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Oxygen isotope exchange in a two-layer model of oceanic crust

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ABSTRACT

A numerical model is presented for the transport and exchange of oxygen isotopes in an idealized two-layer oceanic crust (basalt–carbonate) that is saturated with a non-advecting pore fluid open to the overlying ocean. The model allows for time-varying sedimentation rate, porosity, chemical diffusivity, and temperature-dependent ^{18}O fractionation factors. Reaction is modeled as solution-precipitation of calcite in the carbonate sediment and as modified solution-precipitation (basalt dissolves, smectite precipitates) in the basalt layer. Generic models, using input parameters that are typical of those measured in DSDP-ODP cores, and constant sedimentation rates, illustrate the behavior of the system sufficiently well to allow first-order effects to be discerned that have important implications for paleotemperature and ocean floor weathering studies.

The solution-precipitation reactions allow oxygen to be exchanged between the low- $\delta^{18}\text{O}$ basalt layer and the high- $\delta^{18}\text{O}$ carbonate sediment through the medium of the pore fluids. This results in $\delta^{18}\text{O}$ increasing upwards in the basalt and decreasing downwards in the sediment. Pore fluid $\delta^{18}\text{O}$ values decrease with depth from zero to values of -1 to -3‰ at the basalt–sediment interface, and to values of -7 to -15‰ within the basalt. Because reaction rates are slow relative to diffusion in the pore fluid, high-frequency $\delta^{18}\text{O}$ variations in the solid are preserved indefinitely, but the amplitude of the variations decreases as e^{-Rt} where R is the reaction rate (fraction reacted per unit time). The results suggest that the diagenetic shifts of the $\delta^{18}\text{O}$ values of benthic and high-latitude planktonic foraminifera samples younger than Oligocene age are typically negligible. For samples older than 50 Ma, diagenetic effects are typically significant, and generally cause estimates of bottom and high-latitude surface ocean temperatures in the Cretaceous and early Tertiary to be too high. On the other hand, the model suggests that diagenesis will shift the $\delta^{18}\text{O}$ values of low-latitude planktonic foraminifera to higher values, and that paleotemperature estimates of low-latitude surface waters, particularly in the Eocene and Oligocene, may be too low. Using a synthetic $\delta^{18}\text{O}$ record for DSDP Site 167, we demonstrate how numerical models can be used to correct specific measured records for diagenesis. This approach could provide a means of extracting paleotemperature information from heavily altered Late Cretaceous and older samples, and for quantifying the subtle effects of diagenesis on the $\delta^{18}\text{O}$ record at all sites.

1. Introduction

The upper part of typical oceanic crust consists of basalt overlain by a veneer of sediment. The relatively porous upper parts of the basalt sequence and the highly porous sediment are permeated by seawater-like pore fluid. Oxygen isotopes are sensitive indicators of chemical transport and exchange in this two-layer system be-

cause chemical reactions, particularly between basalt and pore fluid, can result in extensive isotopic redistribution between the three reservoirs. Knowledge of the extent of such redistribution is relevant to several basic questions including that of how the subduction of oceanic crust affects the oxygen isotopic evolution of the mantle, and how the isotopic composition of carbonate sediment is affected by diagenetic recrystallization. Measurements of the concentrations and isotopic compositions of constituents dissolved in pore fluids from Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) cores indicate that, in general, after a few million years,

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when the ocean floor has moved away from the ridge, chemical transport within the pore fluid is accomplished primarily by vertical diffusion with advection playing only a minor role. Consequently, it should be possible to approximate the isotopic evolution of the oceanic crust using a relatively simple one-dimensional model.

In this paper, we present results obtained using mathematical models to describe how the oxygen isotopic compositions of pore fluids and rocks evolve with time in an idealized, two-layer oceanic crust. We employ a mathematical treatment similar to that described by Richter and DePaolo [1,2], who treated Sr chemical and isotopic transport and exchange in carbonate sediments, but in this paper we include the underlying basalt as an integral part of the system. We use a finite difference method rather than a steady-state approximation so that the effects of time-dependent sedimentation rate, temperature, recrystallization rate, porosity, and $\delta^{18}\text{O}$ of pore fluid and seawater can be retained. To simplify the system, we consider only carbonate sediment. Observed pore fluid compositions, sedimentation rates, and porosity–depth relationships are used as guides for calibrating the model. An idealized temperature–depth history, based on a generalized ocean floor–heat flow relationship, is used to determine oxygen isotopic fractionation factors between minerals and water.

The primary objective of this modeling is to estimate qualitatively the magnitude and direction of the shifts in $\delta^{18}\text{O}$ that occur in the sedi-

ment and basalt. These estimates give insights into the way in which post-depositional diagenetic recrystallization may affect the isotopic compositions of foraminiferal tests used to reconstruct ocean paleotemperatures. The results of this effort accord confidence in current paleotemperature estimates by demonstrating that the diagenetic modification is generally small for samples younger than ca. 40 Ma. In addition, if carbonate recrystallization rates can be quantified, this type of modeling could prove useful for extracting paleotemperature information from altered samples by correcting the observed compositions for diagenetic overprinting. This approach is likely to be necessary to obtain ocean paleotemperature information for the Cretaceous and Jurassic, for which few, if any, unaltered samples exist.

There is evidence from the chemistry of pore fluids from DSDP and ODP cores that the processes that form the basis of our model occur in nature (Fig. 1). The pore fluids in both carbonate and non-carbonate sections generally show systematic variations in Ca^{2+} , Mg^{2+} , and $\delta^{18}\text{O}$ with depth below the sediment–water interface. The $\delta^{18}\text{O}$ values typically decrease downsection by 2–3‰ (although values as low as –9‰ exist), correlated with an increase in Ca^{2+} and a decrease in Mg^{2+} [3]. These chemical and isotopic gradients have been interpreted as resulting from slow alteration of the underlying basalt that involves the conversion of igneous minerals with high Ca contents and low $\delta^{18}\text{O}$ values, to smectite and other clay minerals that are low in Ca, high in Mg and have substantially higher $\delta^{18}\text{O}$ values [3,4]. Thus, the underlying basalt is a source of Ca and a sink for Mg and ^{18}O . Because the net contribution of ^{18}O to the pore fluid from recrystallization in the carbonate sediment is relatively small (although volcanic ash in the sediment can affect the profiles), the pore fluid profile in the sediment column is essentially determined by the boundary conditions imposed by the seawater at the top and basalt pore fluids at the bottom [4,5].

Aspects of the modeling developed here have been discussed previously in the literature. Killingly [6] calculated the effect of increasing temperature during burial on the isotopic composition of foraminiferal calcite. His model did not attempt to account for changing pore water $\delta^{18}\text{O}$,

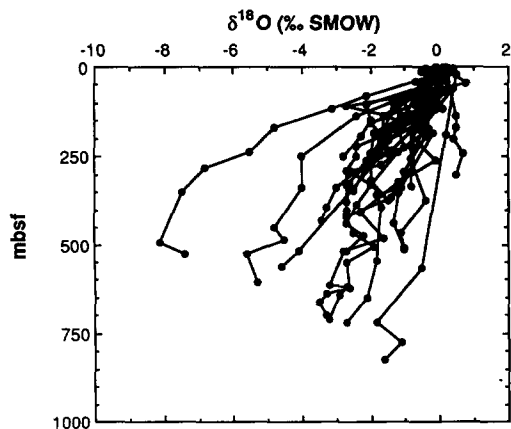


Fig. 1. Interstitial water analyses from 23 DSDP Sites [3] showing decreasing $\delta^{18}\text{O}$ with depth.

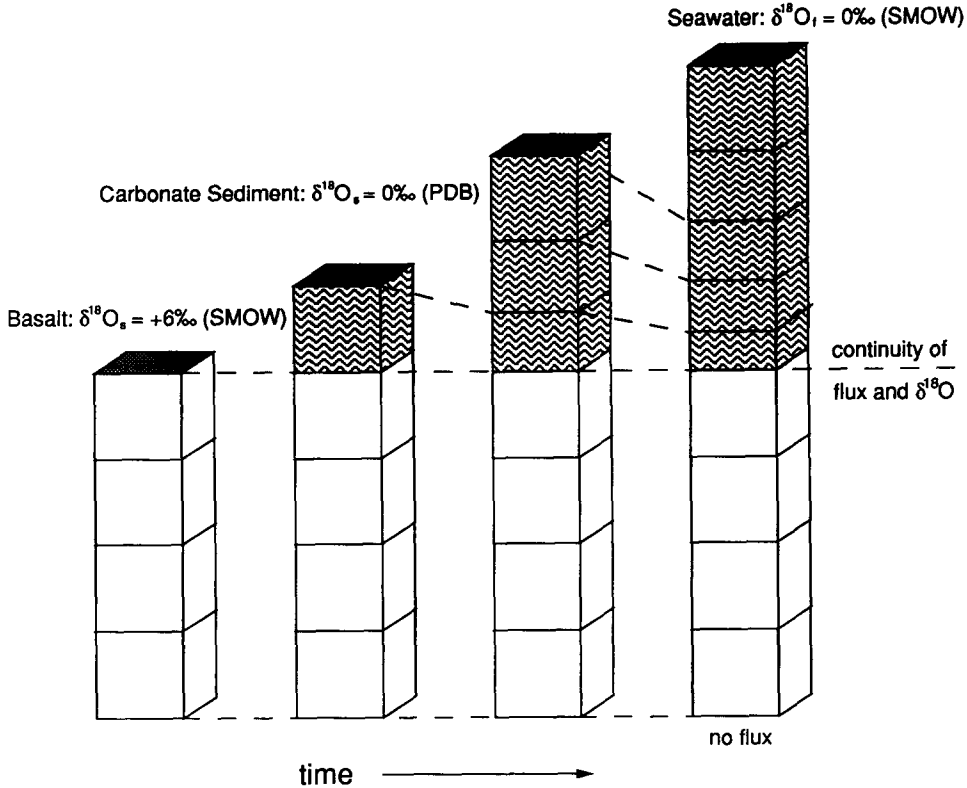


Fig. 2. Schematic representation of the numerical model. Boxes of carbonate sediment ($\delta^{18}\text{O} = 0\text{‰}$ PDB) are added to a column of basalt ($\delta^{18}\text{O} = +6\text{‰}$ SMOW). Compaction occurs as more boxes are added. The $\delta^{18}\text{O}$ of the fluid at the top of the sediment is fixed at zero to simulate seawater; no flux is allowed across the base of the basalt; and at the basalt–sediment interface, there is continuity of flux and $\delta^{18}\text{O}_f$.

but used the assumption that the secondary carbonate precipitated in equilibrium with seawater. Lawrence [7], McDuff and Gieskes [4] and McDuff [5] modelled the transport of ^{18}O , Ca^{2+} and Mg^{2+} in sediment pore fluids, demonstrating that diffusion is the dominant mechanism and that the major source for Ca^{2+} and sink for Mg^{2+} is the underlying basalt.

2. Description of the model

2.1 General description

The geometry of the model is illustrated with a schematic diagram (Fig. 2). The solids are treated as fluid-saturated porous media. We simulate the sedimentation process by successively adding boxes of carbonate sediment, initially 10 m thick, to a 1 km thick section of basalt. Compaction is simulated by allowing the porosity of each box to

decrease as it is buried in a manner consistent with observed porosity–depth relationships. The height of each box is determined from the decrease in porosity, conserving the mass of solid in each box.

The transport of oxygen by diffusion and advection in the pore fluid and reaction between fluid and solid are described by equations of mass conservation for the bulk solids and fluid. Following Richter and DePaolo [1], the conservation equation for a chemical species $C_{i,f}$ (i.e. the concentration of ^{16}O or ^{18}O in mass per unit mass of fluid) in the pore fluid is:

$$\frac{\partial C_{i,f}}{\partial t} = \frac{\partial \left(\phi D \frac{\partial C_{i,f}}{\partial z} \right)}{\phi \partial z} + U_f \frac{\partial (C_{i,f})}{\partial z} + \frac{(1 - \phi) \rho_s}{\phi \rho_f} R(C_{i,s} - k C_{i,f})$$

where ϕ = porosity, D = diffusion coefficient, U = advective velocity, ρ = density, and R = reaction rate (in mass fraction per unit time). The terms on the right-hand side of the equation represent respectively diffusion, advection and the source or sink of $C_{i,f}$ due to solution-precipitation of the carbonate sediment or chemical reaction of basalt to clay minerals. Similarly, the conservation equation for a chemical species $C_{i,s}$ in the bulk solid is:

$$\frac{\partial C_{i,s}}{\partial t} = U_s \frac{\partial(C_{i,f})}{\partial z} + R(C_{i,s} - kC_{i,f})$$

We ignore diffusion in the solid.

As the oxygen isotopic compositions of geologic materials are reported as $\delta^{18}\text{O}$ values, it is also useful to express the conservation equations in terms of $\delta^{18}\text{O}$. Converting the above equations into $\delta^{18}\text{O}$ notation, and defining Δ_{s-f} as the difference between $\delta^{18}\text{O}_s$ and $\delta^{18}\text{O}_f$ at equilibrium, yields the equations for fluid:

$$\begin{aligned} \frac{\partial(\delta^{18}\text{O}_f)}{\partial t} = & \frac{\partial\left(\phi D \frac{\partial(\delta^{18}\text{O}_f)}{\partial z}\right)}{\phi \partial z} + U_f \frac{\partial(\delta^{18}\text{O}_f)}{\partial z} \\ & + \frac{(1-\phi)\rho_s}{\phi\rho_f} \frac{O_s}{O_f} \\ & \times R(\delta^{18}\text{O}_s - \delta^{18}\text{O}_f - \Delta_{s-f}) \end{aligned}$$

and for solid:

$$\begin{aligned} \frac{\partial(\delta^{18}\text{O}_s)}{\partial t} = & U_s \frac{\partial(\delta^{18}\text{O}_s)}{\partial z} \\ & + R(\delta^{18}\text{O}_s - \delta^{18}\text{O}_f - \Delta_{s-f}) \end{aligned}$$

where O_s and O_f are the mass fractions of oxygen in the solid and fluid, respectively. The equations are solved numerically by finite difference.

The reaction terms in the conservation equations, while mathematically identical, represent processes that are different in the basalt than in the carbonate sediment. For the basalt, the reaction term represents the conversion of basalt to smectite. At each time step, a fraction of the fresh basalt dissolves and an equal mass of smectite precipitates in equilibrium with the pore fluid with $\Delta_{\text{smectite-H}_2\text{O}}$ calculated from model thermal gradients using the equation of Yeh and Savin [8]. Once basalt has been converted to smectite in the

model, it is no longer allowed to react. This is consistent with Rb-Sr dates of vein smectites [9] which imply that the smectite, once formed, is not subject to subsequent solution-precipitation. R is the reaction rate of basalt, expressed in mass fraction reacted per unit time.

For the carbonate sediment, the reaction term represents the process of solution and reprecipitation of calcite. At each time step, a fraction of the total carbonate (primary and secondary) dissolves and secondary carbonate precipitates in equilibrium with the pore fluid. The rates of dissolution and precipitation are set equal, so that the mass of carbonate remains constant with time. This is generally consistent with the observed gentle Ca gradients in pore fluids which imply that the mass of the solid is essentially conserved during carbonate diagenesis. As in the basalt alteration, $\Delta_{\text{calcite-H}_2\text{O}}$ is calculated from model thermal gradients using the equation of O'Neil et al. [10], adjusted for the fractionation factor between CO_2 and water reported by Friedman and O'Neil [11]. R is the rate of solution-precipitation, expressed in mass fraction of carbonate dissolved and reprecipitated per unit time.

2.2 Parameters

We have used generalized parameters, suggested by observations from DSDP and ODP cores, to evaluate the magnitude and direction of isotopic redistribution. The temperature gradient through the two-layer section is fixed at 40° km^{-1} with bottom water temperature fixed at 4°C . The model porosity of the sediment decreases with depth from an initial value of 0.7 to a minimum value of 0.4 below a depth of 575 m. The porosity in the basalt decreases with depth from 0.1 at the basalt-sediment interface to 0.01 at 1000 m deeper in the basalt. Diffusion coefficients are calculated from the model temperature gradient using measured values of the self-diffusion of water from 0 to 100°C [12]. We use the model porosity to account for tortuosity in the sediment, where $D = D_0\phi$. D_0 for the top of the sediment is $1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Diffusion coefficients for the pore water in the basalt are calculated as above, but D_0 is increased by a factor of four to account for lower expected tortuosity of fractured basaltic crust. Advection in the system, except

that due to compaction of sediment, is neglected. The results of two runs are shown in Fig. 3. In both runs, $R = 0.01 \text{ Ma}^{-1}$ (see below). Sedimentation rates are fixed at 10 and 20 m Ma^{-1} (uncompacted); this results in the accumulation of 650 and 1150 m of compacted sediment, respectively, after 100 m.y.

The reaction rate for the conversion of basalt to smectite is treated as a fit parameter, adjusted to produce model pore fluid profiles compatible with observations from DSDP and ODP cores. For $R = 0.01 (1\% \text{ Ma}^{-1})$ in the basalt, we are able to reproduce a range of isotopic gradients observed in pore fluids by adjusting the porosity of the basalt. The rate of solution-precipitation of the carbonate sediment has been constrained by several studies of Sr in marine carbonates.

Rates of solution-precipitation calculated in modeling studies using Sr isotopic compositions of sediments and pore fluids at DSDP Sites 575 and 590B are highest at the tops of the holes and decrease rapidly with sediment age after 10 Ma to minimum values between 0.5 and 1.0% Ma^{-1} [1,2]. A similar estimate was obtained by Baker et al. [13]. The rapid recrystallization in the first few million years after burial has been interpreted as due to dissolution of less-stable fractions of the bulk carbonate, whereas the rate of recrystallization that is asymptotically approached after 5 to 10 Ma may be representative of the slow dissolution and reprecipitation of more stable fractions including foraminiferal tests. As our chief interest is in the recrystallization of foraminiferal tests, we use a constant reaction rate, $R = 0.01 \text{ Ma}^{-1}$

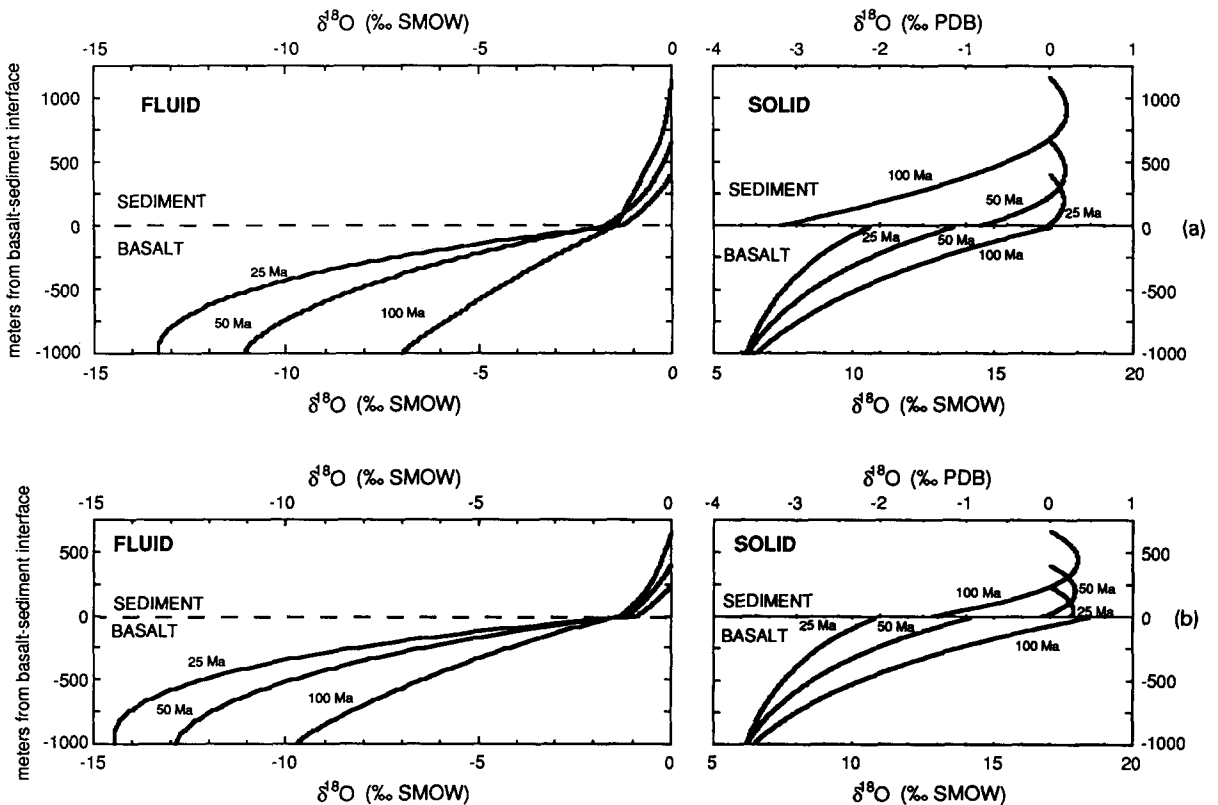


Fig. 3. Model outputs for run times of 25, 50 and 100 m.y. showing $\delta^{18}\text{O}$ profiles for pore fluids, basalt, and carbonate sediment for sedimentation rates of 20 (A) and 10 (B) m Ma^{-1} (uncompacted). In these runs, the rate of solution-precipitation, R , is held constant at 0.01 ($1\% \text{ Ma}^{-1}$). The other parameters used in the calculations are discussed in the text. Note change of scale for $\delta^{18}\text{O}$ of carbonate sediment.

(1% Ma⁻¹). Our decision to hold R constant is consistent with the observation that the preservation of foraminiferal tests decreases with depth [14], although this may not be true in all cases. The effects of changing the value of R are discussed below.

2.3 Boundary conditions

To simplify calculations, the $\delta^{18}\text{O}$ for both solids and fluids are calculated relative to SMOW, including solid carbonate (although we convert the carbonate output values to PDB to compare with published values). The initial $\delta^{18}\text{O}$ of the basalt and the bulk carbonate are set at the beginning of each run; for the generalized model we use initial $\delta^{18}\text{O}_{\text{carbonate}} = +30.86\text{‰}$ (0.00‰ PDB) and $\delta^{18}\text{O}_{\text{basalt}} = +6\text{‰}$. The pore fluid in the basalt and sediment is given an initial $\delta^{18}\text{O}$ value of 0‰. This is a reasonable initial condition for young oceanic crust following hydrothermal circulation of seawater. The $\delta^{18}\text{O}$ of the fluid at the top of the sediment is fixed at 0‰ to simulate the composition of seawater. Changes in the oxygen isotopic composition of seawater could be incorporated in the model by allowing this boundary condition to vary with time; this is not done here so as to evaluate the effects of isotopic redistribution separately from other changes in ocean conditions. At the base of the basalt, we apply a no-flux boundary condition. At the basalt–sediment interface where there is a discontinuous change in porosity and diffusivity, we use a condition satisfying the continuity of flux and isotopic composition of the fluid [15].

3. Results

3.1 Pore fluid

We show pore fluid $\delta^{18}\text{O}$ profiles for calculations with two different sedimentation rates (20 m Ma⁻¹, Fig. 3A; 10 m Ma⁻¹, Fig. 3B) for run times of 25, 50 and 100 m.y. The general geometry of the profiles is the same for all calculations. The $\delta^{18}\text{O}$ in the sediment decreases with depth. The curvature in the profiles is due to the decreasing porosity and diffusivity downsection in the sediment. At the basalt–sediment interface, there is a change in slope of the $\delta^{18}\text{O}$ -depth

profile due to the discontinuous change in porosity and diffusivity. Below the interface, the $\delta^{18}\text{O}$ of pore fluid in the basalt decreases sharply through a diffusive boundary layer. Below this boundary layer, the fluids are near isotopic equilibrium with basalt due to low fluid–rock ratios and the no-flux boundary condition at the base of the basalt. The $\delta^{18}\text{O}$ -depth gradients in the sediment produced with these parameters (2–3‰ km⁻¹) are in the range of observed values. The minimum $\delta^{18}\text{O}$ values in the sediment at any time are within 1‰ of each other. This relatively small range in values reflects primarily the amount of reaction in the basalt which is the same for all calculations. To achieve steeper gradients, the reaction rate can be increased or, alternatively, some advection in the basalt can be added to bring the highly depleted fluids deep in the basalt up to the basalt–sediment interface more rapidly.

The pore fluids at the base of the sediment become more depleted in ¹⁸O with time because the distance from the seawater boundary increases as sediment accumulates. The fluids in the basalt become less depleted in ¹⁸O with time. This is due to increase in temperature in the basalt with time, and the associated decrease in the fractionation factor for the smectite–water system, as well as to the decreased fraction of fresh basalt available for reaction.

The profiles do vary with sedimentation rate but there are two opposing effects. If more distance is placed between a box of sediment and the sea floor, the increased length of the diffusion pathway causes the pore fluid to become more depleted in ¹⁸O. However, the thicker sediment cover causes increased temperatures in the basalt and that causes an increase in the $\delta^{18}\text{O}$ values of the pore fluid. The pore fluid profiles are not sensitive to changes of several per mil in the initial composition of carbonate. Although the effects of non-carbonate phases in the sediment, particularly unaltered volcanic ash, were not studied in the model calculations, it is clear that they will locally influence the pore fluid composition.

3.2 Basalt

The $\delta^{18}\text{O}$ profiles of the altered basalt show extreme isotopic enrichment through the diffu-

sive boundary layer where the $\delta^{18}\text{O}$ values of pore fluids shift, as a result of diffusion, towards the seawater value. The shifts are larger for the lower sedimentation rate because, with thinner sediment cover, the temperatures are lower in the basalt. The evolution of the isotopic composition of the basalt depends on the thickness of the diffusive boundary layer in the pore fluid; increasing the thickness of the boundary layer causes increased enrichment in ^{18}O in the basalt. This can be accomplished by raising the diffusivity and porosity, or lowering the reaction rate. Changing the reaction rate below the boundary layer does not significantly affect the pore fluid composition because the fluids are already near isotopic equilibrium with basalt. The profiles are similar to the $\delta^{18}\text{O}$ profiles observed in ophiolites, which have previously been ascribed to temperature gradients in ridge-proximal hydrothermal systems [16]. These calculations suggest that part of the oxygen isotopic composition of older oceanic crust could be determined to a significant extent by low-temperature weathering reactions away from a ridge hydrothermal system.

3.3 Carbonate sediment

The $\delta^{18}\text{O}$ of the carbonate sediment is calculated by the model to be shifted first very slightly to higher values and then to lower values with increasing depth and age. Shifts are particularly large for the oldest sediments (1–3‰), which in the model have Cretaceous and early Tertiary ages. The $\delta^{18}\text{O}$ values of sediments younger than 40 Ma are shifted by less than 0.2‰. The magnitude of the shift in $\delta^{18}\text{O}$ values of carbonate sediment is dependent on pore fluid composition and temperature. Decreasing the temperature gradient from 40‰ km⁻¹ to 20‰ km⁻¹ decreases the shift in 100 Ma old sediments by approximately 50%. This results in part from the increase in the $\delta^{18}\text{O}$ -depth gradient in the pore fluid caused by lower temperatures in the basalt. This offsets the effect of lower temperatures on the carbonate–water fractionation factor. Increasing the sedimentation rate increases the shift, simply by increasing the burial depth of each package of sediment. This results in increased temperature and decreased $\delta^{18}\text{O}$ of the pore fluid. We conclude that diagenetic modifica-

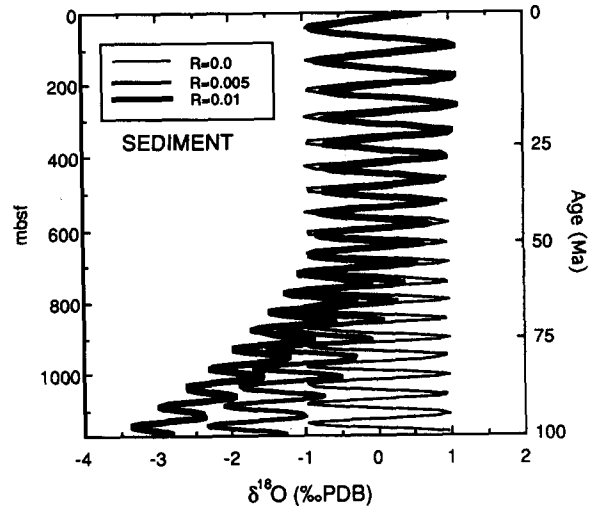


Fig. 4. Model outputs showing $\delta^{18}\text{O}$ profiles for three different rates of solution-precipitation of the carbonate sediment, $R = 0.0$ (light line), $R = 0.005$ (medium line), and $R = 0.01$ (heavy line). All other parameters are the same as in Fig. 6A. An oscillation in the initial $\delta^{18}\text{O}$ of the carbonate sediment illustrates how diagenesis preserves the stratigraphic position of high-frequency signals deposited in the record, but the amplitude of such signals decreases with age.

tion of $\delta^{18}\text{O}$ values should normally be greatest at locations where sedimentation rates are highest.

Figure 4 shows the results of three model calculations for three different recrystallization rates of carbonate sediment, with all other parameters, except for the initial $\delta^{18}\text{O}$ value of the carbonate, the same as in Fig. 3A. In these calculations, we vary the initial $\delta^{18}\text{O}$ value of the carbonate sediment in the model with time by a sine function to illustrate how recrystallization affects high-frequency signals. Increasing R from 0.005 Ma⁻¹ to 0.01 Ma⁻¹ increases the shift in the low-frequency isotopic signal by over 1‰ after 80 Ma (Fig. 4). Recrystallization also affects the high-frequency signal. For $R = 0.0$ Ma⁻¹ (no recrystallization), the original isotopic composition deposited at the sea floor is unaltered. For higher rates ($R = 0.005$ Ma⁻¹ and $R = 0.01$ Ma⁻¹), the high-frequency oscillations are preserved at the precise stratigraphic location at which they were deposited but the amplitudes of these oscillations are diminished. The ratio of the amplitude of the original high-frequency signal (A_0) to the amplitude of the dampened signal

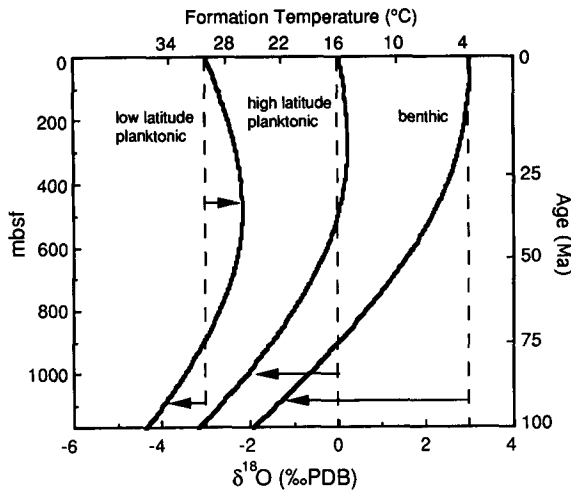


Fig. 5. Model outputs for three different initial $\delta^{18}\text{O}$ values of carbonate: $\delta^{18}\text{O} = +3\text{‰}$ (benthic assemblage), $\delta^{18}\text{O} = 0\text{‰}$ (high-latitude planktonic assemblage), and $\delta^{18}\text{O} = -3\text{‰}$ (low-latitude planktonic assemblage). For all three runs, $R_{\text{sediment}} = 0.01$. All other parameters are the same as in Fig. 6A. The model demonstrates how diagenesis may affect the $\delta^{18}\text{O}$ of low-latitude planktonic foraminifera differently from benthic or high-latitude planktonic foraminifera.

(A) is exponentially related to the recrystallization rate by the equation: $A/A_0 = e^{-Rt}$.

In Fig. 5, we show the sensitivity of the model to the initial $\delta^{18}\text{O}$ of the carbonate sediment with three calculations for initial $\delta^{18}\text{O}$ values of -3 , 0 , and 3‰ (PDB), roughly equivalent to the isotopic compositions of low- and high-latitude planktonic, and benthic assemblages, respectively. All other parameters are the same as for the calculation in Fig. 3A. Changing the initial composition of the carbonate by a small amount does not change the diagenetic environment in the model because the pore fluid composition in the model is controlled primarily by alteration of the underlying basalt. While the $\delta^{18}\text{O}$ of benthic and high-latitude planktonic assemblages are shifted to lower values by diagenesis, the $\delta^{18}\text{O}$ of the low-latitude planktonic assemblage has an initial $\delta^{18}\text{O}$ much lower than the equilibrium values with the cold pore fluids experienced during the initial stages of diagenesis, and is shifted first to higher values, and then to lower values. In this case, the shifts for younger sediments between 20 and 40 Ma are significant.

4. Discussion

4.1 Implications for ocean paleotemperatures

How does the substantial modification of the $\delta^{18}\text{O}$ of the carbonate sediment described by the model relate to possible modification of the $\delta^{18}\text{O}$ of foraminiferal calcite used to reconstruct ocean paleotemperatures? Because the pore fluid composition in the model is controlled primarily by alteration of the underlying basalt, the model describes how the $\delta^{18}\text{O}$ of an individual foraminiferal test with the same initial composition as the model carbonate will change if it were to recrystallize, either by replacement of primary biogenic material or by overgrowth of small crystals onto test surfaces. In the remainder of this section, we discuss specific aspects of the model as they relate to this question regarding interpretation of the foraminiferal oxygen isotopic record. Specifically, we consider whether diagenetic modification might have affected the $\delta^{18}\text{O}$ of foraminiferal tests used for paleotemperature reconstructions through the Cenozoic. In addition, we demonstrate how this modeling approach can be used to extract paleotemperature information from altered samples.

4.2 The Cenozoic paleotemperature record

Researchers have been aware of the potential for diagenetic recrystallization to change the $\delta^{18}\text{O}$ of primary biogenic calcite since Urey et al. first introduced the isotopic method for measuring past ocean temperatures [17]. More recently, Killingly [6] calculated the effect of increasing temperature during burial on the isotopic composition of foraminiferal calcite, concluding that diagenesis could conceivably be responsible for the entire long-term change seen in the isotopic records from the latest Cretaceous to the present. His model did not deal with changes in pore water $\delta^{18}\text{O}$, but assumed that the secondary carbonate precipitated in equilibrium with seawater. More importantly, Killingly assumed that 80% of the carbonate was recrystallized after 60 m.y. It has been reported in most studies of oxygen isotopes in foraminifera that the selected samples have little if any secondary calcite. As a result, Killingly's conclusions have been taken to have

little bearing on what is observed in the sediment [18]. In this discussion, we consider the more relevant question of how a small amount of secondary calcite can change the original $\delta^{18}\text{O}$ of a foraminiferal test.

Many investigators have claimed that it is possible to select pristine, diagenetically unmodified foraminiferal tests from the bulk sediment. However, there is strong evidence that even the best preserved foraminiferal tests do undergo some recrystallization during diagenesis. In numerous SEM studies, euhedral calcite crystals have been observed lining the inner walls of foraminiferal chambers as well as replacing of test walls [e.g. 19,20]. This secondary calcite may be overlooked as specimens are often selected using only binocular microscopy. For example, Barrera et al. [21] in a study of Late Cretaceous and Paleocene foraminifera from Seymour Island, found that while samples appeared well preserved under the binocular microscope, and no overgrowth was observed on outer surfaces of shells, dissolution was ubiquitous and internal infilling and overgrowth existed in all tests where total carbonate in the bulk sample exceeded only 1%. Those tests with infilling or overgrowths were depleted in ^{18}O by 1‰ or 2‰ relative to tests which lacked such alteration. This observation suggests that the predictions of our modeling are qualitatively correct.

The generic model calculations discussed in earlier sections give several important insights into how a foraminiferal test will be affected by diagenetic recrystallization. First, the model shows that the extent of diagenetic modification is dependent on many parameters including sedimentation rate, temperature gradient, $\delta^{18}\text{O}$ -depth gradient, and recrystallization rate. Because each of these parameters may vary with time and from site to site, it is not possible to evaluate the extent of diagenetic modification by comparing measured $\delta^{18}\text{O}$ values from different sites against a single variable such as burial depth. This approach has been used by some researchers to dismiss diagenetic modification as a factor in composite records [22].

The calculations that included a high-frequency oscillation in the initial composition of the carbonate (Fig. 4) show that such high-frequency signals resulting from actual changes in ocean temperature or isotopic composition will not be

eliminated by diagenesis, but the amplitude of these signals will be dampened. Because the amount of dampening is only a function of the recrystallization rate and time, it could be possible to use this relationship to calculate recrystallization rates for actual samples if it were assumed that the original signal was the same at different sites. In any case, the existence of such high-frequency signals at the same stratigraphic position, such as at the Eocene–Oligocene boundary, does not preclude significant diagenetic modification, as some workers have argued [18], because the absolute $\delta^{18}\text{O}$ values of the samples can be systematically shifted without erasing the high-frequency signal.

The model calculations indicate that the direction and magnitude of diagenetic changes in $\delta^{18}\text{O}$ of planktonic foraminifera at different latitudes differ, as do the magnitude of shifts of benthic and planktonic foraminifera, even if the recrystallization rates are the same (Fig. 5). In general, if the tests have undergone partial recrystallization, the measured $\delta^{18}\text{O}$ values of benthic and high-latitude planktonic foraminifera yield overestimates of paleotemperature. The error should normally be negligible for samples younger than 40 Ma. In contrast, the measured $\delta^{18}\text{O}$ values of low-latitude planktonic foraminifera that have been diagenetically altered, should yield underestimates of paleotemperature, with the maximum error occurring in Eocene- and Oligocene-age samples. The $\delta^{18}\text{O}$ values of benthic and planktonic foraminiferal tests are also affected differently by changes in sedimentation rate. Low sedimentation rates generally reduce the diagenetic shift for benthic and high-latitude planktonic foraminifera because shallow burial keeps the foraminiferal tests in a temperature/ $\delta^{18}\text{O}$ environment similar to that in which they formed. Low sedimentation rates have the opposite effect for low-latitude planktonic foraminifera because shallow burial keeps the tests in contact with pore fluids much colder than the surface waters in which they formed.

With these insights into how foraminiferal tests may be affected by diagenetic recrystallization, we conclude that the Cenozoic benthic foraminifera $\delta^{18}\text{O}$ record from the present back to 40 Ma is relatively insensitive to diagenetic modification, and therefore is a robust indicator

of changes in paleotemperature and ice volume. However, for sediment ages greater than 50–60 Ma, the benthic $\delta^{18}\text{O}$ record is suspect. The effect of diagenesis on the Cenozoic record of surface water temperatures from planktonic foraminifera is more complicated to evaluate. For high-latitude sites, the situation is similar to the benthic record. The potential error is relatively small for samples younger than 40 Ma; for older samples, measured $\delta^{18}\text{O}$ values may indicate surface water temperatures as much as 4°C too high (1‰). Low-latitude planktonic foraminifera are most susceptible to modification during early diagenesis because they are deposited on the sea floor far from isotopic equilibrium with the surrounding pore fluid. Consequently, the relatively

low equatorial sea surface temperatures inferred for the Eocene and Early Oligocene [23] could be a diagenetic artifact. This has significant implications, particularly for Eocene climate. The cool low-latitude sea surface temperatures in the Eocene partially balance the warm high-latitude sea surface temperatures, resulting in little or no change in the globally averaged sea surface temperature. Some workers, therefore, have argued that the Eocene ocean–atmosphere system was characterized by a more effective mode of ocean heat transport than today's, rather than by higher atmospheric CO_2 [23,24]. If the low-latitude sea surface temperature estimates are too low and instead the temperatures were comparable to modern values, then the Eocene high-latitude

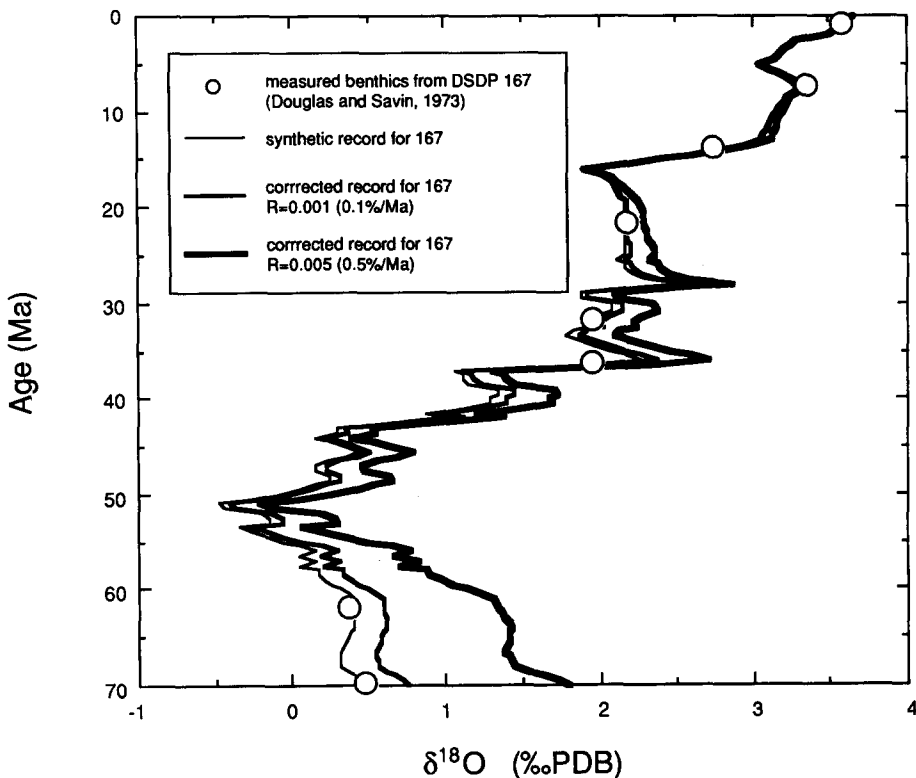


Fig. 6. Model calculation to correct a synthetic benthic foraminiferal record for DSDP Site 167. The heavier lines give the oxygen isotopic compositions of benthic foraminifera corrected for diagenesis. After diagenetic alteration by the model at constant recrystallization rates of $0.5\% \text{ Ma}^{-1}$ (heaviest line) and $0.1\% \text{ Ma}^{-1}$, the lines are shifted to reproduce the synthetic record (lightest line). This calculation demonstrates how the model can be used to correct data collected from specific DSDP and ODP Sites if the parameters can be accurately determined.

warmth may require external forcing such as increased atmospheric CO_2 .

4.3 *Extracting paleotemperature information from altered samples*

If the parameters in our model are measured in situ on DSDP and ODP cores, then a site-specific model can be constructed, and it may be possible to correct measured $\delta^{18}\text{O}$ values of bulk carbonate or foraminiferal tests for the effects of diagenesis. Such corrections to the measured record could allow paleotemperature information to be extracted from Late Cretaceous and possibly older sediments, in which few unaltered foraminifera samples exist. Site-specific models could also be used to enhance confidence in paleotemperature estimates for younger samples.

An important source of uncertainty involves the recrystallization rate of foraminiferal calcite, which is directly proportional to the size of the shift in $\delta^{18}\text{O}$ caused by diagenesis. It may be possible to quantify R using geochemical methods similar to those used by Richter and DePaolo [1,2] and Baker et al. [13] for bulk carbonate. Evaluating the extent of recrystallization of foraminiferal tests over an entire core may prove difficult, however, because the rate of solution-precipitation of foraminiferal tests may depend on attributes such as size, shape, internal structure and subtle variations in shell chemistry which vary between different foraminifera within the same sample.

To illustrate how a measured isotopic record could be corrected for the effects of diagenesis, we have created a synthetic, high-resolution, benthic $\delta^{18}\text{O}$ record for DSDP Site 167 based on data from Douglas and Savin [25] and corrected it for diagenesis which we assume to have occurred at fixed rates of recrystallization of the foraminiferal calcite. We have used sedimentation rates and porosities measured at Site 167. As the isotopic compositions of pore fluids were not measured at Site 167, we used minimal $\delta^{18}\text{O}$ -depth gradients of -1.5‰ km^{-1} . We have allowed the $\delta^{18}\text{O}$ of seawater to change from -1‰ to 0‰ during the model run in two rapid shifts of 0.5‰ at the Eocene–Oligocene boundary and 0.35‰ in the Middle Miocene, with the remaining 0.15‰ occurring since the Pliocene. We cal-

culated the corrected record for two different recrystallization rates, $R = 0.005$ ($0.5\% \text{ Ma}^{-1}$) and $R = 0.001$ ($0.1\% \text{ Ma}^{-1}$). These values correspond to approximately 25% and 5% secondary calcite in foraminiferal tests of Paleocene age, respectively. We obtained the corrected records with a series of forward calculations. For each initial run, we used initial $\delta^{18}\text{O}$ values of carbonate from the synthetic record and ran the model to calculate the shifts from the synthetic record due to diagenesis. We added these shifts to the previous initial compositions, and ran the model using the new initial $\delta^{18}\text{O}$ values. After three iterations, we obtained a set of initial compositions (the corrected record) which produce output values from the model which are within 0.02‰ of the synthetic record.

As expected from the results of the generic model discussed above, the corrected benthic records have higher $\delta^{18}\text{O}$ values than the “measured” (synthetic) record. For ages younger than 50 Ma, the corrections are small ($< 0.3\text{‰}$), even for the higher recrystallization rate. For the oldest sediment (70 Ma), the correction for the low recrystallization rate is still only 0.24‰ . For the higher recrystallization rate, the correction becomes large after 50 Ma. The oldest sediment is corrected by 1.28‰ , which corresponds to an overestimate of bottom water temperature by over 5°C in the uncorrected data set. The corrected record indicates that Late Cretaceous bottom water temperatures were similar to those in the Early Oligocene.

5. Conclusion

A simple numerical model is used to simulate key aspects of the pore fluid–basalt–sediment system and estimate how oxygen isotopic compositions are changed as a result of diagenesis. Calculated $\delta^{18}\text{O}$ values of pore fluids decrease gradually with depth in the sediment column and reach even lower values in the basalt (-7 to -15‰ SMOW). The low $\delta^{18}\text{O}$ values are produced by the conversion of low- $\delta^{18}\text{O}$ fresh basalt to high- $\delta^{18}\text{O}$ smectite. The same reactions cause the basalt to be enriched in ^{18}O , with the enrichment increasing upwards in the section. The basalt $\delta^{18}\text{O}$ profiles produced by the model are similar to those observed in ophiolites, suggesting that

the observed profiles may reflect low-temperature weathering of basalt away from ridge hydrothermal systems. The direction and magnitude of $\delta^{18}\text{O}$ -shifts in the carbonate sediment produced by recrystallization depend on many parameters including sedimentation rate, temperature gradient, $\delta^{18}\text{O}$ -depth gradient in the pore fluid, and recrystallization rate. The shift also depends on the initial isotopic composition of the carbonate; the $\delta^{18}\text{O}$ of calcite formed in warm surface waters is shifted to higher values, whereas the $\delta^{18}\text{O}$ of calcite formed in cold bottom waters is shifted to lower values. The model predicts that diagenetic modification will preserve the stratigraphic position of high-frequency changes in ocean temperature or isotopic composition, but the amplitude of such signals will decrease with continued recrystallization. The results suggest that the diagenetic modification of $\delta^{18}\text{O}$ measured in benthic and high-latitude planktonic foraminifera samples younger than Oligocene is negligible except where there have been extremely high rates of recrystallization ($R > 0.01$). For samples older than 50 Ma, estimates of bottom and high-latitude surface ocean temperatures in the Cretaceous and Early Tertiary may be too high. Estimates of low-latitude surface water temperatures in the Eocene and Oligocene may be too low by as much as 8°C. Using a synthetic $\delta^{18}\text{O}$ benthic record for DSDP Site 167, we demonstrate how numerical models can be used to correct specific measured records for diagenesis. The model-correction approach could provide a means of extracting paleotemperature information from heavily altered Late Cretaceous and older samples, and evaluating the contribution of diagenesis to the $\delta^{18}\text{O}$ record at specific sites, provided that the parameters used in the model can be determined with sufficient accuracy.

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