

EQUATORIAL PACIFIC CALCITE 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 at 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 (Arrhenius; 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 Ekman divergence. Nutrient availability at the sea surface supports high levels of new productivity, potentially

representing a significant fraction of the global total 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.

The geologic record of calcite preservation in the sediments under the equatorial Pacific may serve as a constraint of 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; Arrhenius, 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 [Berger, 1968; Farrell and Prell, 1989]. Generating such a dissolution signal would require a steeper gradient in the saturation state of calcite, ΔCO₂, 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 (tied to productivity at the surface ocean) [Arrhenius, 1988]. In this

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scenario, the water column ΔCO_3 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 roughly homogeneous with depth. A numerical model of the processes controlling calcite dissolution and preservation is applied to the evaluation of these hypotheses.

CARBON CYCLE CONSTRAINTS FROM THE PALEOCEANOGRAPHIC 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 inferences of 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 calcite preservation records were combined into a single time history and contoured, resulting in a plot of the depths of the calcite isopleths (constant calcite content) as a function of time. The reconstruction suggests that the depth of calcite depletion to 10% (the "carbonate critical depth", or "CCrD", defined by Farrell and Prell [1989]) remained constant with depth

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

Location*	Core	Depth, m	Latitude	Longitude
1	V24-55	4189	2°03'N	134°38'W
2	W8402A-14GC	4287	0°57'N	138°57'W
3	DSDP 573A	4301	0°30'N	133°19'W
4	SDSE 59	4370	3°05'N	133°06'W
5	RC11-209	4400	3°39'N	140°04'W
6	RC11-210	4420	1°49'N	140°03'W
7	PLDS 130-131	4471	4°00'N	136°00'W
8	V24-58	4490	2°16'N	141°40'W
9	V28-179	4509	4°37'N	139°36'W
10	SDSE 60	4540	1°35'N	134°57'W
11	DSDP 574	4561	4°13'N	133°20'W
12	V24-59	4662	2°34'N	145°32'W
13	RC12-66	4755	2°37'N	148°13'W
14	V24-62	4834	3°04'N	153°35'W
15	RC12-65	4868	4°39'N	144°58'W
16	RC12-63	4949	5°58'N	142°39'W

* Location numbers correspond to numbers in Figure 2a.

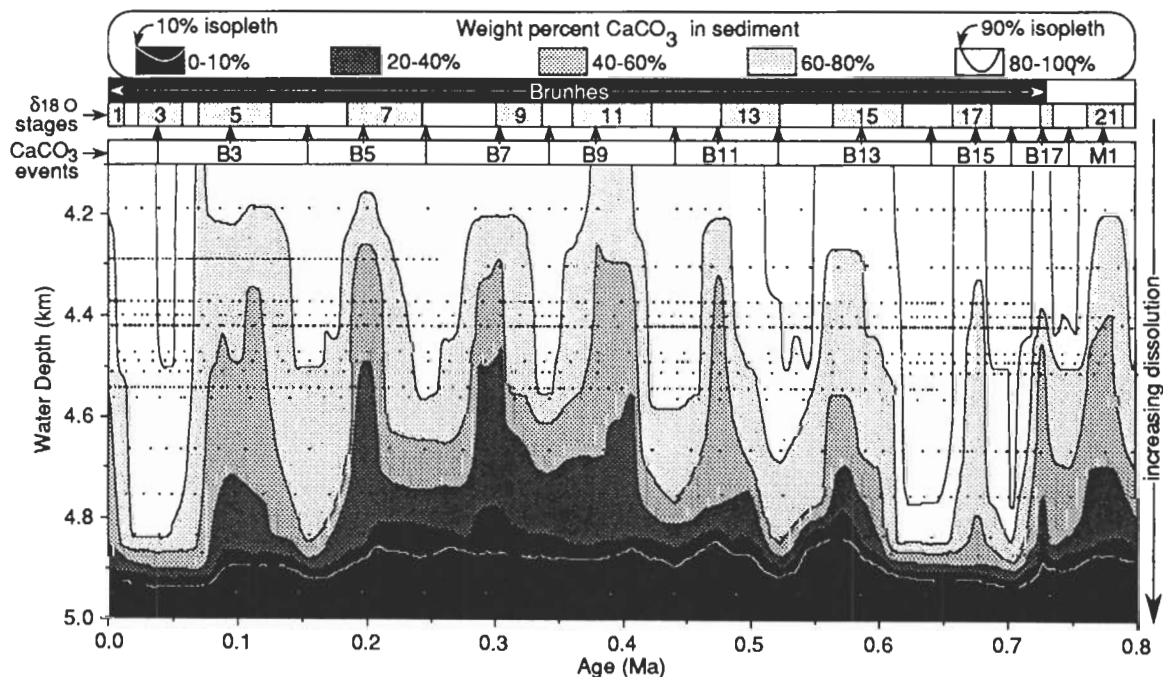


Fig. 1. Shape of the calcite lysocline as a function of time from the equatorial Pacific. From Farrell and Prell [1989].

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 erosion" [Keir, 1984; Farrell and Prell, 1989]. When the steady state surface sediment calcite concentration changes from high calcite to low calcite (in response to a decrease in overlying water CO₃) some of the calcite 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 detrital material in the sediment mixed layer (~8 cm deep) to a condition of no calcite in the mixed layer. At the end of the transition, 8 cm of detrital material is required; this material could either come from the sediment rain or by mixing up from below, by dissolution of old calcite (chemical erosion), depending on which is faster.

The question of chemical erosion is most crucial to the Farrell and Prell dataset at sites RC12-65 and RC12-63 (4868 and 4949 m; 4°39' and 5°5'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 detrital material was about 40 kyr (using a dry bulk density of low-calcite sediment of 0.322 from Farrell [1991]). The time-scale of chemical erosion 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 noncalcite material to the sediment surface faster than it can accumulate by sedimentary rain, the source of the required detrital material might have been by chemical erosion 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 noncalcite material that is needed in the new steady state mixed layer. During the glacial era, the accumulation rates of noncalcite material in sites RC12-63 and RC12065 were 40 and 65 mg cm⁻² yr⁻¹ [Farrell, 1991]. Based on this, the accumulation of a total of 8 cm of detrital material during the glacial era would have taken 40-50 kyr. Thus 40-50 kyr of calcite accumulation could dissolve to supply the needed noncalcite 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 erosion.

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 diagram 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°-2°N, and deeper regions all from 2°-5° latitude. The deepest core (RC12-63) comes from nearly 6°N. During the last glacial maximum (an extreme case), the entire calcite lysocline is interpolated between the 6°N core and the two immediately shallower, located at 3° and 4°39' (V24-62 and RC12-65) (Figure 2b).

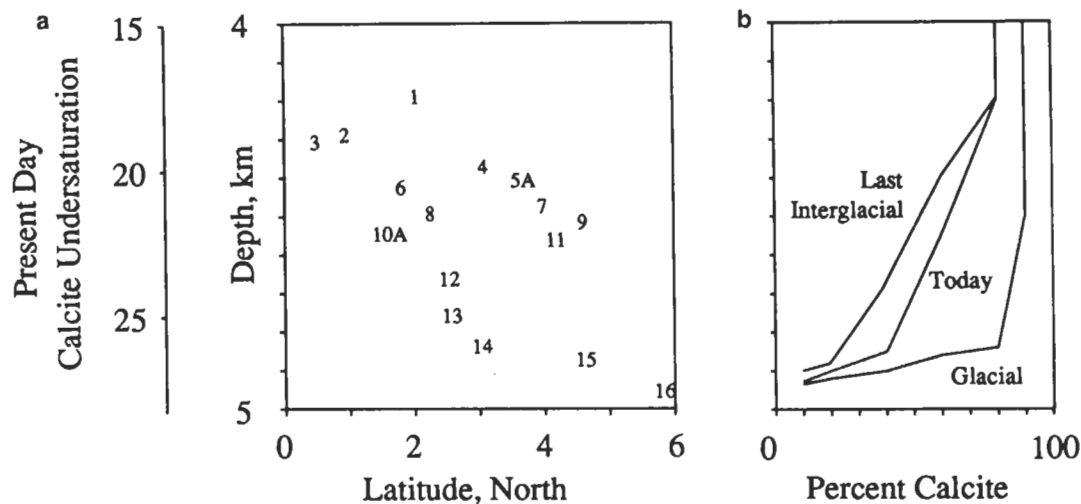


Fig. 2. (a) Bathymetric plot of the locations of the sediment cores used by Farrell and Prell [1991] to create Figure 1. Location numbers correspond to numbers in Table 1. A general trend is evident, with cores used to create the shallower part of the record closer to the equator than cores from the 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 lysocline 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 Farrell [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 (70-120 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 site 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 longitudes of the stations were not the same, in general the equatorial rain rate appears 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; Prahl et al., 1989; Pedersen, 1983; Lyle et al., 1988]. Based on assemblages of fossil 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.

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

Core	Depth, m	Latitude, °N	%CaCO ₃ Glacial	%CaCO ₃ Inter-glacial	Accumulation, Glacial	Accumulation, Inter-glacial	Glacial / Inter-glacial
14GC	4287	0.57	86	72	12.2	4.7	2.6
SDSE 59	4370	3.05	85	61	16.2	6.1	2.7
RC11-210	4420	1.49	86	70	14.5	4.3	3.4
RC11-209	4400	3.39	88	71	13.4	3.6	3.0
PLDS 130	4471	4.00	90	60	5.7	1.7	3.4
SDSE 60	4540	1.35	85	60	20.2	6.1	3.3
V28-179	4509	4.37	80	56	8.7	2.1	4.1

Units are $\mu\text{mol cm}^{-2} \text{yr}^{-1}$.

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

	Latitude	Longitude	Rain Rates		Benthic Carbon Oxidation Rate
			Organic	Calcite	
MANOP C	1 N	139 W	16 ^a	22 ^a	12 ^b , 23 ^c , <14 ^d
H	6 N	93 W	7 ^e	13 ^e	4-11 ^d
M	9 N	104 W	12 ^e	7 ^e	6-8 ^d

Units are $\mu\text{mol cm}^{-2} \text{yr}^{-1}$.

^a Dymond and Collier [1988] (sediment traps)

^b Berelson et al [1990] (benthic flux chamber)

^c Reimers et al. [1984] (oxygen microelectrodes)

^d Emerson et al. [1985] (pore water chemistry)

^e Dymond and Lyle [1985] (sediment traps)

On the basis of the fossil record of calcareous and siliceous 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 siliceous (dominant during the intervals 10-15 kyr and 35-60 kyr BP). 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 $[\text{CO}_3^{2-}]$ between a water sample and the calcite saturation value at in situ pressure (ΔCO_3). A present-day water column profile of ΔCO_3 from GEOSECS is presented in Figure 3. In the depth range of 4-5 km, the increase in ΔCO_3 with depth is largely a function of pressure; the deepwater $[\text{CO}_3^{2-}]$ of the Pacific ocean today is relatively homogeneous [Fiadeiro, 1980].

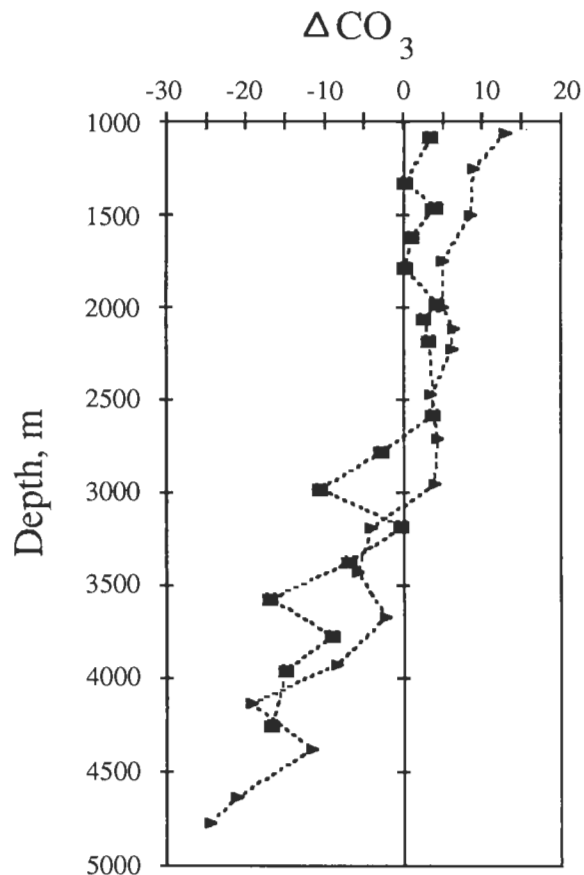


Fig. 3. Present-day ΔCO_3 of the water column in the equatorial Pacific, from GEOSECS stations 334 (triangles) and 337 (squares). The scatter in the data was probably caused by difficulty in measuring $[\text{CO}_3]$ rather than by real variations.

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; Adelseck and Anderson, 1978; Chuey 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 [Luz and Shackleton, 1975; Volat et al., 1980].

In the absence of conclusive data, the best constraints on the glacial water column $[\text{CO}_3^{2-}]$ come from theoretical considerations. Evidence from the $\delta^{13}\text{C}$ of benthic foraminifera 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 biomass [Shackleton, 1978; Broecker 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 periods, although this effect may have been weaker in the Pacific than it was in the Atlantic [Mix, 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 $[\text{CO}_3^{2-}]$ was regulated by the global alkalinity cycle, as it is today [Broecker 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 fluxes 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 water column $[\text{CO}_3^{2-}]$. 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 carbonate ion concentrations may have been $\sim 20 \mu\text{M}$ 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 $[\text{CO}_3^{2-}]$) 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., 1983; Curry and Lohmann, 1983; Mix and Fairbanks, 1985]. This change is consistent with higher glacial preservation of calcite in the Pacific Ocean (as observed by Farrell and Prell [1989], Wu and Berger [1989], and Boyle [1983]), and lower calcite preservation in the Atlantic [Olausson, 1965 and 1971; Berger, 1973; and Berger et al., 1983]. S. Emerson and D. Archer (manuscript in preparation, 1991) repeated Boyle's calculation of the glacial steady state $[\text{CO}_3^{2-}]$, including the effect of the

heterogeneous 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 ΔCO_3 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 $\delta^{13}\text{C}$ of benthic 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 Keigwin [1987]. The existence of multiple water masses in the glacial Pacific could result in gradients in $[\text{CO}_3^{=}]$ 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 $[\text{CO}_3^{=}]$ 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 800,000 years was published by Farrell and Prell [1989]. Any attempt to explain these data must also be consistent with accumulation rates published by Farrell [1991], which show 2.8-3.8 times higher accumulation of calcite during the glacial periods and lower accumulation north of 4°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 periods, such as a source of ventilated deep water, we assume that the $[\text{CO}_3^{=}]$ of the Pacific was relatively homogeneous with depth, as it is today.

MODEL BACKGROUND

A numerical model for sedimentary calcite dissolution is used to calculate the steady state concentration of calcite in the sediment mixed layer under a given set of boundary conditions. These are the rain rates of calcite, organic carbon, and refractory material (defined as the noncalcite sediment that is eventually buried), and the bottom water calcite 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 CO_2 is added by organic carbon respiration and $\text{CO}_3^{=}$ is added by calcite dissolution. The scheme is based on conservation of alkalinity (defined as $[\text{HCO}_3^-] + 2[\text{CO}_3^{=}]$) and total CO_2 (defined as $[\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{=}]$). In steady state, the equations are

$$\begin{aligned} \Phi \frac{\partial \Sigma\text{CO}_2}{\partial t} = 0 = & \frac{\partial}{\partial z} \left(\frac{D_{\text{CO}_2}}{F} \frac{\partial \text{CO}_2}{\partial z} \right) \\ & + \frac{\partial}{\partial z} \left(\frac{D_{\text{HCO}_3}}{F} \frac{\partial \text{HCO}_3}{\partial z} \right) + \frac{\partial}{\partial z} \left(\frac{D_{\text{CO}_3}}{F} \frac{\partial \text{CO}_3}{\partial z} \right) \\ & + j_{\text{O}_2} \text{OC}\% \rho_{\text{oc}} M_{\text{oc}}^{-1} (1 - \phi) \\ & + k_c \text{C}\% \rho_c M_c^{-1} \left(1 - \frac{[\text{CO}_3]}{[\text{CO}_3]_{\text{sat}}} \right)^n \\ & \times H \left(1 - \frac{[\text{CO}_3]}{[\text{CO}_3]_{\text{sat}}} \right) \end{aligned} \quad (1)$$

and

$$\begin{aligned} \Phi \frac{\partial \text{alk}}{\partial t} = 0 = & \frac{\partial}{\partial z} \left(\frac{D_{\text{HCO}_3}}{F} \frac{\partial \text{HCO}_3}{\partial z} \right) \\ & + 2 \frac{\partial}{\partial z} \left(\frac{D_{\text{CO}_3}}{F} \frac{\partial \text{CO}_3}{\partial z} \right) \\ & + 2 k_c \text{C}\% \rho_c M_c^{-1} \left(1 - \frac{[\text{CO}_3]}{[\text{CO}_3]_{\text{sat}}} \right)^n \\ & \times H \left(1 - \frac{[\text{CO}_3]}{[\text{CO}_3]_{\text{sat}}} \right) \end{aligned} \quad (2)$$

where Φ is porosity, D_X is the diffusion coefficient of solute X [Li and Gregory, 1974], F is the sediment formation factor, representing the inhibition of solute diffusion by the sediment lattice [Ullman and Aller, 1982], $\text{OC}\%$ and $\text{C}\%$ are the dry weight fractions of organic carbon and calcite in the sediment, ρ is the solid density, and M_{oc} and M_c are molecular weights; k_c and n are the rate constant and reaction order for calcite dissolution (taken to be 4.5 order [Keir, 1980]). The Heaviside function, $H(1 - [\text{CO}_3]/[\text{CO}_3]_{\text{sat}})$, reflects the kinetic barrier to calcite pre-cipitation from supersaturated solutions [Emerson and Bender, 1981].

A required third constraint is that the pH reaction,



is maintained in equilibrium at all depths, such that

$$\frac{[\text{CO}_2][\text{CO}_3^{=}]}{[\text{HCO}_3^-]^2} = \frac{K_1'}{K_2'} \quad (4)$$

where K_1' and K_2' 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

(gradient) at $z = 10$ cm. The effects of pore water advection and biological irrigation are negligible in the deep sea and are neglected. Solutions to these equations under a given set of conditions were found using a relaxation algorithm (FORTRAN code given by Archer [1990]).

Solid calcite in the sediment was assumed to be well mixed [Keir, 1982]. At a given calcite concentration and dissolution rate, the rate of calcite burial can be calculated as,

$$\text{calcite burial} = (\text{mass rain} - \text{mass dissolution}) \times \% \text{CaCO}_3. \quad (5)$$

At the steady state calcite concentration, the sources and sinks for sedimentary calcite balance, such that

$$\text{calcite rain} = \text{calcite dissolution} + \text{calcite burial}. \quad (6)$$

The shape and position of the calcite lysocline is predicted by calculating the steady state calcite concentration as a function of overlying water chemistry, under conditions of constant rain rates of calcite and organic carbon.

The model correctly reproduced the observed shape and depth of the calcite lysocline, and the accumulation rate of calcite above the saturation horizon, in 13 basins in the present-day ocean [Archer, 1991]. The simulation required a dissolution rate constant for calcite that was consistent with microelectrode data [Archer et al., 1989] and incorporated observed near-bottom sediment trap fluxes of organic carbon and calcite. A value of the molar ratio of organic carbon to carbonate carbon rain rates (abbreviated "org/inorg") of ~ 0.7 to 1.0 was required to fit the observations; this value is consistent with available sediment trap data. In most parts of the ocean, a value of the calcite concentration in the case of no dissolution ($\% \text{CaCO}_3^{\text{initial}}$) of 90% was required to reproduce the concentration of calcite at and above the saturation horizon, and the shape of the calcite lysocline.

The best fit value for the parameter org/inorg is sensitive to the extent of anoxic diagenesis. An "oxygen-only" version of the model is based on the sediment respiration model of Emerson [1985], which was developed for the equatorial Pacific. Application of this respiration model to calcite dissolution in sediments required that the value of org/inorg be close to 0.7. The "oxic/anoxic" model attempts to represent the maximum possible effect of anoxic carbon diagenesis on calcite dissolution. In this case, a value ranging from 0.7 to 1.0 was required to simulate the data. Since this difference in org/inorg is small relative to the variation in sediment trap data, the distinction between the two models will be regarded as a subtlety, and the oxygen-only model will be used henceforth.

MODEL APPLICATION TO THE PRESENT-DAY EQUATORIAL PACIFIC

From the analysis presented by Archer [1991], we can infer the values of the various model parameters that are required to simulate the preservation of calcite in the equatorial Pacific today. This will be a useful prelude to

interpreting the geological record from the glacial era. The necessary model parameters are the rain rates of organic carbon, calcite, and detrital material. The rain rate of refractory material was expressed by Archer [1991] relative to the calcite rain as $\% \text{CaCO}_3^{\text{initial}}$, 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 Farrell and Prell [1989] record [Archer, 1991] and with the concentration of calcite in the shallowest cores in the record ($> 80\%$ at $\Delta \text{CO}_3 = -10 \mu\text{M}$). A value of the 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 rates of calcite from the last interglacial 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 sediment. The position of the top of the present-day lysocline is defined by the estimated ΔCO_3 at ~ 4300 m (-10 to $-15 \mu\text{M}$) and rain rates from sediment trap data [Dymond and Collier, 1988]. This position is marked "H" 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 label "H"; ΔCO_3 is the present-day estimate). The bottom of the Farrell and Prell record is located at 6°N (site RC12-63, 4949 m). This is located on Figure 4 using the calcite rain rate from MANOP site H (6°N), and an estimated ΔCO_3 of $\sim 30 \mu\text{M}$ (Figure 3). The "path" of the Farrell and Prell Holocene lysocline is traced between these two locations (heavy line).

MODEL APPLICATION TO THE GLACIAL 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 rates, the rain rate 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 practicality there will be a continuum of model solutions that can explain the glacial calcite preservation signal. Thus, rather than argue that we can infer quantitatively specific results from the model, we will limit our interpretation of the model output to comments about its broad behavior.

The range of accumulation rates of calcite 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 "Diss.") by increasing the water column carbonate ion concentration. Alternatively, the production hypothesis (labeled "Prod") would increase the calcite rain rate by a bit more than a factor of 2, to about $50 \mu\text{M cm}^{-2} \text{yr}^{-1}$. A third possibility

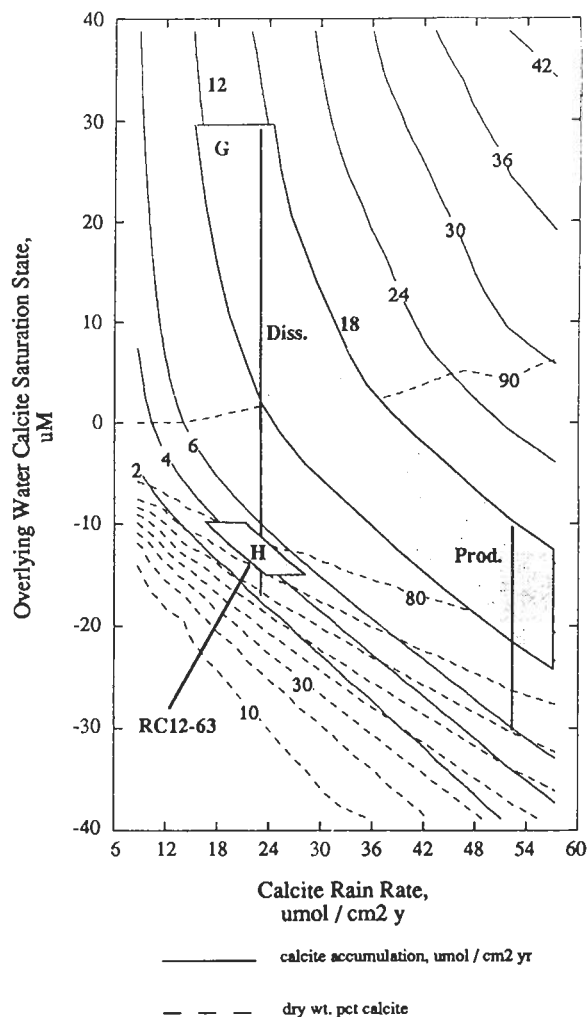


Fig. 4. Contours of model sedimentary calcite concentration and accumulation rate, in the space of water column ΔCO_3 (calcite saturation state) and calcite rain rates. The molar ratio of organic carbon to calcite rain rates for these simulations is 0.7. The value of the sedimentary calcite concentration assuming no dissolution is 95% (referred to in text as $\% \text{CaCO}_3^{\text{initial}}$). The position of the top of the lysocline in the equatorial Pacific today (indicated by "H") is determined by the water column chemistry (-10 to $-15 \mu\text{M} \Delta\text{CO}_3$) and the rain rate of calcite from sediment traps (from MANOP 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 lysocline is determined by MANOP 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_3 of up to $40 \mu\text{M}$ (the 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.").

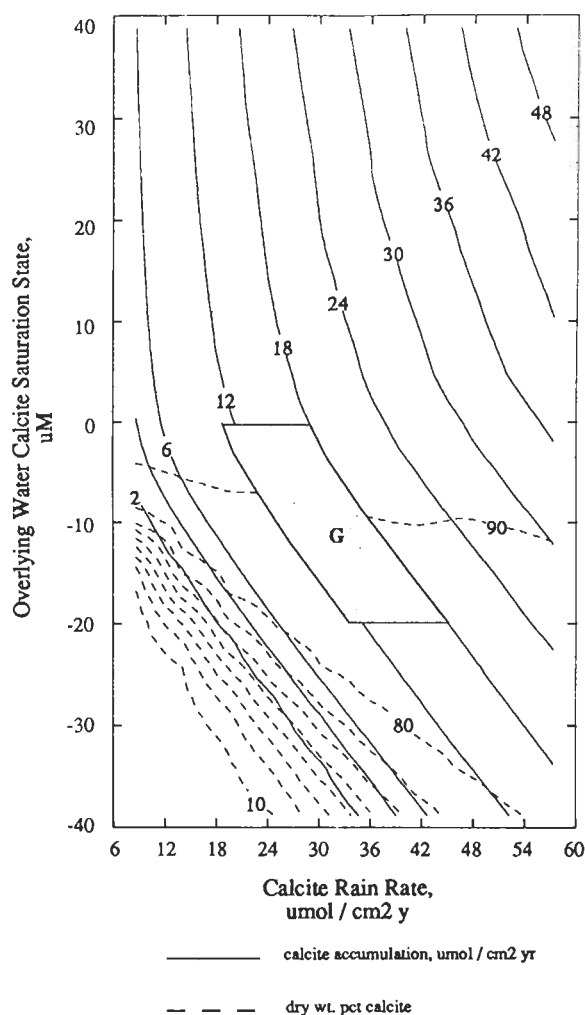


Fig. 5. Increasing calcite accumulation by lowering the organic carbon / calcite molar rain rate ratio. The stippled region is the observed glacial calcite accumulation rate. In the case of similar water column ΔCO_3 to today, a calcite rain rate of $\sim 30 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ would 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 top of the lysocline, as observed in the Farrell and Prell record.

In order to generate the observed glacial accumulation rates of calcite (which ranged to $20 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ at site SDSE 60) without changing production rates, an increase in overlying water carbonate ion of up to $40 \mu\text{M}$ would be required. This is larger than the estimates of 10 - $20 \mu\text{M}$ for the change in ΔCO_3 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 $[\text{CO}_3^{2-}]$ of up to 60 μM over the 800 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 ($\Delta z = 110 \text{ m}$). The required gradient in ΔCO_3 of 180 $\mu\text{M}/\text{km}$ (from the second constraint) can be compared with a present-day gradient between NADW and AABW in the western Atlantic of 40-80 $\mu\text{M}/\text{km}$ (from GEOSECS stations 53-56). Clearly maintenance of a gradient of ΔCO_3 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 $\sim 5^\circ\text{N}$. The possibility of higher production in the glacial equatorial Pacific is supported by sedimentary organic carbon [Pedersen, 1983], manganese [Finney et al., 1988], lipid biomarkers [Prah et al., 1989], accumulation of other biogenic sedimentary components [Arrhenius, 1988], and plankton assemblages (from the Atlantic, Mix [1989]). This scenario assumes that the chemistry of the water column was relatively homogeneous, 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] (Emerson and Archer, manuscript in preparation, 1991); these predictions are compatible but not required or well constrained by the calcite production hypothesis.

Alternative scenarios. 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 sedimenting material. This has the effect of diminishing respiration-driven calcite dissolution [Archer, 1991]. Figure 5 is a contour plot similar to Figure 4, but generated using a ratio of organic carbon to calcite of 0.5 instead of 0.7. Without making any changes in the water column calcite saturation state, 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 rain rates would have to be lower if the water column $[\text{CO}_3^{2-}]$ were higher than at 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 [Pedersen, 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; Emerson and Hedges, 1988], it is likely that the 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 somewhat. 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 their predicted lysoclines 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 $\sim 36\text{-}42 \mu\text{M cm}^{-2} \text{ yr}^{-1}$ (an increase by a factor of 1.6-2.0 over present-day rates), which is lower than the estimate of $\sim 50 \mu\text{M cm}^{-2} \text{ yr}^{-1}$ (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 lysocline and in the accumulation rate for calcite are documented in the Equatorial Pacific geologic record. One potential explanation for the observations (the "dissolution hypothesis") is that the gradient of the calcite saturation state with water depth became more intense during the last glacial period. By comparing a numerical model for the calcite lysocline to the observed calcite concentration and accumulation data, we show that the required change in ΔCO_3 is 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 requires a gradient in ΔCO_3 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 lysocline and increase the accumulation rate to the extent observed. Homogeneous changes in the water column $[\text{CO}_3^{2-}]$ within the range of previous theoretical predictions are not inconsistent with or required by this scenario.

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