EQUATORIAL PACIFIC CALCIITE PRESERVATION CYCLES: PRODUCTION OR DISSOLUTION?

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Abstract: In the Equatorial Pacific Ocean, the depth and shape of the calcite lysocline appears to have changed significantly in response to climate forcing (Farrell and Prell, 1989). Taking the Farrell and Prell record as face value, the lysocline apparently became steeper during each of the last eight glacial stages. Also, the accumulation rate of calcite during the last glacial maximum was 2-4 times higher than it was during the previous interglacial (Archer, 1952, 1988; Broecker, 1971; Farrell, 1991). A numerical model for calcite dissolution in sediment is used to interpret these observations. The model was validated by comparison with observations from the present day ocean; these results are presented elsewhere. If the lysocline fluctuations in the equatorial Pacific are primarily a dissolution record, then changes in the glacial Pacific [CO2] of 20-40 μM can be inferred. Here I offer the alternative explanation that cycles in equatorial production are responsible for the observations. Higher rates of calcite and organic carbon rain to the sediment in the equatorial region would have depressed the calcite lysocline and increased the calcite accumulation rate, as observed. A twofold increase in glacial production appears to be adequate to explain the observations, but a precise determination is prevented by uncertainties in some of the model parameters.

INTRODUCTION

The character of the central equatorial Pacific Ocean is dominated by upwelling of nutrient-rich water driven by the Ekmann divergence. Nutrient availability at the sea surface supports high levels of new productivity, potentially representing a significant fraction of the global new production (Chavez and Barber, 1987). During El Niño, the dynamics of the upper equatorial ocean change such that the upwelling ceases. The impact of El Niño is felt around the world in patterns of rainfall, wind, and temperature (Enfield, 1989). These observations attest to the pivotal nature of the Equatorial Pacific to the Earth's climate. The equatorial Pacific may have been as significant to the glacial climate as it is to today's climate. The geologic record of calcite preservation in the sediments under the equatorial Pacific may serve as a constraint on the glacial production and water column chemistry in this region. The depth and shape of the glacial lysocline changed regularly in response to glacial forcing, with higher calcite preservation during glacial times than during interglacials (Farrell and Prell, 1989). Also, the accumulation rate of calcite near the equator was 2-4 times higher during the last glacial than it was during the previous interglacial (Farrell, 1991; Archer, 1952, 1988; Broecker, 1971; Lyle et al., 1988).

Two alternative explanations have been offered. The "dissolution hypothesis" is that the observed cycles reflect changes in dissolution driven by bottom water chemistry (Bjerg, 1998; Farrell and Prell, 1989). Generating such a dissolution signal would require a steeper gradient in the saturation state of calcite, AODC, with depth in the glacial Pacific, of a magnitude similar to or greater than the present-day transition between North Atlantic Deep Water (NADW) and Antarctic Bottom Water (AABW) in the western Atlantic. Thus, this explanation could be interpreted as evidence for the existence of two distinct water masses in the glacial deep Pacific Ocean. Alternatively, the "production hypothesis" is that the calcite preservation cycles are driven by changes in the rain rates of calcite and organic carbon to the sediments (led to productivity at the surface ocean) (Archer, 1988). In this
scenario, the water column $\text{ACO}_2$ may have changed in response to glacial forcing, but in the absence of a major change in glacial Pacific circulation, this change would probably be much different. A numerical model of the processes controlling calcite dissolution and preservation is applied to the evaluation of these hypotheses.

**CARISSON CYCLE CONSTRAINTS FROM THE PALEOCENOCHRONOGRAPHIC LITERATURE**

Because of the importance of the equatorial Pacific to understanding global climate, and because calcite is preserved in this region, there are many constraints on the glacial carbon cycle in this region that can be inferred from the paleoceanographic literature. These include records of the concentration and accumulation rate of calcite in sediments as a function of depth and latitude, and inferred changes in the surface productivity rate based on various sedimentary indicators. Also, changes in the water column carbonate chemistry have been suggested based on changes in the depth distribution of nutrients in the ocean and on our understanding of the global alkalinity cycle. A summary of these constraints on the glacial carbon cycle in the equatorial Pacific will be elaborated, before the model results are presented.

**The Shape of the Glacial Lysocline**

Recently, an elegant reconstruction of the equatorial Pacific lysocline over the last eight glacial cycles was presented by Farrell and Prell [1989]. This reconstruction is reproduced in Figure 1. The calcium carbonate content (dry weight %) was measured in 16 cores as a function of depth (Table 1). The calcium preservation records were combined into a single time history and compared, resulting in a plot of the depths of the calcite lysocline (constant calcite content) as a function of time. The reconstruction suggests that the depth of calcite depletion to 10% (the "carbonate critical depth", or $\text{CCD}$, as defined by Farrell and Prell [1989]) remained constant with depth.

**TABLE 1. Cores Comprising the Farrell and Prell [1989] Data Set**

<table>
<thead>
<tr>
<th>Location*</th>
<th>Core</th>
<th>Depth, m</th>
<th>Latitude</th>
<th>Longitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>V24-55</td>
<td>4189</td>
<td>203N</td>
<td>13438W</td>
</tr>
<tr>
<td>2</td>
<td>WB402A-14GC</td>
<td>4287</td>
<td>073N</td>
<td>13550W</td>
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<td>4</td>
<td>SDOE 59</td>
<td>4370</td>
<td>312N</td>
<td>13796W</td>
</tr>
<tr>
<td>5</td>
<td>RC11-209</td>
<td>4400</td>
<td>255N</td>
<td>14074W</td>
</tr>
<tr>
<td>6</td>
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<td>4420</td>
<td>149N</td>
<td>14095W</td>
</tr>
<tr>
<td>7</td>
<td>PLDS 130-131</td>
<td>4471</td>
<td>400N</td>
<td>13600W</td>
</tr>
<tr>
<td>8</td>
<td>V24-58</td>
<td>4490</td>
<td>210N</td>
<td>14540W</td>
</tr>
<tr>
<td>9</td>
<td>V28-179</td>
<td>4509</td>
<td>137N</td>
<td>13936W</td>
</tr>
<tr>
<td>10</td>
<td>SDOE 60</td>
<td>4540</td>
<td>132N</td>
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<td>DSDP 574</td>
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<td>12</td>
<td>V24-59</td>
<td>4606</td>
<td>254N</td>
<td>14332W</td>
</tr>
<tr>
<td>13</td>
<td>RC12-66</td>
<td>4737</td>
<td>33N</td>
<td>14813W</td>
</tr>
<tr>
<td>14</td>
<td>V24-62</td>
<td>4834</td>
<td>304N</td>
<td>15735W</td>
</tr>
<tr>
<td>15</td>
<td>RC12-65</td>
<td>4868</td>
<td>479N</td>
<td>14458W</td>
</tr>
<tr>
<td>16</td>
<td>RC12-63</td>
<td>4919</td>
<td>58N</td>
<td>14739W</td>
</tr>
</tbody>
</table>

* Locations numbers correspond to numbers in Figure 2a.

Fig. 7. Shape of the calcite lysocline as a function of time from the equatorial Pacific. From Farrell and Prell [1989].
over the last eight glacial cycles, while the depth of the 80% isopleth (the "top" of the lysocline) fluctuated systematically between deeper positions during glacial and shallower during interglacials. Thus the thickness of the lysocline appears to have changed in response to glacial forcing.

The first potential pitfall that must be considered when interpreting these data is the possibility of "chemical resides" [Keir, 1984; Farrell and Prell, 1989], When the steady state surface sediment calcium concentration changes from high calcium to low calcium (in response to a decrease in overlying water Ca²⁺) some of the calcium from the high-calcite era, preserved below the sediment mixed layer, may dissolve. This transient behavior could potentially alter the glacial (high-calcite) parts of the calcite record.

We will consider the worst-case scenario of no calcite preservation during the low-calcite era, that is, a transition from a mixture of calcite and denitral material in the sediment mixed layer (~4 cm deep) to a condition of no calcite in the mixed layer. At the end of the transition, 8 cm of denitrational material is required, this material could either come from the sediment rain or be mixing up from below, by dissolution of old calcite (chemical resides), depending on which is faster.

The question of chemical resides is most crucial to the Farrell and Prell dataset at sites CRC12-63 and CRC12-63 (4808 and 4809 m; 4°39′ and 5°19′N). The accumulation rates of non-calcitic material from these locations were about 65 mg cm⁻² kyr⁻¹ during the past 70 ka [Farrell, 1991]; based on this, the time scale for the accumulation of 8 cm of denitrational material was about 40 kyr (using a dry bulk density of low-calcite sediment 0.322 from Farrell [1991]). The time-scale of chemical resides has been estimated to be up to 10 kyr or less [Keir, 1984], depending on the magnitude of the change in bottom water chemistry. Since dissolution can apparently supply the needed non-calcite material to the sediment surface faster than it can accumulate by sedimentary rain, the source of the required denitrational material might have been by chemical resides of glacial sediments below the mixed layer.

The second question is, how much of the glacial age calcite dissolves at the glacial/interglacial transition? The answer can be calculated as the proportion of the total glacial inventory of non-calcite material that is needed in the new steady state mixed layer. During the glacial era, the accumulation rates of non-calcite material in sites CRC12-63 and CRC12-63 were 40 and 65 mg cm⁻² kyr⁻¹ [Farrell, 1991]. Based on this, the accumulation of a total of 8 cm of denitrational material during the glacial era would have taken 40-50 kyr. Thus 40-50 kyr of calcite accumulation could dissolve to supply the needed non-calcite material to the mixed layer. This time scale is similar to the 50-60 kyr duration of the high-calcite periods recorded in the shallower part of the Farrell and Prell record. We conclude that the potential exists for the deeper part of the Farrell and Prell record to be affected by chemical residues.

The second potential complication to the interpretation of the Farrell and Prell record is a latitudinal bias in the record. Figure 2a is a bathymetric plot of the depths of the cores used in the reconstruction, plotted as a function of latitude (station depths and locations in Table 1). A general trend is evident, with shallowest depths in Figure 1 represented by cores from within 0°-3°N, and deeper regions all from 2°-5° latitude. The deepest core (CRC12-63) comes from nearly 9°N. During the last glacial maximum (an extreme case), the entire calcite lysocline is interpreted between the 8°N core and the two immediately shallower, located at 3° and 4°39′ (V24-62 and CRC12-63) (Figure 2b).

Fig. 2. (a) Bathymetric plot of the locations of the sediment cores used by Farrell and Prell [1991] to create Figure 1. Location numbers correspond to members in Table 1. A general trend is evident, with cores used to create the shallower part of the record closer to the equator than cores from the deeper part of the record. The shallower part of the record may be affected by changes in equatorial productivity. (b) The shape of the lysocline today, during the last glacial maximum, and during the last interglacial, from the Farrell and Prell record.
Thus the glacial calcite lysolines could be explained by variations in production with latitude as easily as by changes in dissolution with depth.

Calcite Accumulation Rate

Another constraint to the dynamics of calcite rain and dissolution comes from the inferred calcite accumulation rate from the equatorial region. The best available accumulation rate data come from Parfiell [1991], some of which are presented in Table 2. Because of the difficulty of evaluating present-day accumulation rates, values from the previous low-calcite period (75–120 ka) are used. To independently evaluate the effects of latitude and depth, the data are divided into groups of roughly constant depth, and ordered as a function of latitude. Through all depths and latitudes, the glacial accumulation rates are greater than the interglacial by a factor of 2.8–3.8. For both time periods, the accumulation rates tend to fall off north of about 4° latitude.

Surface Productivity and Carbon Rain

The rain rates of organic and inorganic carbon to the seafloor at MANOP sites C (1°N, 139°W) have been measured in sediment traps and are given in Table 3.

Assuming that most of the organic rain to the seafloor is oxidized within the sediment (as opposed to on the sediment surface; this assumption is based on the pore water data in Table 3), the organic carbon rain should be equivalent to the sediment respiration rate, measured using pore water techniques (also in Table 3). The organic and inorganic carbon rain rates at MANOP sites M and H (6°N, 93°W and 9°N, 104°W, respectively) are also presented (Table 3) for comparison. Although the comparison may be unfair because the durations of the stations were not the same, in general the equatorial rain rates appear to be higher than the region north of the equator, consistent with the distribution of surface nitrate [Chavez and Barber, 1987].

Although available evidence is not conclusive, it is thought that surface productivity and the resulting carbon rain rates to equatorial Pacific sediments were higher during the last glacial period than they are today [Berger et al., 1983; Finney et al., 1988; Pradl et al., 1989; Pedemont, 1983; Lyle et al., 1984]. Based on assemblages of faunal plankton preserved in Atlantic sediments, Mix [1989] has concluded that equatorial productivity was about 90% higher during the glacial period than today; non-equatorial pelagic regions were about 40% more productive. Thus changes in carbon rain rates may have been more pronounced in equatorial regions than in other regions.

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**TABLE 2.** The equatorial accumulation rate data presented by Parfiell [1991]

<table>
<thead>
<tr>
<th>Core</th>
<th>Depth, m</th>
<th>Latitude, °N</th>
<th>%CaCO₃ Glaclal</th>
<th>%CaCO₃ Interglacial</th>
<th>Accumulation, Glacial</th>
<th>Accumulation, Interglacial</th>
<th>Glacial / Interglacial</th>
</tr>
</thead>
<tbody>
<tr>
<td>H4G1</td>
<td>4287</td>
<td>0.57</td>
<td>85</td>
<td>72</td>
<td>12.2</td>
<td>6.7</td>
<td>2.6</td>
</tr>
<tr>
<td>SDB9</td>
<td>4370</td>
<td>3.05</td>
<td>85</td>
<td>61</td>
<td>16.2</td>
<td>6.1</td>
<td>2.7</td>
</tr>
<tr>
<td>RC11-210</td>
<td>4420</td>
<td>1.49</td>
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<td>70</td>
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<td>3.4</td>
</tr>
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<td>3.99</td>
<td>88</td>
<td>71</td>
<td>13.4</td>
<td>3.6</td>
<td>3.0</td>
</tr>
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<td>PLDS 130</td>
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<td>4.00</td>
<td>90</td>
<td>60</td>
<td>5.7</td>
<td>1.7</td>
<td>3.4</td>
</tr>
<tr>
<td>SDB6</td>
<td>4540</td>
<td>1.35</td>
<td>85</td>
<td>60</td>
<td>20.2</td>
<td>6.1</td>
<td>3.3</td>
</tr>
<tr>
<td>YZ6-179</td>
<td>4509</td>
<td>4.37</td>
<td>80</td>
<td>56</td>
<td>8.7</td>
<td>2.1</td>
<td>4.1</td>
</tr>
</tbody>
</table>

**TABLE 3.** Rain Rates of Organic and Inorganic Carbon in the Deep Equatorial Pacific Today, Measured with Sediment Traps

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Organic Carbon</th>
<th>Benthic Carbon Oxidation Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>MANOP C</td>
<td>1 N</td>
<td>139 W</td>
</tr>
<tr>
<td></td>
<td>16°</td>
<td>22°</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>6 N</td>
</tr>
<tr>
<td></td>
<td>93 W</td>
<td>7°</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>9 N</td>
</tr>
<tr>
<td></td>
<td>104 W</td>
<td>12°</td>
</tr>
</tbody>
</table>

Units are m/yr.

1 Dyndon and Collier [1988] (sediment traps)
2 Ibbotson et al. [1990] (benthic flux chamber)
3 Raisens et al. [1984] (oxygen microelectrode)
4 Imeson et al. [1985] (pore water chemistry)
5 Dyndon and Lyle [1985] (sediment traps)
On the basis of the fossil record of calcareous and silicaceous plankton tests in the equatorial Pacific, Lyle et al. (1988) have concluded that the surface planktonic community oscillates on geologic time scales between two distinct assemblages, one of them calcareous and the other silicaceous (dominant during the intervals 10-15 kyr and 35-60 kyr A.D.). By changing the ratio of organic carbon to calcite in the sinking material, such a biological cycle should have had a major effect on the preservation of calcite in the equatorial Pacific sediments (Archer, 1991).

### Water Column Calcite Saturation State

The saturation state of calcite is typically expressed as the difference in [CO$_3^{2-}$] between a water sample and the calcite saturation value at its site pressure ($\Delta$CO$_3$). A present-day water column profile of $\Delta$CO$_3$ from GECOESCS is presented in Figure 3. In the depth range of 4-5 km, the increase in $\Delta$CO$_3$ with depth is largely a function of pressure; the deepwater [CO$_3^{2-}$] of the Pacific ocean today is relatively homogeneous (Flaiddens, 1988).

![Fig. 3. Present-day $\Delta$CO$_3$ of the water column in the equatorial Pacific, from GECOESCS stations 334 (squares) and 337 (triangles). The scatter in the data was probably caused by difficulty in measuring [CO$_3^{2-}$] rather than by real variations.](image-url)

The water column chemistry of the glacial Pacific Ocean is not extremely well constrained by direct observational data. Many of the calcite preservation records are located in regions of high productivity near the equator (Wu and Berger, 1989; Adlebeck and Anderson, 1978; Chary et al., 1987) or in near-coastal regions (Boyle, 1983) so that interpretation of the bottom water chemistry changes are complicated by possible changes in production. Other locations contain high concentrations of calcite throughout the record, so that the calcite concentration record is not sensitive to changes in overlying water chemistry (Lan and Shackleton, 1975; Votol et al., 1980).

In the absence of conclusive data, the best constraints on the glacial water column [CO$_3^{2-}$] come from numerical considerations. Evidence from the $^{13}$C of biogenic foraminifers preserved in sediments suggests that the total CO$_2$ of the glacial oceans was higher than it is today, presumably because of a decrease in terrestrial biosphere (Shackleton, 1978; Bronk and Peng, 1982). Carbon isotopes and cadmium data (Boyle, 1988) suggest that the present-day nutrient maximum at intermediate water depths in the water column shifted to deeper water during the glacial period, although this effect may have been weaker in the Pacific than it was in the Atlantic (Mo et al., 1991). Both of these changes, taken alone, would tend to make the bottom waters more corrosive to calcite.

In the face of these perturbations, the average ocean [CO$_3^{2-}$] was regulated by the global algal-biologic cycle, as it is today (Bronk and Peng, 1982). The idea is that production of calcite at the sea surface exceeds the supply rate of alkalinity from rivers, so that for the alkalinity flux to balance, only a fraction of the calcite production can be removed from the oceans by burial. The burial fraction is controlled by the depth of the saturation horizon, which is determined by the seawater [CO$_3^{2-}$]. On time frames of thousands of years or longer, the average depth of the saturation horizon is maintained such that the total ocean burial rate of calcite matches the input rate of alkalinity from rivers. In response to changes in ocean total CO$_2$ and nutrient distributions, Boyle (1988) estimates that the glacial deep-sea carbonic anhydride concentrations may have been ~28 $\mu$M lower than today. Local variations in the saturation horizon depth arise due to the large-scale patterns of oceanic circulation. Today, well-ventilated (and hence high [CO$_3^{2-}$]) North Atlantic Deep Water makes the Atlantic ocean more preserving to calcite than the rest of the world's oceans. During the last glacial, NADW either formed more slowly or was less ventilated than it is today (Boyle and Keigwin, 1982; Shackleton et al., 1985; Chery and Lohmann, 1985; Mix and Fairbanks, 1985). This change is consistent with higher glacial preservation of calcite in the Pacific Ocean (as observed by Farrell and Peltier, 1988; Wu and Berger, 1989; and Boyle, 1983), and lower calcite preservation in the Atlantic (跨越式, 1969 and 1971; Berger, 1975; and Berger et al., 1983). S. Emerson and D. Archer (manuscript in preparation, 1993) repeated Boyle's calculation of the glacial steady state [CO$_3^{2-}$], including the effect of the
homogeneous basins (Atlantic vs. Pacific and Indian). This refinement lowers the predicted change in Pacific deep-water carbonate ion to an increase of 7-11 µM. We will consider the possibility of an increase in water column ΔCO₂ of the order of these estimates (10-20 µM).

As a final complication, it is conceivable that a source of ventilated water in the North Pacific existed during the glacial times. This discussion is based on the δ¹³C of beech foraminifera preserved in the North Pacific relative to the record in the Antarctic Circumpolar Current. The discussion remains open because the evidence is contradictory, with data in support of the hypothesis published by Moore et al. (1978), Corliss et al. (1986), and Curry et al. (1988), and data to the contrary by Kingwin (1997). The existence of multiple water masses in the glacial Pacific could result in gradients in [CO₂] with depth such as are found today at the boundary between North Atlantic Deep Water and Antarctic bottom water in the Atlantic ocean. In the absence of ventilated Pacific deep water formation, I assume that the water column [CO₂] would have been relatively homogeneous with depth, as it is today.

Summary of Carbon Cycle Constraints from the Literature

A provocative reconstruction of the calcite lysocline through the last 100,000 years was published by Farquhar and Prell (1989). Any attempt to explain these data must also be consistent with accumulation rates published by farquhar (1991), which show 1.8-3.8 times higher accumulation of calcite during the glacial periods and lower accumulation north of 6°N than closer to the equator during glacial and interglacial periods. Various sedimentary indicators suggest that surface productivity was higher during the glacial than it is today, but the estimates are not quantitatively strong. The water column carbonate chemistry of the glacial Pacific is not well constrained by calcite preservation data, but can be estimated from theoretical considerations. Unless there was a major change in the circulation of the deep Pacific during the glacial intervals, and in the presence of ventilated deep water, we assume that the [CO₂] of the Pacific was relatively homogeneous with depth, as it is today.

MODEL BACKGROUND

A numerical model for sedimentary calcite diagenesis is used to calculate the steady state concentration of calcite in the sedimentary waters under a given set of boundary conditions. These are the rain rates of calcite, organic carbon, and a redox zone (defined as the noncalcareous sediments that are essentially buried), and the bottom water carbonate saturation state. Details of the model were presented by Archer (1991) and will be summarized here. The pore water chemistry is formalized as a diffusive medium to which CO₂ is added by organic carbon respiration and CO₂ is added by calcite dissolution. The scheme is based on equilibrium balances (HCO₃⁻ + CO₂ = 2 CO₃⁻) and CO₂ (defined as CO₂ = [HCO₃⁻] + CO₃⁻). In steady state, the equations are

\[
\begin{align*}
\frac{d}{dt} [\text{CO}_2] &= 0 = \frac{d}{dt} \left( \frac{[\text{HCO}_3^-] + [\text{CO}_3^{2-}]}{F} \right) \\
\frac{d}{dt} \left( \frac{[\text{CO}_2]}{F} \right) &= \frac{d}{dt} \left( \frac{[\text{HCO}_3^-]}{F} \right) \times [\text{H}] \\
\frac{d}{dt} \left( \frac{[\text{CO}_3^{2-}]}{F} \right) &= \frac{d}{dt} \left( \frac{[\text{CO}_2]}{F} \right) + \frac{d}{dt} \left( \frac{[\text{HCO}_3^-]}{F} \right) \\
\end{align*}
\]

and

\[
\begin{align*}
\frac{d}{dt} [\text{CO}_2] &= 0 = \frac{d}{dt} \left( \frac{[\text{HCO}_3^-] + [\text{CO}_3^{2-}]}{F} \right) \\
\frac{d}{dt} \left( \frac{[\text{CO}_2]}{F} \right) &= \frac{d}{dt} \left( \frac{[\text{HCO}_3^-]}{F} \right) \times [\text{H}] \\
\frac{d}{dt} \left( \frac{[\text{CO}_3^{2-}]}{F} \right) &= \frac{d}{dt} \left( \frac{[\text{CO}_2]}{F} \right) + \frac{d}{dt} \left( \frac{[\text{HCO}_3^-]}{F} \right) \\
\end{align*}
\]

where F is porosity, D is the diffusion coefficients of solute X (Li and Gregory, 1974), F is in the sediment formation factor, representing the inhibition of solute diffusion by the sediment lattice (Ulssam and Aller, 1982), OC and C are the dry weight fractions of organic carbon and calcite in the sediment, p is the solid density, and M₀ and Mₛ are molecular weights; kₐ and kₐ are the rate constant and reaction order for calcite dissolution (taken to be 4.5 order [Kre, 1960]). The Hinweiske function, K₁ = [CO₂][CO₃^-], reflects the kinetic barrier to calcite pre-epilation from supersaturated solutions (Emerson and Bender, 1981). A required third constraint is that the pH reaction,

\[
\text{CO}_2 + \text{H}_2\text{O} + \text{CO}_3^- \leftrightarrow 2 \text{HCO}_3^- ,
\]

is maintained in equilibrium at all depths, such that

\[
\frac{[\text{CO}_2]}{[\text{HCO}_3^-]} = K_1 \\
\frac{[\text{HCO}_3^-]}{[\text{CO}_3^-]} = K_2
\]

where K₁ and K₂ are the first and second apparent dissociation constants for carbonic acid.

The boundary conditions for solutes are the bottom water values at the sediment-water interface and zero flux.
Calculating the geologic record from the glacial era. The necessary model parameters are the rain rate of organic carbon, calcite, and detrital material. The rain rate of refractory material was expressed by Archer [1991] relative to the calcite rain as "9CaCO3rain" defined as the maximum possible sedimentary calcite concentration (i.e., the case of no dissolution). A value of 95% is consistent with the shape of the present-day lysocline in the Farrel and Perill [1995] record [Archer, 1991] and with the concentration of calcite in the shallowest cores in the record (> 80% at δCaO > -10 μm). A value of organic / inorganic carbon rain rate ratio of 0.7 is consistent with the sediment trap data of Dymond and Collier [1988], with the shape of the lysocline in the region [Archer, 1991], and with the accumulation rate of calcite from the last glacial period [Farrell, 1991] (Table 2). The results of the model simulations using these values of the rain rate ratios are summarized in Figure 4. In the space of calcite saturation (oriented vertically because of its analogy to depth in the ocean) and calcite rain rate, contours are plotted for calcite accumulation rate and calcite concentration in the sediments. The position of the top of the present-day lysocline is defined by the estimated δCaO at ~4500 m (~10 to -15 μm) and rain rates from sediment trap data [Dymond and Collier, 1988]. This position is marked "D" on Figure 4. The accumulation rate of calcite predicted by the model for these conditions is similar to accumulation rate data from the last interglacial (Table 2: indicated in Figure 4 by the stippled region enclosing the labeled "6", δCaO in the present-day estimate). The boundary of the Farrel and Perill record is located at 6° N (site RC21-63, 4949 μm). This is located on Figure 4 using the calcite rain rate from M0N0 site H (67N), and an estimated δCaO of ~30 μm (Figure 5). The "peak" of the Farrel and Perill Holocene lysocline is marked between these two locations (heavy line).

MODEL APPLICATION TO THE PRESENT-DAY EQUATORIAL PACIFIC

Given the uncertainty in many of the parameters to which the calcite dissolution model is sensitive (the ratio of the organic carbon to calcite rain rate, the rain rates of detrital material, and the extent of anoxic respiration), it is difficult to apply the model in a strictly quantitative way to today's ocean; when interpreting data from the past this problem can only be compounded. In particular, the extent to which the model output can explain the glacial calcite preservation signal. Thus, rather than argue that we can infer the relative contributions of different processes to the model, we will limit our interpretation of the model output to comments about its broad behavior. The range of accumulation rates during the last glacial is described by the region labeled "G" on Figure 4. It can be seen that these accumulation rates can be generated by the dissolution hypothesis (labeled "D"): increased by the increased carbon dioxide concentration. Alternatively, the production hypothesis (labeled "P") would have the result of more calcite rain by a bit more than a factor of 2, to about 50 μm cm^-2 yr^-1. A third possibility
Fig. 4. Contours of model sedimentary calcite concentration and accumulation rate, in the space of water column $\Delta CO_2$ (calcite saturation state) and calcite rain rates. The molar ratio of organic carbon to calcite rain rates for these simulations is 0.7. The value of the sedimentary calcite concentration assuming no dissolution is 95% (referred to in text as $\% CaCO_3$). The position of the tip of the hyalocline in the equatorial Pacific today (indicated by “H”) is determined by the water column chemistry (-10 to -15 $\mu$M $\Delta CO_2$) and the rain rate of calcite from sediment traps (from MANIP site C data; Table 3). Calcite concentration and accumulation rates predicted by the model are similar to observations (stippled region enclosing the marker “H”). The bottom of the hyalocline is determined by MANIP site M rain rate data and is indicated by “RC12-63”. During the glacial, the accumulation rate at 4200-4400 meters was higher than it is today (indicated by stippled region “G”). Generating this accumulation rate using the numerical model requires an increase in water column $CO_2$ of up to 40 $\mu$M (dissolution hypothesis, labeled “Diss.”) or increasing the rain rate of calcite and organic carbon by approximately a factor of 2 (the production hypothesis, labeled “Prod.”).

Fig. 5. Increasing calcite accumulation by lowering the organic carbon / calcite molar rain rate ratio. The stippled region is the observed glacial calcite accumulation rate. In the case of similar water column $\Delta CO_2$ to today, a calcite rain rate of ~30 $\mu$mol cm$^{-2}$ yr$^{-1}$ would be required. In this case, the organic rain rate would be similar to today. This possibility is discounted by the observed higher accumulation of organic carbon during glacial periods.

(not shown) would be some combination of these two scenarios. Any of these possibilities would also increase the concentration of calcite in the sediment to > 80% at the tip of the hyalocline, as observed in the Farrell and Prell record.

In order to generate the observed glacial accumulation rates of calcite (which ranged to 20 $\mu$mol cm$^{-2}$ yr$^{-1}$ at site SD10; 60) without changing production rates, an increase in overlying water carbonate ion of up to 40 $\mu$M would be required. This is larger than the estimates of 10-20 $\mu$M for the change in $\Delta CO_2$ reviewed previously. Also, the...
dissolution hypothesis implies either that the lack of calcite preservation at site RC12-63 is an artifact of chemical erosion, or that the circulation patterns in the glacial Pacific were very different from today. If the calcite preservation signal is real, there must have been a differential in [CO_2] of up to 60 μM over the 160 meter depth range of the Farrell and Prell record, and of the order 20 μM over the interval between core V24-62 and RC12-63 (δc = 110 m). The inverse estimate of 18O of 110 μM (from the second constraint) can be compared with a present-day gradient between NAPO and NAWR in the western Atlantic of 40-80 μM (from GEOFSEC stations 53-56). Clearly maintenance of a gradient of 18CO_2 of this magnitude would require heterogeneous water mass formation in the Pacific similar to the present-day Atlantic. While the dissolution hypothesis is not disproved by the current analysis, Figure 4 shows that the production hypothesis is also feasible. When the calcite rain rate is increased in the model, calcite is preserved to greater depth in the water column, even in the absence of changes in the overlying water chemistry. Simulation of the data requires that the rain rate of calcite was nearly double its current value south of ~7N. The possibility of higher production in the glacial equatorial Pacific is supported by sedimentary organic carbon (Pedenen, 1983), manganese (Finney et al., 1988), lipid biomarkers (Pabst et al., 1989), accumulation of other biogenic sedimentary components (Archer, 1988), and planktonic assemblages (from the Atlantic, Mix [1989]). This scenario assumes that the chemistry of the water column was relatively homogenous, as it is today; that is, the hypothesis does not require glacial ventilated Pacific deep water. Homogeneous changes in water column chemistry are predicted theoretically (Boyle, 1988) (Eisehorn and Archer, manuscript in preparation, 1991); these predictions are compatible but not required or well constrained by the calcite production hypothesis.

Alternative scenario. The observed increase in calcite accumulation during the last glacial can also be generated in the model by decreasing the ratio of organic carbon to calcite in the sedimentary material. This has the effect of diminishing respiration-driven calcite dissolution (Archer, 1991). Figure 5 is a contour plot similar to Figure 4, but generates a ratio of organic carbon to calcite of 0.5 instead of 0.7. Without making any changes in the water column organic carbon accumulation, the required calcite accumulation rates can be generated by increasing calcite production over today's values by roughly 50%, maintaining organic carbon rain rates similar to today (These rates would have to be lower if the water column [CO_2] was higher as present, following Boyle [1988]). The problem with this scenario is the observation that organic carbon accumulation rates in equatorial Pacific sediments were higher during the glacial periods (Pedenen, 1983; Emerson, 1985). Although precise interpretation of organic carbon accumulation data is limited by uncertainty about the processes that control organic carbon burial (Emerson, 1985; Eisehorn and Hedges, 1985), it is clear that organic carbon rain rates were higher during the glacial than they are today, discounting this hypothesis.

The other potential degree of freedom in the analysis that must be addressed is the partitioning between oxic and anoxic organic carbon degradation. Archer (1991) presented two models of organic carbon respiration in sediments and showed that calcite preservation predictions of the two models differ significantly. Since the two models were intended to bracket our uncertainty in the processes by which organic carbon is respired, the differences between the two models represent the propagation of this uncertainty to the prediction of calcite preservation. For present-day equatorial Pacific conditions, the two models are essentially identical in the shape of the predicted lysinoclines and in their predicted preservation rates of calcite (these conclusions are based on figures presented by Archer, 1991)]. However, the higher glacial calcite accumulation rates can be simulated using the oxic/anoxic model with calcite rain rates of ~64-65 μM cm^-2 yr^-1 (an increase by a factor of 1.6-2.0 over present-day rates), which is lower than the estimate of ~50 μM cm^-2 yr^-1 (factor of 2.2 increase) required for the "production" scenario using the oxygen-only model.

SUMMARY

Glacial interglacial changes in the shape and depth of the lysinocline and in the accumulation rate for calcite are documented in the Equatorial Pacific geologic record. One possible explanation for the observations (the "dissolution hypothesis") is that the gradients of the calcite saturation state with water depth became more intense during the last glacial period. By comparing a numerical model for the calcite lysinocline to the observed calcite concentration and accumulation data, we show that the required change in 18CO_2 in 20-40 μM, higher than recent estimates based on sedimentary or theoretical considerations. The lack of calcite preservation at site RC12-63 is either an artifact of chemical erosion or it required a production rate with depth that is similar to or greater than the present-day gradient between North Atlantic deep water and Antarctic bottom water in the Atlantic. Thus this explanation might imply a source of ventilated deep water in the Pacific Ocean during the last glacial.

The model suggests an alternative explanation, however, that does not require a major change in the Pacific circulation pattern. A doubling of the present-day calcite and organic carbon rain rates to the sediments would depress the lysinocline and increase the accumulation rate to the extent observed. Homogeneous changes in the water column [CO_2] within the range of previous theoretical predictions are not inconsistent with or required by this scenario.

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