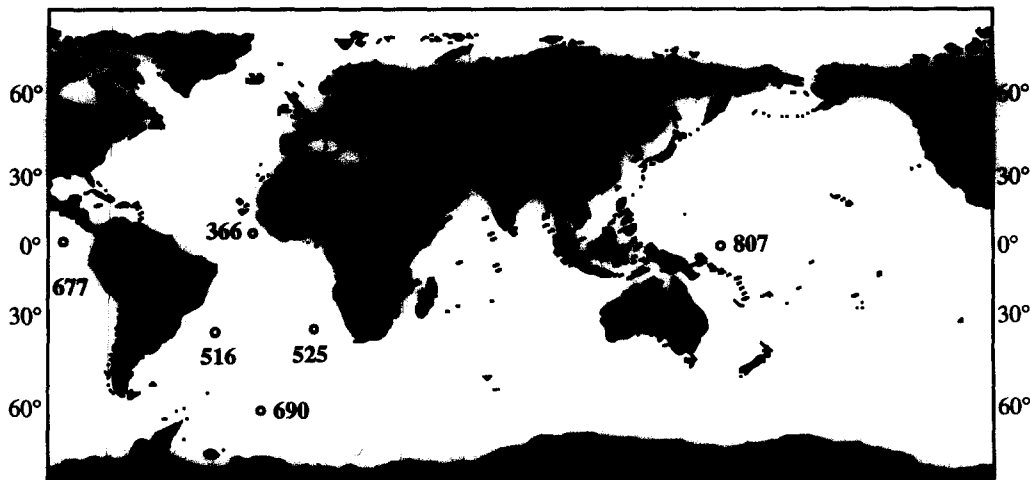

Fig. 2. Map showing location of DSDP and ODP sites investigated in this study.

impact on $\delta^{18}O$ records, we examine data from DSDP site 366 and ODP site 807 (Tables 1, 4). Site 366 is located in the eastern equatorial Atlantic, and sits on Early Paleocene oceanic crust. Site 807 is located in the Western Pacific and sits on 120 Ma oceanic flood basalt on the Ontong Java Plateau. While both sites have similar sedimentation rates, heat flow is much higher at site 366 than on the Ontong Java Plateau. Comparison of these two sites allows us to investigate how the vertical temperature gradient through the sediment column affects the impact of diagenesis on $\delta^{18}O$ records. Finally, to evaluate how well the $\delta^{18}O$ value of bulk carbonate records changes in sea surface temperature, we compare bulk carbonate data (Table 3) and planktonic foraminiferal data (Shackleton and Hall, 1984) for Pleistocene sediment from ODP site 677 in the eastern equatorial Pacific.

METHODS

Analytical Procedures

Isotopic data for bulk carbonates from DSDP sites 366 (Table 1) and 516 (Table 2) and ODP sites 677 (Table 3) and 807 (Table 4) 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. Precision based on measurements of standard calcite spaced throughout each run averages 0.04‰ for $\delta^{18}O$. Reproducibility of bulk analyses given by the average difference between twenty-five pairs of replicate analyses is 0.06‰.

Numerical Modeling

Model calculations described here simulate oxygen isotope exchange during deposition and compaction of sediment on the seafloor, and are based on the model described by Schrag et al. (1992). Calculations include time-varying sedimentation rates and depth-dependent porosities based on shipboard measurements for the sites investigated (Lancelot et al., 1977; Barker et al., 1983; Moore et al., 1984; Kroenke et al., 1991; Barker et al., 1988). The basic steps in the model are outlined as follows:

1) Add 5 m thick box of sediment with initial porosity to existing sediment column.
2) Calculate new porosities for lower boxes due to compaction and calculate new thickness of each box (and height of entire sediment column).
3) Calculate temperature for each box from model temperature gradient and deep ocean temperature curve (which sets temperature of top box).
4) Calculate pore fluid $\delta^{18}O$ value for each box from pore fluid $\delta^{18}O$-depth gradient and model $\delta^{18}O_{seawater}$ (which sets pore fluid $\delta^{18}O$ value of top box).
5) Calculate amount of recrystallization and $\delta^{18}O$ of secondary carbonate for each box over model time interval.
6) Repeat from steps 3 and 4 when deep ocean temperature and isotopic composition changes through model run.
7) For additional sedimentation, repeat from step 1.

The model calculates the $\delta^{18}O$ value and the amount of secondary calcite that precipitates during a run. Because none of the parameters that set the $\delta^{18}O$ value of secondary calcite are affected by the $\delta^{18}O$ of the calcite we specify as an initial condition for the model, we can correct measured $\delta^{18}O$ values from the conservation relationship:

$$\delta^{18}O_{primary} = (\delta^{18}O_{measured} - \delta^{18}O_{secondary}x_{secondary})/(1 - x_{secondary}) .$$

We express the results in terms of the shift caused by diagenesis defined as the difference between the measured $\delta^{18}O$ value and the primary (model calculated) $\delta^{18}O$ value.

Table 2. Oxygen isotope data for bulk carbonate from DSDP Site 516.

depth (m)	Age (Ma)	$\delta^{18}O$ (‰ PDB)	depth (m)	Age (Ma)	$\delta^{18}O$ (‰ PDB)
0.04	0.0	1.98	426.20	31.7	0.77
7.18	1.2	1.16	455.23	33.0	0.45
16.78	2.8	1.51	483.27	34.3	0.32
24.82	4.1	1.89	511.18	35.5	0.37
29.22	4.3	1.32	540.28	36.9	-0.38
43.33	4.8	1.72	540.28	36.9	-0.36
52.31	5.9	1.22	568.71	38.1	-0.16
60.71	6.9	1.18	596.67	39.4	-0.30
69.72	15.0	1.06	626.54	40.8	-0.35
73.89	15.2	1.07	654.80	42.2	-0.41
87.18	16.0	0.82	682.96	43.6	-0.63
91.40	16.3	1.17	711.37	45.0	-0.32
104.24	17.0	1.11	729.83	45.9	-1.28
112.93	17.5	1.08	756.89	47.3	-0.91
122.31	18.1	0.64	784.05	48.6	-0.68
125.77	18.3	0.71	796.58	49.3	-1.60
139.98	19.1	0.99	815.33	50.2	-1.77
148.20	19.6	0.77	895.97	57.0	-2.30
156.89	20.1	1.15	895.97	57.0	-2.32
166.19	20.7	1.00	919.81	58.7	-2.08
171.00	21.0	0.87	948.70	62.0	-1.93
181.78	21.6	0.89	977.11	66.0	-1.86
169.97	20.9	0.88	1006.32	68.0	-2.18
169.97	20.9	0.85	1030.32	70.0	-1.57
197.98	22.5	0.87	1044.46	72.0	-1.87
226.51	24.2	0.73	1060.61	73.0	-2.41
255.59	25.9	0.82	1087.47	74.7	-2.35
255.59	25.9	0.86	1110.47	76.1	-2.74
283.91	27.6	0.50	1136.81	77.7	-3.17
311.83	28.4	0.55	1163.27	79.3	-3.48
340.76	29.2	1.00	1190.98	83.0	-3.43
369.62	30.0	0.51	1190.98	83.0	-3.40
369.62	30.0	0.36	1212.90	83.7	-4.65
397.79	30.9	0.50			

Table 3. Oxygen isotope data for bulk carbonate from ODP Site 677A.

depth (m)	$\delta^{18}O$ (‰ PDB)	depth (m)	$\delta^{18}O$ (‰ PDB)
0.05	0.07	5.75	0.48
0.15	0.28	5.85	0.08
0.25	0.45	5.95	0.13
0.35	0.42	6.02	0.18
0.45	0.32	6.11	0.36
0.55	0.60	6.25	0.76
0.65	0.90	6.35	0.87
0.75	0.97	6.45	0.65
0.85	1.34	6.55	0.88
0.95	1.31	6.65	0.57
1.05	1.39	6.75	0.75
1.15	1.25	6.85	0.64
1.25	1.44	6.95	0.69
1.35	1.54	7.05	0.27
1.45	1.41	7.15	0.48
1.55	1.40	7.25	0.31
1.65	1.49	7.35	0.44
1.75	1.38	7.45	0.41
1.85	1.55	7.55	0.41
1.95	1.25	7.65	0.56
2.05	1.12	7.79	0.76
2.15	1.00	7.92	0.72
2.25	0.91	7.99	0.83
2.35	1.03	8.12	0.71
2.45	0.86	8.20	0.83
2.55	0.92	8.31	0.81
2.65	0.91	8.31	0.79
2.75	1.02	8.40	0.74
2.85	1.05	8.50	0.75
2.95	0.79	8.60	0.68
3.05	0.68	8.80	0.41
3.15	0.58	8.90	0.43
3.25	0.73	9.00	0.32
3.35	0.60	9.10	0.83
3.45	0.88	9.20	1.16
3.55	0.83	9.30	1.16
3.65	0.99	9.30	1.20
3.75	1.00	9.40	1.13
3.85	1.05	9.50	1.08
3.95	0.95	9.60	0.80
4.05	1.04	9.69	1.02
4.15	0.79	9.90	1.35
4.25	0.76	9.90	1.41
4.35	0.84	10.00	1.44
4.43	0.59	10.21	1.15
4.55	0.50	10.31	1.05
4.65	0.85	10.40	0.84
4.75	0.84	10.50	0.82
4.85	0.53	10.59	0.70
4.95	0.45	10.70	0.82
5.05	0.60	10.80	1.04
5.15	0.56	10.90	0.93
5.25	0.43	11.00	0.84
5.35	0.76	11.10	0.91
5.45	0.81	11.20	0.85
5.55	0.68	11.30	0.78
5.65	0.76	11.40	0.65
11.50	0.69	17.32	0.64
11.60	0.78	17.42	1.10
11.60	0.80	17.52	0.68
11.70	0.63	17.62	0.99
11.80	0.45	17.72	0.76
11.90	0.57	17.72	0.70
12.00	0.33	17.82	0.85
12.10	0.24	17.92	0.98
12.10	0.27	18.03	0.88
12.10	0.20	18.12	0.88
12.20	0.16	18.22	0.93
12.30	0.29	18.32	0.66
12.40	0.53	18.42	0.78
12.51	0.04	18.52	0.90
12.51	0.20	18.62	1.01
12.61	1.02	18.73	0.90
12.69	1.49	18.83	0.91
12.79	1.83	18.93	0.75
13.00	1.52	19.02	0.67
13.09	1.39	19.02	0.67
13.20	1.55	19.12	0.78
13.30	1.59	19.22	0.60
13.39	1.55	19.32	0.57
13.62	1.49	19.32	0.55
13.70	1.45	19.42	0.49
13.80	1.42	19.53	0.62
13.91	1.18	19.62	0.73
14.00	0.93	19.72	0.99

Table 3 (cont.).

depth (m)	$\delta^{18}O$ (‰ PDB)	depth (m)	$\delta^{18}O$ (‰ PDB)
14.00	0.99	16.12	1.59
14.10	0.95	16.22	1.51
14.19	0.83	16.42	1.40
14.19	0.72	16.53	0.96
14.29	0.59	16.63	1.59
14.41	1.05	16.73	1.39
14.49	0.81	16.82	1.02
14.59	0.42	16.82	1.22
14.70	1.05	16.93	1.18
14.78	0.78	17.02	1.53
14.91	0.37	17.12	1.35
14.98	0.50	17.20	1.19
15.11	0.40	19.82	0.87
15.74	1.29	19.92	0.79
15.83	2.17	20.03	0.78
15.92	1.94	20.12	0.93
16.03	1.36		

Rather than tracking the porewater composition through time by modeling isotopic exchange and diffusive transport as was done in our previous study (Schrag et al., 1992), we specify the composition of the pore fluid, fixing the $\delta^{18}O$-depth gradient at $-3‰\ \text{km}^{-1}$ from the seawater boundary at the top of the sediment, an average value based on observed profiles from DSDP cores (Lawrence and Gieskes, 1981). This simplification is reasonable based on results from previous modeling which demonstrate that the oxygen isotopic composition of the pore fluid composition is controlled primarily by low temperature alteration of underlying basalt, not by carbonate recrystallization (Schrag et al., 1992). We allow the $\delta^{18}O$ of seawater and the temperature of the deep ocean to change during the model run. 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 (Fig. 3) based on estimates of the impact of continental ice on $\delta^{18}O$ of seawater by Shackleton and Kennett (1975). Our $\delta^{18}O_{seawater}$ curve contains two major steps; one at the Eocene-Oligocene boundary and one in the Middle Miocene. 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. Following Richter and DePaolo (1987, 1988), we use recrystallization rate-age relationships of the form $R = \alpha + \beta e^{-t/\gamma}$. Values of α, β, and γ used for each site are listed in Table 5. For sites 366 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. Because no strontium isotopic data are available for these sites, we set $\gamma = 0.005$, a value in the upper range of those calculated by Richter and Liang (1993). For site 366, we run a second calculation for $\gamma = 0.01$. For sites 516, 525, and 690, we use values of α, β, and γ from Richter and Liang (1993) calculated from strontium concentration and isotopic data for site 516. Vertical temperature gradients in the sediment column are estimated from global compilations of oceanic heat flow data (Louden, 1989). At sites 366, 516, 525, and 690, the vertical temperature gradient is set initially at $60°\ \text{km}^{-1}$ and decreases linearly to $40°\ \text{km}^{-1}$ by the end of the run. For site 807, which sits on 122 Ma oceanic flood basalt on the Ontong Java Plateau, a lower gradient was applied, initially $35°\ \text{km}^{-1}$. The decrease in the gradient over the duration of the model run was half as much as for the other sites, decreasing to $25°\ \text{km}^{-1}$ by the end of the run. Model runs using a temperature gradient which decreases as $t^{-1/2}$ yield very similar results to those presented here, although this is probably an inaccurate representation of the cooling history because it neglects the early effects of hydrothermal circulation of seawater at mid-ocean ridges (e.g., Stein and Stein, 1992).

Table 4. Oxygen isotope data for bulk carbonate from ODP Site 807.

depth (m)	Age (Ma)	$\delta^{18}O$ (‰ PDB)	depth (m)	Age (Ma)	$\delta^{18}O$ (‰ PDB)
0.02	0.0	-1.21	809.90	33.1	-0.21
16.94	1.1	-0.73	828.52	33.6	-0.08
35.94	2.2	-0.71	828.52	33.6	-0.03
92.94	4.0	-0.59	888.95	35.3	-0.14
104.50	4.3	-0.24	899.22	35.9	-0.88
104.50	4.3	-0.23	899.22	35.9	-0.88
112.08	4.6	-0.31	908.98	36.5	-0.84
130.95	5.1	0.16	918.95	36.9	-0.81
130.95	5.1	0.16	933.91	37.6	-0.79
149.94	5.5	-0.23	943.71	38.0	-0.87
149.94	5.5	-0.14	958.30	38.6	-0.81
168.94	6.0	0.08	977.58	39.4	-0.66
188.05	6.4	0.39	977.58	39.4	-0.66
216.50	7.1	0.39	996.93	42.5	-0.39
244.94	7.7	0.38	1016.23	43.1	-1.00
244.94	7.7	0.38	1034.70	43.6	-1.52
302.33	9.5	0.06	1054.08	44.3	-0.86
302.33	9.5	0.06	1073.56	48.6	-0.93
330.94	11.1	-0.14	1092.49	50.2	-0.90
359.98	12.8	-0.01	1092.49	50.2	-0.97
389.27	14.5	-0.19	1102.46	53.2	-1.70
418.34	16.2	0.24	1116.07	54.7	-1.64
447.34	18.0	0.26	1135.39	55.8	-1.73
476.35	19.8	0.15	1145.39	56.4	-2.02
476.35	19.8	0.11	1155.59	57.1	-2.06
505.17	21.5	0.29	1170.11	59.5	-1.99
562.76	24.1	0.18	1222.64	68.6	-1.48
591.70	25.3	0.20			
620.68	26.6	-0.07			
639.98	27.4	0.06			
697.00	29.9	-0.54			

RESULTS AND DISCUSSION

Oxygen Isotopic Composition of Bulk Carbonate as a Measure of Surface Ocean Temperature and Composition

While the vast majority of researchers since 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 make up 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) recently presented a bulk carbonate oxygen isotope record for the last 120 kyrs, illustrating how bulk carbonate can be used in place of foraminifera for chronostratigraphy of Pleistocene sediments. To examine the relationship between bulk carbonate and foraminiferal oxygen isotope records in more detail, we measured the $\delta^{18}O$ of bulk carbonate from ODP site 677A, the same site where Shackleton and Hall (1984) produced a high resolution foraminiferal isotopic record for the Pleistocene. In Fig. 4, we compare bulk carbonate and planktonic foraminiferal $\delta^{18}O$ records for sediment from the last several hundred thousand years, young enough so that diagenesis should have negligible effects. The average $\delta^{18}O$ value for bulk carbonate is 2‰ higher than that for the planktonic foraminifera *Globigerinoides ruber*. This is likely due to vital effects in coccoliths, which make up most of the mass of bulk carbonate. Aside from the offset in average value, the records are highly correlated ($r = 0.78$), both tracking the changes in temperature and ice volume caused by episodes of glaciation over the last 500,000 years. The amplitude of the variations in the bulk carbonate record are slightly lower than those in the forami-

nifera record. This may be due to bioturbation that mixes finer grains (coccoliths) more effectively than coarser ones (foraminifera), a phenomenon similar to that observed for bioturbation of different size fractions of volcanic glass (Ruddiman and Glover, 1972).

Diagenesis of Bulk Carbonate at High Latitudes—ODP Site 690

Because the vertical temperature gradient is relatively small at high latitudes, carbonate precipitated in high latitude surface oceans has a primary $\delta^{18}O$ value that is not far from equilibrium with the cold pore fluid to which carbonate is exposed during early diagenesis. This means that rapid recrystallization during early diagenesis at high latitude sites results in relatively small changes in the $\delta^{18}O$ values. If the sedimentation rate is low, this condition continues, and further recrystallization has only minor effects.

Results of our model calculations for ODP 690 are consistent with this qualitative description (Fig. 5). Shifts in $\delta^{18}O$ values caused by diagenesis are calculated to be small, less than 0.3‰ throughout the record. This implies that the bulk carbonate $\delta^{18}O$ record should accurately describe the evolution of sea surface temperatures through the Paleogene, biased by no more than 1°C due to diagenetic effects. This also applies to planktonic foraminiferal $\delta^{18}O$ records provided that foraminiferal calcite recrystallizes at a rate less than or equal to the recrystallization rate for bulk carbonate.

In Fig. 6, we compare stable isotope data on bulk carbonates from Shackleton et al. (1993) (collected primarily for obtaining a carbon isotope record of the Paleogene) with data

benthic foraminifera
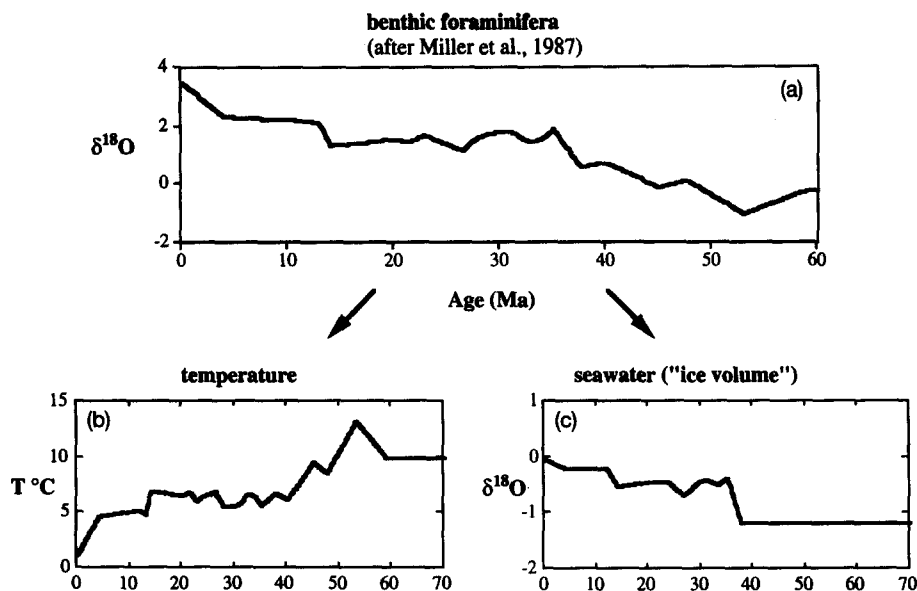**(after Miller et al., 1987)**

FIG. 3. We divide the benthic oxygen isotope record from Miller et al. (1987) (a) into a deep ocean temperature component (b) and a seawater $\delta^{18}O$ component (c), which are used as boundary conditions in the model calculations.

on planktonic foraminifera of the genus *Subbotina* from Stott et al. (1989). The two records are nearly identical, both recording the Early Eocene warming of the surface ocean at high latitudes followed by cooling through the rest of the Paleogene. There is no offset between planktonic foraminiferal and bulk carbonate $\delta^{18}O$ values similar to that seen at site 677. This may be explained by the fact that *Subbotina* species grow deeper in the surface ocean; Stott et al. (1989) also measured *Acarina* species which have $\delta^{18}O$ values 1–2‰ lower than the *Subbotina* values. There is less scatter in the bulk data, perhaps because sampling bulk carbonate integrates all the carbonate, making the record less sensitive to variations between individual shells. The similarity of the two records gives further support to our claim that the $\delta^{18}O$ of bulk carbonate is a robust proxy for surface water temperature and isotopic composition, and therefore much of the same information on the evolution of high latitude sea surface temperatures can be retrieved from the bulk record, but with far less effort in sample preparation.

Correcting for Diagenetic Overprinting at Mid-Latitudes: DSDP Sites 516 and 525

As at high latitudes, the effects of rapid recrystallization during early diagenesis at mid-latitude sites is relatively small because primary $\delta^{18}O$ values are near the equilibrium values with cold pore fluid. However, as sediment is buried deeper, recrystallization at elevated temperatures in the sediment col-

umn adds secondary carbonate with lower $\delta^{18}O$ values, shifting the composition of the bulk assemblage. Thus, diagenetic effects on bulk carbonate from mid-latitude sites should be most pronounced where sedimentation rates are highest.

Comparison of data and model calculations from sites 516 and 525 allows us to test this prediction. Data on bulk carbonates from both sites, plotted against depth and age, are shown in Fig. 7. The $\delta^{18}O$ values of carbonate from both sites decrease with age and depth, although this decrease is much more rapid at site 516, reaching values below $-4‰$ at 1200 m depth. If we interpret the data as reflecting changes in temperature alone, the bulk record from site 516 implies that the surface ocean in the South Atlantic cooled by over 25°C from the Late Cretaceous to the present-more than twice the change observed at high latitudes! For site 525, the implied cooling is only 12°C.

In Fig. 8, we compare model-calculated shifts for fits of the data (lines, Fig. 7). For site 516, we show three calculations with different choices of parameters. The curve labeled 516(a) uses an initial vertical temperature gradient of 50° km^{-1}, and the recrystallization-age relationship from Richter and Liang (1993): $R = 0.002 + 0.015e^{-t/12.5}$. The curve labeled 516(b) uses the same recrystallization rate, but with a higher initial temperature gradient of 60° km^{-1}. In both calculations, the temperature gradient decreases by 20° km^{-1} through the model run to simulate slow cooling of the oceanic crust. The curve labeled 516(c) uses an initial temperature gradient of 60° km^{-1}, and has a higher recrystallization rate

Table 5: Recrystallization rate constants used in model calculations. The recrystallization rate, in units of m.y.$^{-1}$, is of the form $\alpha+\beta e^{-t/\gamma}$ where t is time in millions of years.

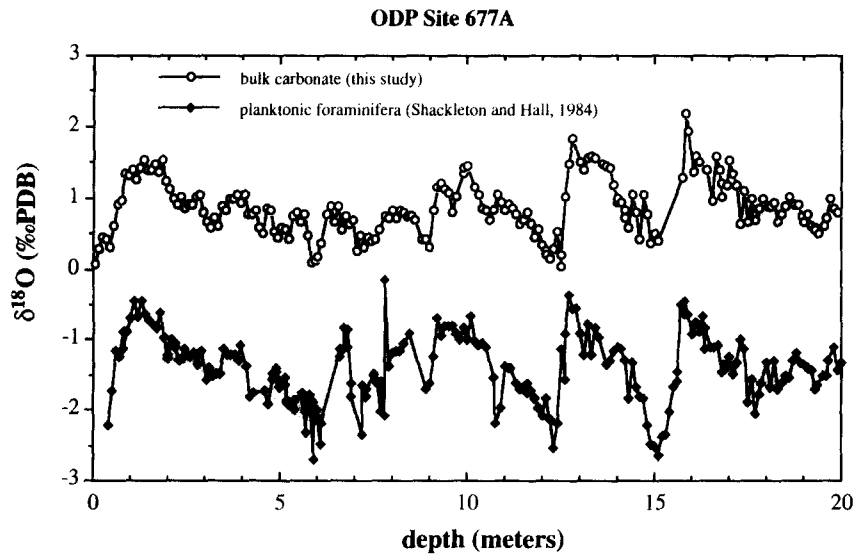| Site	α (m.y.$^{-1}$)	β (m.y.$^{-1}$)	γ (m.y.)
366	0.005,0.01	0.06	6
516	0.002,0.004	0.015	12.5
525	0.002	0.015	12.5
690	0.002	0.015	12.5
807	0.005	0.07	9

ODP Site 677A

FIG. 4. Comparison of bulk carbonate and planktonic foraminiferal (*G. ruber*) oxygen isotope data from ODP Site 677A (data from Table 3 and from Shackleton and Hall, 1989).

for older sediment: $R = 0.004 + 0.015e^{-t/12.5}$. All model-calculated shifts greater than 0.2‰ are toward more negative $\delta^{18}O$ values, consistent with our prediction that early recrystallization has only minor effects. Shifts are small for sediment younger than 30 Ma because the $\delta^{18}O$ of primary calcite is close to the value for equilibrium with the pore fluid. For site 525, which has a much slower sedimentation rate as well as a hiatus between 45 and 25 Ma, shifts are small even at the base of the hole where diagenesis has lowered the $\delta^{18}O$ value of bulk carbonate by only 0.5‰. For site 516, shifts are greater than at 525 because the sediment has spent much more

time in contact with lower $\delta^{18}O$ pore fluid at elevated temperature. For Late Cretaceous through Late Eocene sediment from site 516, the model calculations with a lower recrystallization rate predict shifts of approximately 1‰. A 10° difference in vertical temperature gradient (equivalent to a change in the $\delta^{18}O$-depth gradient in the pore fluid of -2.5‰ km^{-1}) reduces the shifts for sediment of this age by only 0.2‰. The calculation using a higher recrystallization rate
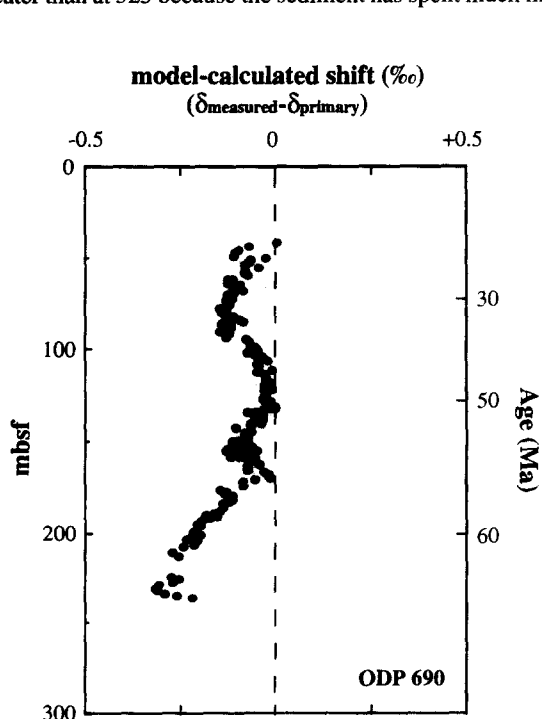
FIG. 5. Model-calculated shifts for bulk carbonate from ODP Site 690. Details of the model calculations are described in the text.
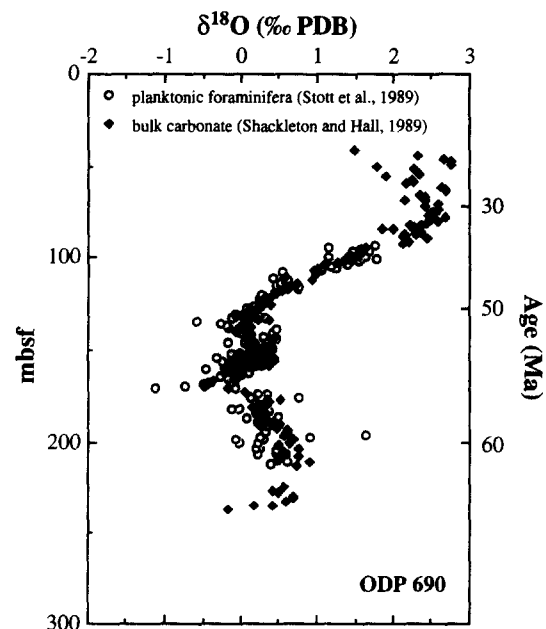
FIG. 6. Comparison of bulk carbonate and planktonic foraminiferal $\delta^{18}O$ records from ODP Site 690 (data from Shackleton and Hall (1989) and from Stott et al., 1989). Because diagenetic effects are relatively small (see Fig. 5), the similarity of the two records indicates that the $\delta^{18}O$ of bulk carbonate is a good proxy for surface water temperature and isotopic composition.
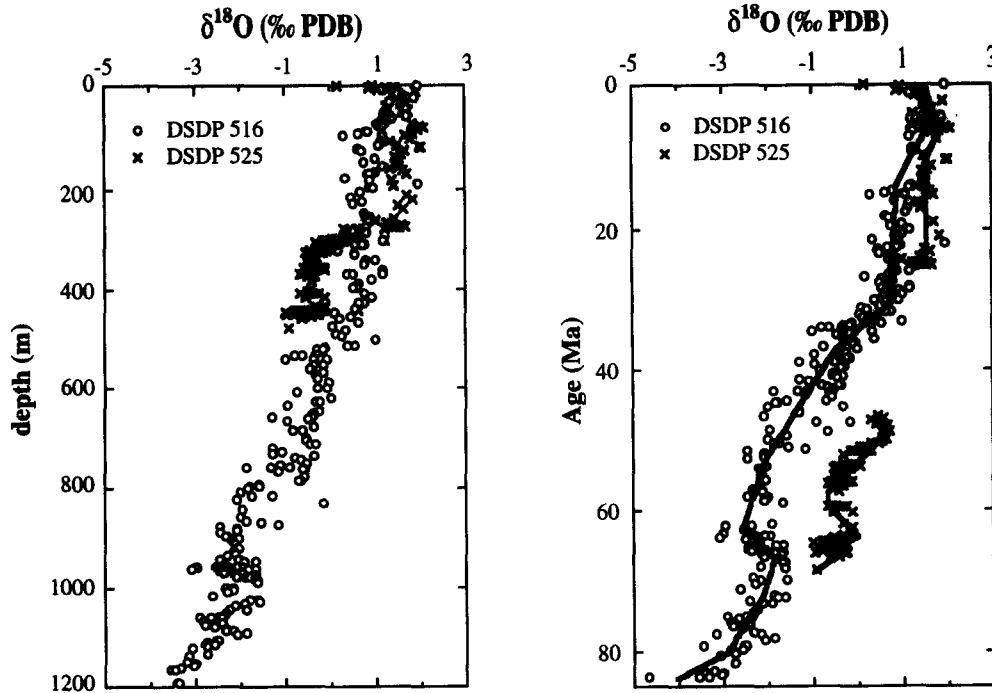
FIG. 7. Bulk carbonate oxygen isotope data for DSDP Sites 516 and 525, plotted against sediment age and burial depth. Data for Site 516 are from this study (Table 2) and Renard (1984). Data for Site 525 are from Shackleton and Hall (1984). Heavy lines in the plot of $\delta^{18}O$ vs. age are fits of the data used for calculating diagenetic shifts and reconstructing sea surface temperatures.

predicts much larger shifts—over 2‰ for Late Cretaceous sediment.

In Fig. 9, we show sea surface temperatures reconstructed from the corrected data for sites 516 and 525. We express the data in terms of change in sea surface temperature relative to modern isotopic temperatures to avoid problems associated with vital effects of coccoliths. However, based on the good correlation between planktonic foraminifera and bulk carbonate $\delta^{18}O$ records from sites 677 (Fig. 4) and 690 (Fig. 6), as well as work on coccoliths grown in culture showing that $\delta^{18}O$ values vary with temperature with the same slope as for foraminiferal carbonate (Dudley and Goodney, 1979), we submit that relative changes in sea surface temperature are reflected accurately in these reconstructions. To calculate the temperatures, we use our model $\delta^{18}O_{seawater}$ curve and the $\delta^{18}O$-temperature relationship from O'Neil et al. (1969), adjusted for the fractionation factor between CO_2 and water from Friedman and O'Neil (1977) [$1000 \ln \alpha = 2.78 * 10^6/T^2 - 2.89$]. For site 516, we use the calculation with the higher recrystallization rate ($\alpha = 0.004$). We choose this calculation for two reasons; first the lower rate ($\alpha = 0.002$) results in less than %25 total recrystallization at the end of the calculation, an amount in apparent contradiction with the textural state of the sediment (i.e., limestones). In addition, the strontium isotopic data on which the values from Richter and Liang (1993) are based place poor constraints on the value for alpha as the isotopic composition of the solids and pore fluids at depth at Site 516 are nearly identical—information about the recrystallization rate comes only when disequilibrium conditions exist. The recrystallization rate is the largest source of uncertainty in the calculation; we estimate this uncertainty at

roughly ±1‰ or ±4°C in inferred paleotemperature. Changes in the $\delta^{18}O_{seawater}$ curve used here could also affect our reconstruction since the Oligocene. For older time periods, the reconstruction would not be affected as there exists consensus among workers that large continental ice sheets did not exist, and therefore $\delta^{18}O_{seawater}$ was constant, prior to the Eocene-Oligocene boundary (Shackleton and Kennett, 1975; Miller et al., 1987).

Temperature reconstructions for both sites indicate a general cooling of mid-latitude surface oceans by approximately 4°C through the Cenozoic. The record from site 516 gives warmest temperatures in the period between 80 and 85 Ma. Sea surface temperatures decreased in the latest Cretaceous, followed by warming in the Paleocene and early Eocene. Like the high latitude record from Site 690 (Fig. 6), the record from site 516 shows a steady cooling from the early Eocene through the Oligocene. The early Miocene is the only other warm episode in the record when temperatures were 2–4° higher than present. The record from site 525 gives a similar picture of Cenozoic climate change. Temperatures reach maximum values in the late Paleocene and early Eocene, dropping off towards the late Eocene where the discontinuity interrupts the record. The most significant aspect of the two records is that the sea surface temperatures reconstructed for the Paleocene and Eocene are in good agreement despite the fact that measured $\delta^{18}O$ values over this interval differ by more than 2‰. The successful reconciliation of the two oxygen isotope records, one (516) highly affected by diagenesis, the other (525) only slightly affected, is an important confirmation that our model-correction strategy can extract temperature information from otherwise irreconcilable data. For Cretaceous
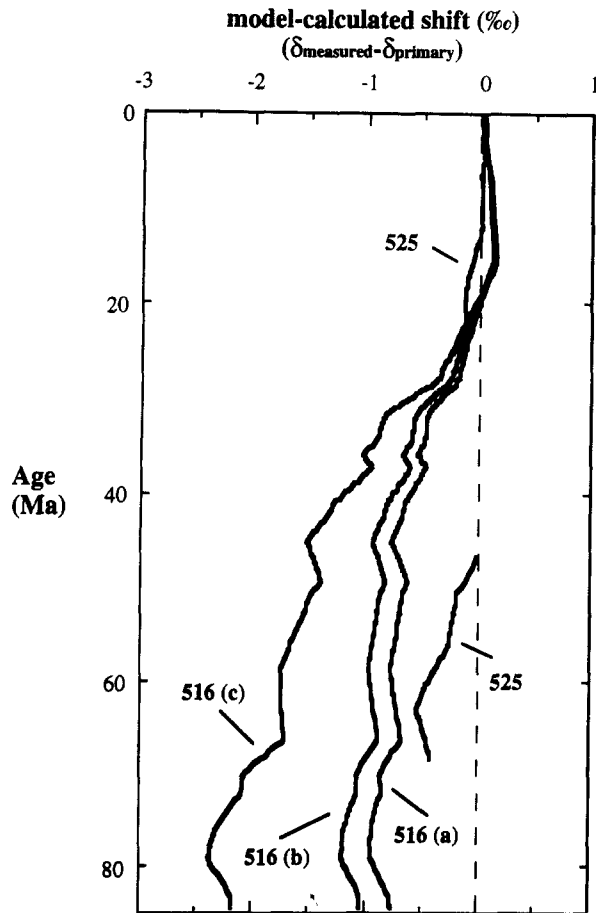
model-calculated shift (‰)
($\delta_{measured} - \delta_{primary}$)

Fig. 8. Model-calculated shifts for DSDP Sites 516 and 525. Curve 516(a) uses a temperature gradient of $-50°$ km^{-1} and a recrystallization rate, $R = 0.002 + 0.015e^{-t/12.5}$; curves 516(b) and 525 use a temperature gradient of $-60°$ km^{-1} and the same recrystallization rate as 516(a); curve 516(c) uses a temperature gradient of $-60°$ km^{-1} and a recrystallization rate, $R = 0.004 + 0.015e^{-t/12.5}$.

and older sediments, diagenesis will almost always have significant impact on $\delta^{18}O$ values, and application of this strategy may provide the best way to obtain reliable paleotemperature estimates.

Diagenesis of Carbonate at Low Latitudes: The Record of Equatorial Sea Surface Temperatures

Our model predicts that carbonate formed in low latitude surface oceans is highly susceptible to diagenetic effects because (1) the oxygen isotopic composition of primary calcite is far from equilibrium with the cold seawater encountered early during the burial process and (2) recrystallization is most rapid in the first few million years after deposition. Recrystallization shifts the $\delta^{18}O$ of bulk carbonate towards higher values until, with continued burial and increasing temperatures in the sediment column, the $\delta^{18}O$ value of secondary calcite drops below the $\delta^{18}O$ value of the total carbonate assemblage. Further recrystallization then causes $\delta^{18}O$ values to decrease (see Fig. 1). Measured $\delta^{18}O$ profiles for bulk carbonate from site 366 in the eastern equatorial Atlantic, and from site 807 on the Ontong Java Plateau in the western Pa-

cific are generally consistent with this description (Fig. 10). In both records, $\delta^{18}O$ values increase with depth initially, consistent with rapid recrystallization at cold temperature near the seafloor, and then decrease deeper in the section as recrystallization proceeds at higher temperatures deeper in the sediment. The major difference between the data from the two sites is that $\delta^{18}O$ values from 807 decrease slowly with depth, achieving minimum values of $-2‰$ at 1200 m below the seafloor, whereas $\delta^{18}O$ values from 366 decrease rapidly with depth, reaching minimum values of $-4.5‰$ at 800 m below the sea floor. An important question, therefore, is whether our model for bulk carbonate diagenesis can account quantitatively for the measured changes in $\delta^{18}O$ values observed in the records from these sites, including differences between the two records.

Models for both sites were constructed as described above (see Methods section). For site 366, we ran two calculations for $\alpha = 0.005$ and $\alpha = 0.01$ to show the sensitivity of the calculation to the recrystallization rate. For site 807, we show a single calculation for $\alpha = 0.005$. As an input to the model, we set the isotopic composition of the carbonate sediment

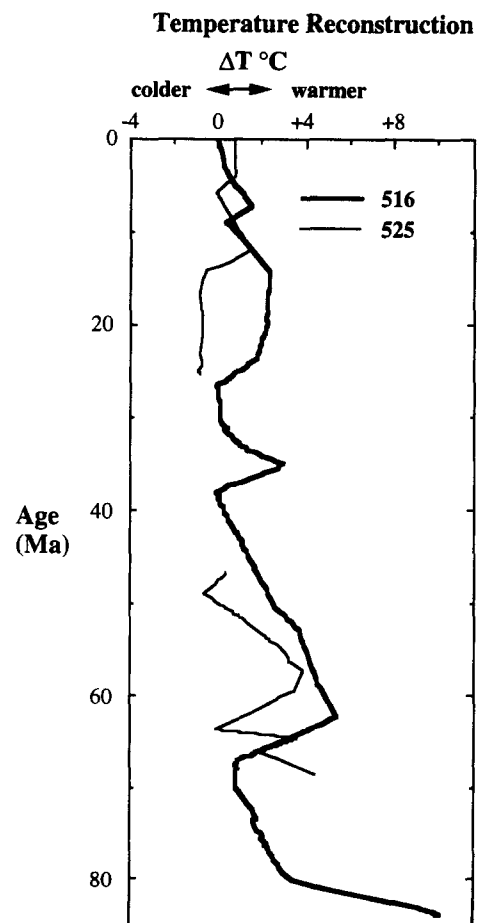## Temperature Reconstruction
ΔT °C
colder ◄———► warmer

Fig. 9. Relative change in sea surface temperatures reconstructed from the corrected data for sites 516 and 525. To calculate the temperatures, we use the model $\delta^{18}O_{seawater}$ (Fig. 3) and the $\delta^{18}O$-temperature relationship from O'Neil et al. (1969), adjusted for the fractionation factor between CO_2 and water from Friedman and O'Neil (1977). For site 516, we use the calculation with the higher recrystallization rate ($\alpha = 0.004$).
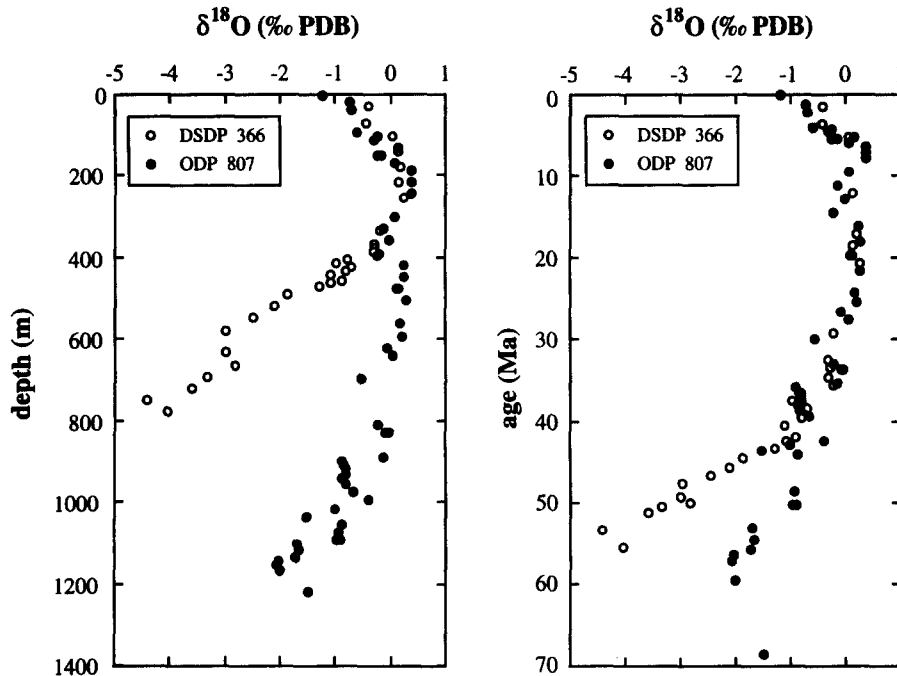
Fig. 10. Bulk carbonate oxygen isotope data for DSDP Site 366 (Table 1) and ODP Site 807 (Table 4), plotted against sediment age and burial depth.

deposited at a certain time during a model run at the $\delta^{18}O$ value for calcite in equilibrium with the model $\delta^{18}O_{seawater}$ for that time at a constant temperature of 19° for site 366 and 21° for site 807. The assumed temperature difference between the two sites accounts for slightly warmer temperatures in the Western Pacific relative to the Eastern Atlantic and reproduces an offset of 0.5‰ observed between $\delta^{18}O$ values of modern bulk carbonate from the two sites. Because we assume no change in sea surface temperature with time, all changes in the initial $\delta^{18}O$ of calcite used as an input for the model calculations are due solely to changes in the model $\delta^{18}O$ seawater; this allows us to determine whether diagenesis can explain the observed patterns assuming no change in low latitude sea surface temperature with time. The major difference between calculations for the two sites is in the vertical temperature gradients in the model sediment column. For site 366, which sits on Early Paleocene "normal" oceanic crust, the vertical temperature gradient is set initially at 60° km^{-1} and decreases linearly to 40° km^{-1} by the end of the run to simulate cooling of oceanic crust. For site 807, which sits on 120 Ma oceanic flood basalt on the Ontong Java Plateau, a lower gradient was applied, initially 35° km^{-1} decreasing to 25° km^{-1} by the end of the run. Results from the model calculations are compared with measured $\delta^{18}O$ values in Fig. 11.

For site 366, the model-calculated $\delta^{18}O$ records fitting the observed data well. Rapid recrystallization at low temperature during early diagenesis produces the initial increase in $\delta^{18}O$ values in the first 10 million years. Then, as recrystallization proceeds at slower rates and higher temperatures deeper in the sediment column, the $\delta^{18}O$ values decrease. One prominent feature of the measured record is perfectly reproduced by the model and gives further confidence that the model provides a realistic simulation of oxygen isotope exchange during dia-

genesis. In the measured record, a change in slope occurs in the $\delta^{18}O$ vs. age curve at 44 Ma (Fig. 11). This change in slope is generated in both model runs even though there is no change in the $\delta^{18}O$ value of carbonate used as an input through this age range. The cause of the change in slope is a change in sedimentation rate, from 27 m/m.y. before 44 Ma, to 9 m/ m.y. 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 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. This change in slope is relatively insensitive to later recrystallization as model curves for $\alpha = 0.005$ and $\alpha = 0.01$ are nearly identical over this interval. For sediment older than 44 Ma, the agreement between the model and the data is not as good. Measured $\delta^{18}O$ values of sediment older than 44 Ma decrease rapidly with age, reaching minimum values of −4.5‰ at 53 Ma. The model calculation using the higher recrystallization rate (heavy line, Fig. 11) reproduces the curve quite well down to 50 Ma old sediment, but cannot reproduce $\delta^{18}O$ values less than −3.5‰. The model calculation using the lower recrystallization rate (thin line, Fig. 11) gives minimum values of −3‰.

The fit of the model curve to the data is similarly good at site 807. Model-predicted $\delta^{18}O$ values increase by over 1.5‰ in the first 10 million years, and then decrease slowly. The model is unable to reproduce the more negative $\delta^{18}O$ values of sediment in the age range 50–60 Ma. This is the same interval over which the model for site 366 predicted higher values than observed.

There are two ways two explain the discrepancy between the model and the data for early Paleogene sediment. One
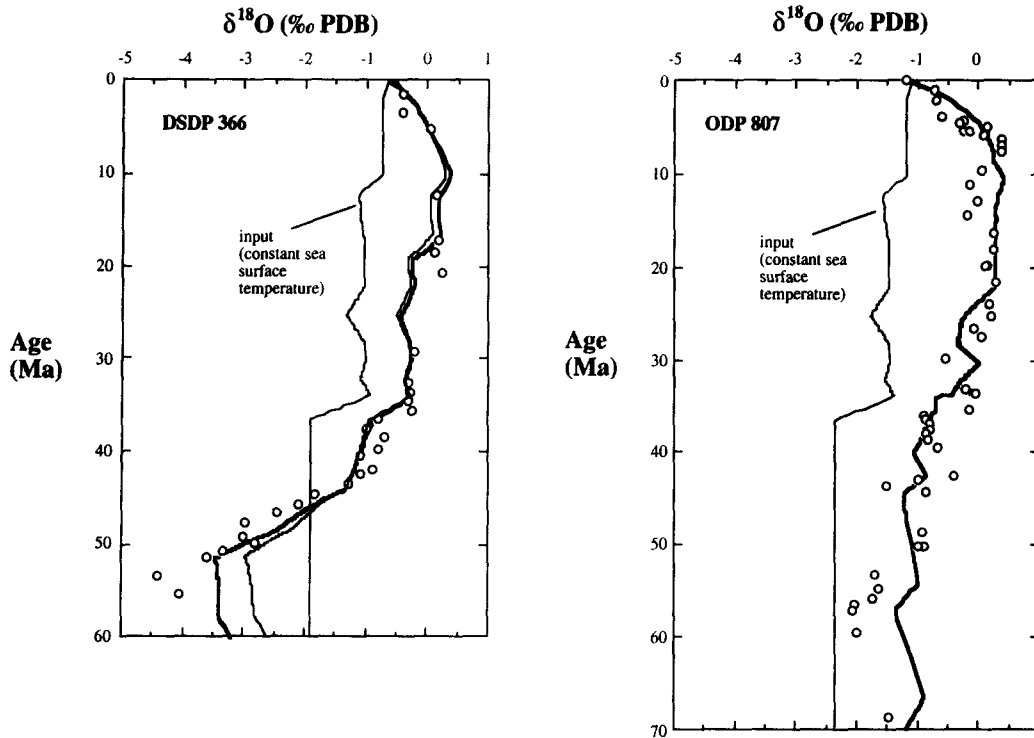
FIG. 11. Comparison of measured $\delta^{18}O$ values and model calculated values assuming that sea surface temperatures were constant through time. Two calculations are shown for site 366, using two different recrystallization rates (thin line: $\alpha = 0.005$; heavy line: $\alpha = 0.01$). For both sites, the model does an excellent job of fitting the data, except for sediment in the age range 50–60 Ma for which the measured $\delta^{18}O$ values are lower than model predictions. To fit the data over the 50–60 Ma range, equatorial sea surface temperatures would have to be higher by 2–6°C.

explanation is that recrystallization rates are faster at depth than the values we used. For both sites, strontium concentration data was used to calculate values for β and γ, but the concentration data places no constraint on the recrystallization rate of older sediment set by the value for α. We cannot rule out the possibility that the recrystallization rates for older sediment increases as higher temperatures are achieved deep in the sediment column. This might be testable by looking for changes in the strontium isotopic composition of older sediment. Another possibility is that equatorial sea surface temperatures were several degrees higher during the Early Eocene. This is plausible considering that deep ocean and high latitude surface ocean temperatures reached maximum values during this interval (Miller et al., 1987; Stott et al., 1989).

Overall, the model results successfully explain (and reconcile) the principle difference between the measured $\delta^{18}O$ records from sites 366 and 807. The major cause of the different $\delta^{18}O$ records from the two sites is the lower heat flow at site 807. Moreover, the model shows how the observed variations in $\delta^{18}O$ values from sites 807 and 366 are consistent with little or no change in average equatorial sea surface temperature through the Cenozoic with the possible exception of the early Eocene, when temperatures would have to be higher by a few degrees for our model curve to reproduce the measured oxygen isotope record. In contrast, oxygen isotope records based on planktonic foraminifera from sites at low latitudes indicate that average equatorial sea surface temperatures

were 5–10°C colder than present during the Eocene and early Oligocene (Douglas and Savin, 1973; Shackleton and Boersma, 1981). These reconstructed temperatures have met with some skepticism (e.g., Horrel, 1990; Barron, 1987; Crowley, 1991), because they conflict with the warm Eocene climate implied by terrestrial fossil records, and by oxygen isotope records for deep oceans and high latitude surface oceans (Miller et al., 1987; Stott et al., 1989). One possible explanation proposed by Zachos et al. (1994) is that the isotope records which show cold equatorial sea surface temperatures are from sites in upwelling zones. The comparison of model results and bulk carbonate data for sites 366 and 807 indicates that diagenetic effects provide another explanation because they can increase $\delta^{18}O$ values of carbonate formed at low latitudes by nearly 2‰ resulting in lower apparent temperatures. Moreover, the general shape of the bulk carbonate $\delta^{18}O$-age curves from sites 366 and 807, which can be reproduced by our model assuming no change in low latitude sea surface temperature, is similar to the shape of the $\delta^{18}O$-age curve for low latitude planktonic foraminifera. We propose that the inferred cooling of low latitude surface oceans during the Eocene and Early Oligocene is an artifact of recrystallization. This interpretation requires that foraminiferal calcite has recrystallized to approximately the same extent as bulk carbonate. Although the recrystallization rate of foraminiferal calcite is yet undetermined, we submit that potential diagenetic effects on low latitude planktonic foraminifera are large enough that it is impossible to reconstruct accurately equa-

torial sea surface temperatures without explicitly accounting for diagenetic overprinting.

SUMMARY

We have shown that application of our model-correction approach to reconstructing past sea surface temperatures explains the observed patterns of measured $\delta^{18}O$ values of bulk carbonate. Comparison of bulk carbonate and planktonic foraminiferal $\delta^{18}O$ records from ODP site 677 indicates that the oxygen isotopic composition of bulk carbonate does reflect changes in sea surface temperature and $\delta^{18}O$. This is also supported by the similarity of bulk carbonate and planktonic foraminiferal $\delta^{18}O$ records from ODP Site 690, where the model-calculated shifts from diagenesis are small. The model successfully reconciles differences in measured $\delta^{18}O$ values from DSDP sites 516 and 525; the resulting paleotemperature reconstruction indicates a 4°C cooling of mid-latitude surface oceans since the Eocene. The strongest support of our model-correction strategy comes from comparison of model predictions with data from low latitude sites where most of the variation in measured $\delta^{18}O$ values can be accounted for by diagenetic effects including variations in the $\delta^{18}O$ record caused by changes in sedimentation rate. We show that the bulk carbonate data are consistent with approximately constant equatorial sea surface temperatures through most of the Cenozoic, with the possible exception of the early Eocene when slightly higher temperatures are indicated. This result emphasizes the importance of explicitly accounting for diagenetic overprinting in reconstructing past ocean temperatures from oxygen isotope records.

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