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Calcium carbonate preservation in the ocean

By S. R. Emerson and D. Archer
University of Washington, School of Oceanography, Seattle, Washington 98195, *U.S.A.*

Recent microelectrode pH and O_2 measurements across the sediment–water interface suggest $CaCO_3$ dissolution kinetics substantially slower than laboratory values and support a dissolution response to organic matter degradation near the sediment surface. We report a modelling exercise, motivated by these results, that indicates the pattern of calcium carbonate preservation in the equatorial Atlantic and Indian oceans is most readily reproduced using a dissolution rate constant 10 to 100 times smaller than those measured in the laboratory. The model suggests that 40% or more of the particulate $CaCO_3$ rain dissolves at the calcite saturation horizon in response to organic matter degradation within the sediments, and that this effect is insensitive to the choice of dissolution rate constant in ranges measured. Implications are that the dissolution flux from the sediments is greater than previously thought, and that calcium carbonate preservation in the deep sea should be strongly dependent on the particulate organic carbon to calcium carbonate rain ratio.

Introduction

Calcium carbonate dissolution in marine sediments is one of the processes responsible for determining the carbonate chemistry of ocean water and the largest eventual buffer for neutralizing anthropologically produced carbon dioxide. Recent models derived to explain glacial–interglacial changes in atmospheric CO_2 content include the response of marine carbonate sediments to variations in the ocean's carbon cycle as an important component. That there have been changes in the pattern of $CaCO_3$ preservation in the ocean coincidentally with glacial cycles has been known through studies of marine sediments since the work of Arrhenius (1952). Factors that control $CaCO_3$ dissolution are the particulate rain rates of calcium carbonate and organic carbon to the ocean bottom, the degree to which the minerals calcite and aragonite are saturated in bottom waters overlying the sediments and the dissolution rates of these minerals in undersaturated waters. When these values are accurately quantified it will be possible to construct and test a realistic model of calcium carbonate preservation. This paper may be viewed as a part of the evolution toward this goal.

The accumulation rate of $CaCO_3$ in deep ocean sediments located above the saturation horizon is on the order of (1.0 ± 0.5) g $CaCO_3$ cm^{-2} ka^{-1} (see, for example, Broecker & Peng 1982). Sediment trap studies reveal a much wider range of carbonate flux to the sediments, but because there are seasonal and interannual variations in the particulate flux, the sediment accumulation rate measurements should be a more accurate estimate of the long-term average (if it can be assumed that the dissolution of $CaCO_3$ is insignificant in sediments that underlie supersaturated waters). The increasing detail and quantity of sediment trap studies over the past decade have established that the molar ratio of organic and calcium carbonate carbon in particulate material that reaches the deep sea floor is about 1.0 ± 0.5 (Wefer 1989; Dymond & Lyle 1985). This is important because most of the organic carbon that reaches the sediment is degraded at the interface and within the top few centimetres of the sediments, and the metabolic CO_2 that is released could play an important role in $CaCO_3$ dissolution. Emerson & Bender (1981) estimated that this effect has the potential for dissolving a large fraction of the particulate carbonate rain even in sediments that are bathed with waters supersaturated with respect to calcite. This prediction is valid only if a major fraction of the particulate organic carbon rain is degraded within the sediments rather than at the interface, and if the rate of solid carbonate dissolution is rapid enough to dissolve before metabolic CO_2 is neutralized by carbonate ion diffusion from bottom water. Pore-water measurements coupled with sediment trap deployments in the equatorial Pacific have verified the first of these criteria (Emerson *et al.* 1985), but direct evidence for the second is still rare.

One might expect that the importance of organic matter degradation and bottom water saturation to $CaCO_3$ preservation could be evaluated by comparing indicators of dissolution observed in sediments with the degree of saturation in accompanying bottom waters. Because the particulate $CaCO_3$ content of sediments is a strong nonlinear function of the fraction that is preserved, and therefore insensitive to dissolution until roughly half of the carbonate is dissolved, other indices such as the degree of carbonate shell fragmentation and the relative abundance of shells resistant to dissolution are used to judge the extent of calcium carbonate loss (see, for example, Berger *et al.* 1982; Peterson & Prell 1985). Quantifying the amount of dissolution that brings about changes in these indices, however, has proved to be very erratic (Ku & Oba 1978; Adelseck 1977; Peterson & Prell 1985).

Evaluating the degree of saturation of bottom water is less ambiguous than quantifying the extent of dissolution of sediments, but also imperfectly known. Advances in our ability to measure carbonate parameters in seawater during GEOSECS and TTO surveys, and recent laboratory studies of calcite solubility products, have improved estimates of the depth where seawater becomes unsaturated with respect to calcium carbonate minerals (the saturation horizon). Still, present lack of reproducibility among different experimental determinations of the solubility product causes uncertainty in the saturation horizon depth of at least ±0.5 km (see later). For these reasons, direct comparison of seawater saturation state with indicators of sediment dissolution alone is too poorly understood to provide a reliable method of evaluating the mechanisms of calcium carbonate preservation.

Laboratory studies of calcite and aragonite dissolution rates as a function of the degree of undersaturation using suspended particles in a stirred reactor have shown that the rate of dissolution, r, follows the law:

$$r = kX(1-[CO_3]_m/[CO_3]_s)^n, \tag{1}$$

where X is the concentration of solid $CaCO_3$ in the sediments (mol cm^{-3}_{bulk}) and the subscripts m and s refer to measured and saturated carbonate ion concentration. The rate constant for natural carbonate-rich sediment is on the order of 30 d^{-1} and is roughly of order 4.5 with respect to the normalized degree of undersaturation (Morse 1978; Keir 1980). (A rate constant of 30 d^{-1} leads to daily dissolution of roughly $\frac{1}{4}\%$ of the solid $CaCO_3$ for a 10 μmolar degree of undersaturation.) This value was only slightly greater than that derived for reagent grade calcite in the same experiments. Although these two $CaCO_3$ particles give close to the same result, Keir (1980) observed in his study of biogenic calcite that the larger size fraction of the sediment and individual foraminifera shells dissolved two orders of magnitude more slowly.

Laboratory results for reagent grade calcite and whole sediments represent only an upper limit for the *in situ* dissolution rate, because it is possible that the process in the ocean might be inhibited by factors such as solid surface coatings and the presence of dissolved organic matter in pore waters. Keir (1983) conducted a laboratory dissolution experiment using a 6 mm layer of sediment rather than a suspension. This study revealed much lower dissolution kinetics but was flawed by the potential for dissolution impedence caused by a millimetre scale benthic boundary layer. Sensitivity to boundary layer thickness in this study was due mainly to the high degrees of undersaturation he used (see Archer *et al.* 1989). There have been only a few attempts to determine the dissolution rate *in situ*. Benthic flux measurements of alkalinity and dissolved inorganic carbon (DIC) by Berelson *et al.* (1987) from California borderland sediments indicate rate constants that are at least two orders of magnitude slower than those determined using whole sediment in the stirred reactor laboratory experiments. There are, however, reasons to be cautious about deriving rate constants from the benthic flux experiments, because alkalinity fluxes may have been influenced by sulphate reduction, greatly complicating the interpretation.

The only other *in situ* study of the response of deep-sea calcitic sediments to undersaturation is the microelectrode investigation of Archer *et al.* (1989). They measured fine scale gradients of O_2, pH and conductivity across the sediment–water interface at locations above and below the calcite saturation horizon in the equatorial Atlantic Ocean. The pH data within the surface centimetre of sediments from this study could be explained only if calcite dissolved in response to the metabolic CO_2 input estimated from microelectrode O_2 profiles, and only if the dissolution rate constant was between 0.1 and 1 d^{-1}. While there is a large uncertainty caused by the insensitivity of pH to the reaction rate constant, these results, like the benthic flux experiments, are incompatible with the fast dissolution rate constants derived in the stirred reactor laboratory experiments. Furthermore, they provide the first direct evidence that calcite dissolves both above and below the saturation horizon in response to metabolic CO_2 input.

Another approach to evaluating the dissolution rate constant is to model the distribution of $CaCO_3$ content in oceanic sediments. Keir (1982) demonstrated the sensitivity of the dissolution rate constant determined in this way to the depth of the saturation horizon in the water column. His model did not include the effect of organic matter metabolism within surface sediments. Emerson & Bender (1981) included this effect but used relatively rapid, first-order reaction kinetics following a previous study of Takahashi & Broecker (1977).

Since the last modelling attempts to assess our understanding of factors controlling the preservation of calcium carbonate, the boundary conditions (particle flux, water column saturation state and the *in situ* dissolution rate kinetics) have become more accurately quantified. The purpose of this paper is to provide a status report on our understanding of the mechanisms controlling $CaCO_3$ preservation in the ocean. Our strategy is to compare the first-order predictions of model derived carbonate distributions with observations in three locations of the ocean where boundary conditions and sediment accumulation rates have been studied in detail. The model we use to describe the pore water chemistry is that in Archer *et al.* (1989).

Oceanic observations

Rather than attempting to model the detailed depth distribution of calcium carbonate content in marine sediments at various locations in the ocean, we choose three criteria that describe the pattern of carbonate preservation and compare these with model predictions. The criteria that must be reproduced in the model are: (1) the accumulation rate of $CaCO_3$ above the saturation horizon; (2) the difference between the degree of carbonate ion saturation ($\Delta CO_3 = [CO_3]_s - [CO_3]_m$) at the depth where the sedimentary carbonate content shows first signs of a strong depth dependence (referred to here as the calcite lysocline; $\Delta CO_{3,\,lys}$) and the degree of saturation at the depth where sedimentary carbonate reaches negligible levels (the carbonate compensation depth (CCD); $\Delta CO_{3,\,CCD}$). We refer to this difference as $\delta\Delta CO_{3,\,lys-CCD}$, and it is an estimate of the intensity of undersaturation required to decrease the fraction of solid carbonate from 80–90% to negligible values; (3) the final criterion is similar to number (2) except that it is a measure of the difference in ΔCO_3 between the water column saturation horizon (SH) and the CCD ($\delta\Delta CO_{3,\,SH-CCD}$). By definition this value is equal to ΔCO_3 at the carbonate compensation depth. It is more variable than criterion number (2) because of the uncertainty in the depth of the saturation horizon (see later).

There are three locations containing carbonate sediments that have been studied in detail and where the water column chemistry is well defined from GEOSECS and TTO surveys (table 1). The locations are all in the equatorial oceans, which is in some ways unfortunate because it diminishes the variation in boundary conditions that control calcium carbonate preservation. Nevertheless, it does not bias our interpretation of the relative importance of the boundary conditions at this location, and we must study areas that are well characterized to derive any sort of test for the model. Table 1 lists the calcium carbonate accumulation rates and the two $\delta\Delta CO_3$ criteria. We do not include the central equatorial Pacific Ocean because the lysocline may be strongly influenced by lateral differences in the particulate flux.

TABLE 1. SEDIMENTATION RATE (S) REFRACTORY MATERIAL AND $CaCO_3$ ACCUMULATION RATES (P_r AND P_{Ca}), DEPTH OF THE SEDIMENTARY LYSOCLINE AND CCD, THE ΔCO_3 DIFFERENCES BETWEEN THE LYSOCLINE AND CCD, AND THE SATURATION HORIZON AND THE CCD

	S	P_r	P_{Ca}	lysocline depth	CCD	$\delta\Delta CO_{3,\,lys-CCD}$	$\delta\Delta CO_{3,\,SH-CCD}$
location	($cm\ ka^{-1}$)	($g\ cm^{-2}\ ka^{-1}$)		km		($\mu mol\ kg^{-1}$)	
east Atlantic	1.5^a	0.27^c	$0.8–0.9^c$	4.4^b	6.0^b	30	20–30
west Atlantic	—	0.38^c	$0.9–1.0^c$	$4.2^{c,d}$	$5.5^{a,d}$	50	40–50
Indian	1.7^e	0.15^e	$1.3–1.4^e$	3.8^e	5.0^e	25	25–35

[a] Curry & Lohman (1985); [b] Biscaye *et al.* (1976); [c] W. B. Curry & G. P. Lohrmann (unpublished); [d] Thunell (1982); [e] Peterson & Prell (1985).

Depth profiles of measured dissolved carbonate ion concentration and the values estimated to be in equilibrium with calcite in the equatorial Atlantic and Indian Oceans are illustrated in figure 1. The carbonate ion concentrations were calculated from alkalinity and DIC data from TTO and GEOSECS surveys (Takahashi *et al.* 1980; Williams 1986). Data were corrected to be consistent among the oceans and between surveys in the manner outlined by Takahashi *et al.* (1985). Carbonate ion was calculated using the procedures presented by Broecker & Takahashi (1978) except that first and second carbonate ion dissociation constants were those suggested by Dickson & Millero (1987) rather than Merbach *et al.* (1973). This change makes little difference in the resultant carbonate concentration because the two sets of equilibrium data are very similar. (This is also true at 2 °C temperature for the constants determined by Goyet & Poisson (1990); see also Goyet & Brewer (1990).) Alkalinity and DIC data for the Indian Ocean profile were extrapolated to correspond to core top locations on the 90° E ridge by Peterson & Prell (1985).

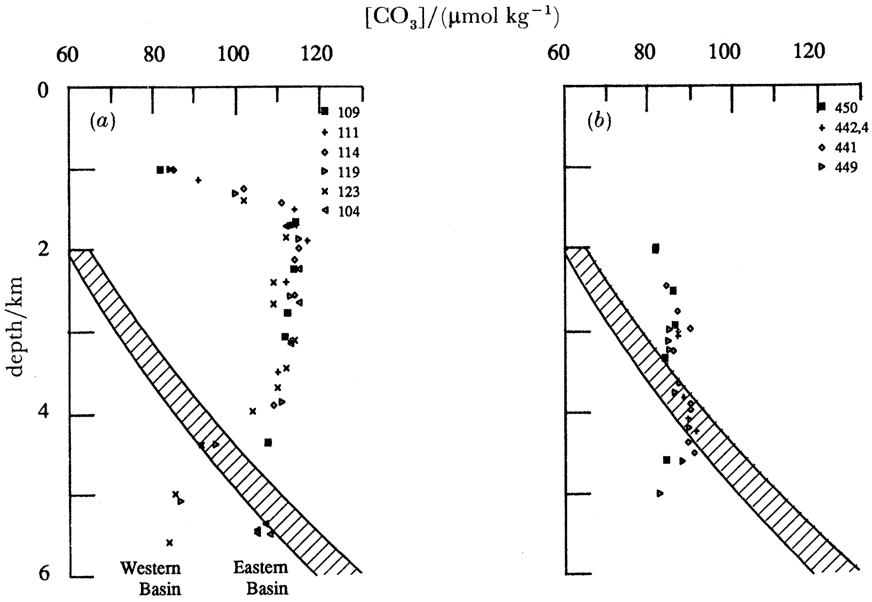

FIGURE 1. Carbonate ion concentrations and the depth dependence of the concentration in equilibrium with calcite for (*a*) the equatorial Atlantic Ocean and (*b*) the Indian Ocean. Symbols in the Atlantic Ocean represent different TTO stations (0–9° N and ≈28° W); in the Indian Ocean they are the extrapolations given by Peterson & Prell (1985) from the GEOSECS stations listed. The difference in saturation value curves reflect the range of uncertainty in the one atmosphere solubility measurements of Mucci (1983). See text for details.

The calcite solubility product at one atmosphere used to calculate the carbonate saturation value is that reported by Mucci (1983), $(4.4 \times 10^{-7} \pm 0.2 \times 10^{-7})$ $\mathrm{mol^2\,kg^{-2}}$ at 2 °C and 35‰. The range in his experimental values incorporates the best estimate of Morse *et al.* (1980) when corrected to 2 °C using Mucci's temperature dependence. His value, however, is 0.3×10^{-7} and 0.5×10^{-7} $\mathrm{mol^2\,kg^{-2}}$ lower than the 2 °C, 35‰ results of Ingle *et al.* (1973) and Plath *et al.* (1980) respectively. We chose the results of Mucci (1983) because of the long equilibration times and large number of experiments reported. The range in the equilibrium carbonate ion concentration in figure 1 corresponds to the $\pm 0.2 \times 10^{-7}$ $\mathrm{mol^2\,kg^{-2}}$ error reported by Mucci (1983). Pressure dependence on the solubility product determines the change in the saturation carbonate ion value with depth. We used the dependence presented by Millero (1982) and confirmed by the pore water measurements of Sayles (1985).

The saturation horizon is represented by the intersection of the carbonate ion saturation values with the sea water measurements in figure 1. These estimates are shallower than the 'critical' CO_3^{2-} ion depth estimated by Broecker & Takahashi (1978) by 0.25–0.5 km mainly because of the solubility pressure dependence used here. Uncertainty in the one atmosphere value for the solubility product, alone, creates a range of possible saturation horizon depths of ±0.25 km in the Atlantic Ocean and ±0.5 km in the Indian Ocean. As it is not possible to evaluate the extent of error in the solubility product pressure dependence and the dissolved carbonate ion concentration without further studies, we assume, for the argument that follows, that these values are perfectly known. The range of possible saturation horizon depth is, thus, probably a lower limit. This variation is the reason for the range in the $\delta\Delta CO_{3,\,\mathrm{SH-CCD}}$ values in table 1.

MODEL RESULTS

Model predictions described here were generated from the diffusion-reaction pore water scheme of Archer *et al.* (1989) combined with a sediment surface layer that is homogeneous in $CaCO_3$ concentration (on a weight–weight basis). Boundary conditions for the problem are the particulate rain rates of $CaCO_3$, refractory material, and organic carbon, coupled with the degree of bottom water saturation, ΔCO_3. The relation between the pore water and solid calcium carbonate is embodied in the expression for the rate of calcium carbonate dissolution (equation (1)). The only unknown besides the boundary conditions is the value of the rate constant, k.

The pore water model presented in Archer *et al.* (1989) includes the porosity gradients measured by their *in situ* microelectrode profiler, dissolved carbonate species equilibrium and the single ion diffusion coefficients. The preservation rate of calcium carbonate and the $CaCO_3$ fraction within the mixed layer are generated by calculating the steady-state pore water profile and calcite dissolution flux, F_{Ca}, as a function of the content of calcite in the sediment mixed layer. The $CaCO_3$ content X is then adjusted until a balance is achieved between the $CaCO_3$ rain rate R_{Ca} the dissolution flux out of the sediments and the preservation rate, P_{Ca}:

$$R_{Ca} = F_{Ca}(X) + P_{Ca}(X). \qquad (2)$$

The numerical scheme used here was checked by decreasing time steps until constant results were achieved and against the analytical solution given by Keir (1982) for the condition of no porosity gradient and no organic carbon degradation.

Model derived mixed layer calcium carbonate content, the dissolution flux of calcium from the sediments and the $CaCO_3$ preservation rate above the saturation horizon are presented in figure 2 and summarized in table 2. A matrix of solutions were generated for: (1) two different dissolution rate constants (the maximum value expected from the stirred reactor experiments of Keir (1980), 30 d^{-1}, and a value near the lower limit required to explain the microelectrode pH data of Archer *et al.* (1989), 0.15 d^{-1}); (2) calcium carbonate rain rates of 12 and 17.5 $\mu mol\ cm^{-2}\ a^{-1}$ (1.2 and 1.75 g $CaCO_3$ $cm^{-2}\ ka^{-1}$) (this is the range that generates observed accumulation rates and conforms to sediment trap particulate-organic-carbon:calcium-carbonate ratio); (3) a particulate organic carbon rain rate of 12 $\mu mol\ cm^{-2}\ a^{-1}$, which is the average value determined by recent microelectrode oxygen measurements in the equatorial Atlantic and is in agreement with range of values reported in equatorial Pacific sediment trap and benthic flux measurements (Emerson *et al.* 1985); and (4) a range of ΔCO_3 values from 40 to -40 $\mu mol\ kg^{-1}$.

Percent $CaCO_3$-depth curves for the rapid carbonate dissolution rate constant in figure 1 indicate that this expression of calcium carbonate preservation in the ocean is relatively insensitive to the range in particulate $CaCO_3$ and organic carbon fluxes. The main effect of variations in the particulate $CaCO_3$ and organic carbon input is the position of the depth gradient with respect to the saturation horizon, and the maximum difference is only 10 $\mu mol\ kg^{-1}$ ΔCO_3. The reason for the lack of sensitivity is that nearly all the predicted change in $CaCO_3$ fraction is below the saturation horizon and, in the case of rapid kinetics, the dissolution in this region is promoted primarily by bottom-water undersaturation that occurs very near the sediment–water interface rather than dissolution driven by organic matter degradation, which occurs at a $1/e$ depth of 1.5–2.0 cm.

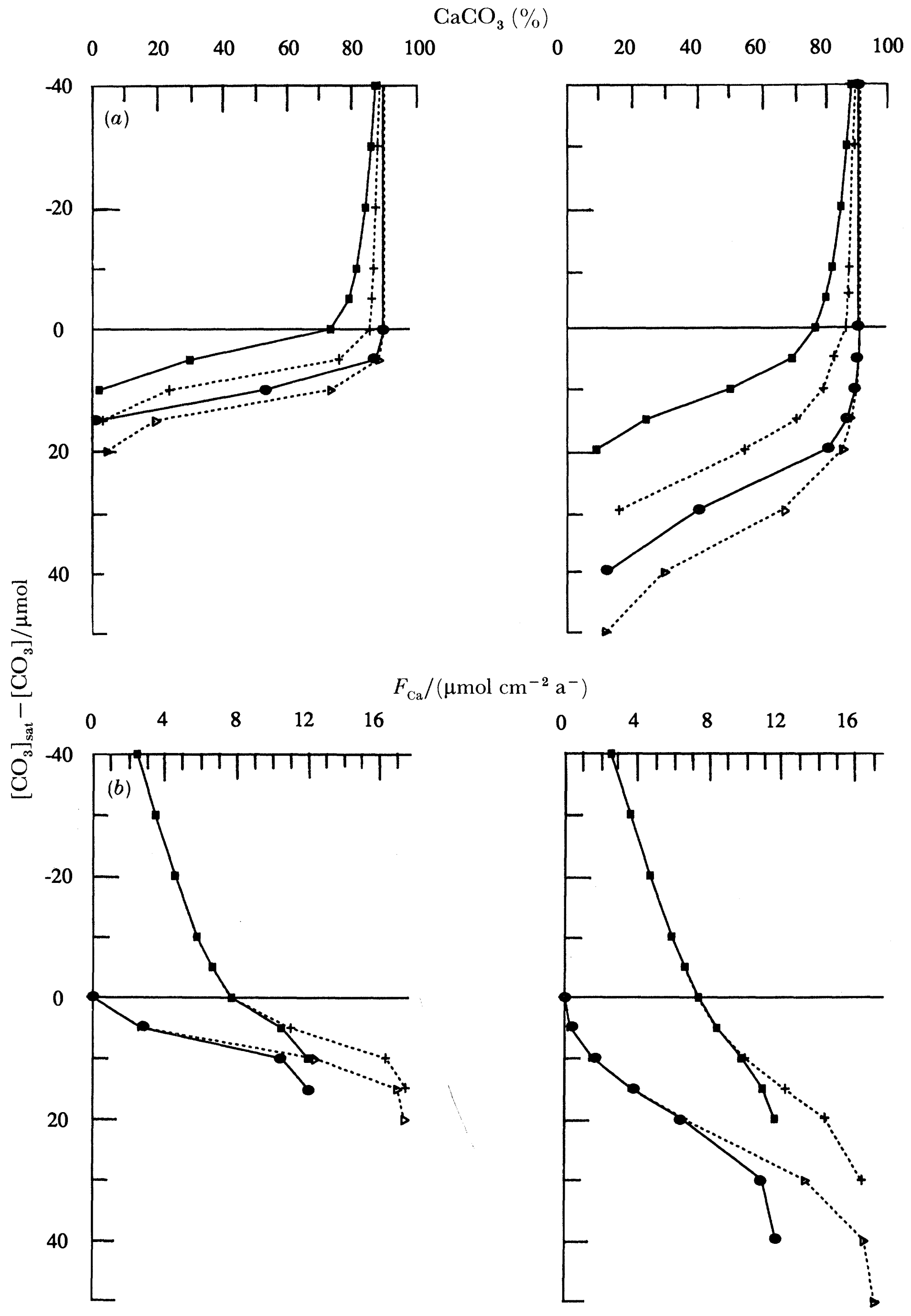

FIGURE 2. Model derived curves for (*a*) the sedimentary content of CaCO$_3$ as a function of depth and (*b*) the flux of dissolved calcium from CaCO$_3$ dissolution out of the sediments. The curves were generated for two different dissolution rate constants and a range of CaCO$_3$ and organic carbon particle rain rates (see text). ——, $R_{Ca} = 12$; ----, $R_{Ca} = 17.5$. ■+, $R_{oc} = 12$; ●△, $R_{oc} = 0$. For the left-hand figures $k = 30\ d^{-1}$, for the right-hand figures $k = 0.15\ d^{-1}$.

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TABLE 2. SUMMARY OF MODEL RESULTS FOR P_{Ca} (AT $\Delta\mathrm{CO}_3 = -25\ \mu\mathrm{mol\ kg}^{-1}$), $\delta\Delta\mathrm{CO}_{3,\,\mathrm{lys-CCD}}$ AND $\delta\Delta\mathrm{CO}_{3,\,\mathrm{SH-CCD}}$

(k is the calcite dissolution rate constant, R_{Ca} and R_{oc} the particulate $\mathrm{CaCO_3}$ and organic carbon rain rates. All refractory rain rates are $0.1R_{\mathrm{Ca}}$ except where indicated.)

	R_{Ca}	R_{oc}	$R_{\mathrm{oc}}/R_{\mathrm{Ca}}$	P_{Ca} (at $\Delta\mathrm{CO}_3 = -25\ \mu\mathrm{mol\ kg}^{-1}$)	$\delta\Delta\mathrm{CO}_{3,\,\mathrm{lys-CCD}}$	$\delta\Delta\mathrm{CO}_{3,\,\mathrm{SH-CCD}}$
$k\ d^{-1}$	$\mu\mathrm{mol\ cm^{-2}\ a^{-1}}$			$\mathrm{g\ cm^{-2}\ ka^{-1}}$	$\mu\mathrm{mol\ kg}^{-1}$	
30	12	0	—	1.2	10	15
	17.5	—	—	1.75	15	20
	12	12	1.0	0.8	10–15	10
	17.5	12	0.6	1.4	15	15
0.15	12	0	—	1.2	25–30	45
	17.5	0	—	1.75	35	55
	12	12	1.0	0.8	25	25
	17.5	12	0.6	1.4	25–30	35
	17.5[a]	12	0.6	1.4	25–30	35

[a] The refractory sediment content in this experiment was 40 rather than 10% of the particulate carbonate flux.

Results using the slower dissolution rate constant ($0.15\ \mathrm{d}^{-1}$) are much more sensitive to the particulate rain rate. The difference between the presence and absence of organic-matter-driven dissolution is nearly $20\ \mu\mathrm{mol\ kg}^{-1}$ and variation of the $\mathrm{CaCO_3}$ rain rate causes another $15\ \mu\mathrm{mol\ kg}^{-1}$. The effect of increasing the calcite rain rate is to deepen the $\%\mathrm{CaCO_3}$ depth gradient, whereas increased organic matter rain causes it to shoal. Increased sensitivity to organic matter degradation is caused by relative insensitivity to bottom-water-driven dissolution because of the slower rate constant, with unchanged response to metabolically promoted dissolution. The reason for the latter effect is that organic matter degradation occurs deep enough in the sediment that the amount of $\mathrm{CaCO_3}$ dissolved by this process is independent of the range of dissolution rate constants used in our model runs.

Insensitivity of metabolically driven calcium carbonate dissolution to the rate constant is illustrated dramatically in plots of the flux of calcium out of the sediment in figure 2. Fluxes at a given depth above the saturation horizon are nearly the same for the widely differing rate constants used here. Emerson & Bender (1981) illustrated that the extent of $\mathrm{CaCO_3}$ dissolution in situations where bottom waters are above saturation depends upon the relative depths of the onset of pore water undersaturation and the 1/e depth of organic matter degradation. Model derived curves of pore water $\mathrm{CO_3^{2-}}$ ion as a function of depth (figure 3) indicate that, for both dissolution rate constants, the depths in the sediments where undersaturation begins are substantially above the 1/e organic carbon degradation depth of 1.5–2.0 cm. The consequence is that the organic matter promoted dissolution is insensitive to the rate constant. Results in figure 2 demonstrate the nonlinearity of the relation between sediment calcite content and the dissolution flux. The model predicts that between 40 and 70% of the particulate calcite rain is dissolved at the saturation horizon for the cases where organic matter degradation is included. This effect is manifested in the sediments by a range in $\mathrm{CaCO_3}$ content of only 75 to 85%.

Comparison of model results and oceanic observations

The criteria for judging which set of rate constants and boundary conditions most closely describe the oceanic observations are summarized in tables 1 and 2. The $\delta\Delta\mathrm{CO}_3$ values

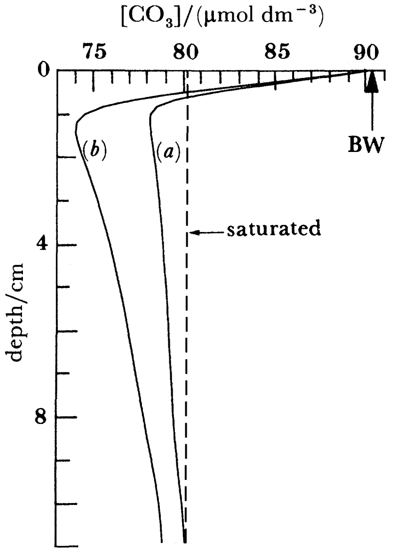

FIGURE 3. Model derived depth profile for CO_3^{2-} in pore waters for two different rate constants: (*a*) 30 d^{-1} and (*b*) 0.15 d^{-1}. $\Delta CO_3 = -10$ µmol kg^{-1}; $R_{Ca} = R_{oc} = 12$ µmol cm^{-2} a^{-1} for these solutions.

produced by the model using the fast kinetic rate constant (30 d^{-1}) are all substantially smaller than those observed in the equatorial Atlantic and Indian Oceans. Model results for the conditions $R_{Ca} = 17.5$ µmol cm^{-2} a^{-1} and $R_{oc} = 0$ nearly match the observations, but for this case the CaCO$_3$ accumulation rate is outside the measured range. Results from the slower dissolution rate constant (0.15 d^{-1}) runs produce $\delta\Delta CO_3$ values that are closer to the observations. The greatest $\delta\Delta CO_3$ values generated for the case of no carbon rain ($R_{oc} = 0$) are close to the observations, but in these model runs $\delta\Delta CO_{3,\text{SH-CCD}}$ is 50–80% larger than the $\delta\Delta CO_{3,\text{lys-CCD}}$ indicating that this condition produces a lysocline depth that is as much as 1–2 km deeper than the saturation horizon (figure 2). This is not observed in the sediment and water column saturation estimates for these oceanic locations. Apparently, deepening of the CaCO$_3$ lysocline–CCD depth transition caused by the slower dissolution kinetics is compensated in the real world by the shoaling effect of CaCO$_3$ dissolution prompted by metabolic CO$_2$ produced in the sediments. This is illustrated by the model results created from slow kinetics with $R_{Ca} = 17.5$ and $R_{oc} = 12$ µmol cm^{-2} a^{-1}. $\delta\Delta CO_3$ values for this case are in the same range as the observations from the eastern equatorial Atlantic and Indian Oceans. $\delta\Delta CO_3$ values from the western Atlantic Ocean are greater than the predictions. As this is an area of high burial rates of refractory material from the Amazon River, the effect of detrital dilution on the depth gradient of sedimentary carbonate content was examined in the final model run in table 2 and found to make very little difference. We do not know the reason for the greater degrees of undersaturation required to rid the sediments of CaCO$_3$ in this region.

CONCLUSIONS

Our best estimate of the conditions required to reproduce the pattern of CaCO$_3$ preservation in the equatorial Atlantic and Indian Oceans requires a relatively slow dissolution rate of calcium carbonate. We are somewhat cautious about suggesting that the modelling results, by themselves, unequivocally require that the organic matter flux to the ocean bottom play a critical role in the pattern of $CaCO_3$ preservation, as two of the three criteria we use to compare model and observational results could be met without this process. The argument for the necessity of metabolically promoted dissolution within the sediments is that it is not possible to satisfy all three criteria without it, and that recent sediment trap, benthic flux and microelectrode studies leave us no choice.

The key result of the modelling exercise is that increases in our understanding of particle fluxes, the *in situ* $CaCO_3$ dissolution rate and processes controlling the dynamics at the sediment–water interface do not dramatically change the conclusion of Emerson & Bender (1981) regarding the effect of organic matter degradation on $CaCO_3$ preservation. The reason is that this process is relatively insensitive to the rate of calcium carbonate dissolution. Our results reinforce the conclusion that greater than 40 % of the calcite rain dissolves in sediments that lie at the saturation horizon depth and 15–30 % dissolves several kilometres above this depth. The slow dissolution rate constant is an argument against the hypothesis that calcium carbonate preservation is influenced by the presence of a benthic sublayer with thickness of the order of 1 mm (Schink & Guinasso 1977). A dissolution rate constant of 0.15 d^{-1} results in a 1/e penetration depth into the sediments of *ca.* 0.6 cm at typical oceanic undersaturations, rendering diffusion depths differences of a millimetre insignificant.

The conclusion that a large fraction of $CaCO_3$ rain dissolves in response to organic matter degradation above the saturation horizon is at odds with some sediment observations. For example, the dissolution depth curve in figure 2 predicts that the accumulation rate of $CaCO_3$ ought to decrease by a factor of two from a depth of say 2.5 km to the saturation horizon. In the two locations where detailed accumulation rates have been measured over a wide depth interval: the Serra Leone rise and the Ontong-Java plateau (Curry & Lohman 1985; Berger & Killingly 1982; DuBois & Prell 1989), changes in the accumulation rates are not observed until near the saturation horizon. Although these observations do not follow our prediction, there are explanations that do not require invalidation of the model results. First, the model derived $CaCO_3$ contents are all generated by using a constant organic carbon rain rate, whereas it has been shown in most sediment trap studies that the particulate carbon rain rate decreases with depth below one kilometre by a factor of 50–100 % (Dymond & Lyle 1985; Dymond & Collier 1988). This would increase the metabolically driven dissolution at shallower depths offsetting the depth trend in figure 2. It is also possible that the accumulation rates measured at these two locations incorporate the effect of a significant down slope transport which would tend to decrease an expected trend of smaller accumulation rates with depth. In fact, the ^{14}C derived sedimentation rates reported by DuBois & Prell (1989) cannot be interpreted as steady-state deposition because there is no change in sedimentation rate throughout the entire depth range, even below the lysocline where mixed layer ages indicate roughly 40 % of the carbonate rain has dissolved.

Another inconsistency between our predictions and sediment observations is that the amount of $CaCO_3$ dissolution above the saturation horizon indicated in figure 2 is greater than that suggested by sediment studies in the Indian (Peterson & Prell 1985) and western equatorial Pacific (Berger *et al.* 1982) oceans. The discrepancy between our values and that derived using foraminiferal indices or degree of fragmentation might be caused by the ‘transparent’ contribution of coccoliths and pteropods to the $CaCO_3$ particle flux. Coccoliths make up roughly 30 % of the carbonate in deep-sea sediments (Roth & Berger 1975) and an unknown fraction of the particle flux, whereas aragonitic shells are virtually absent in deep sediments but comprise at least 10% of the flux (Berner & Honjo 1981). This explanation for the discrepancy between our predictions and sediment observations is more a guess than defensible observation at this point, but given the uncertain nature of the sedimentary methods used to infer calcite dissolution and the strength of the observations supporting the role of organic matter degradation in the process of dissolution, we suggest it as an attractive hypothesis.

An important implication of adopting the role of organic matter driven $CaCO_3$ dissolution is that the lysocline–CCD transition relies more on kinetic processes than previously thought. The concept of a sedimentary lysocline that is controlled by calcite equilibria in seawater is too simple. Further implications are that calcium carbonate rain rates derived from measuring accumulation rates above the saturation horizon are minimum values. The results in figure 2 and table 2 suggest that the rain rate is underestimated by roughly 20% ((1.75 − 1.4)/1.4). If we are right, the benthic flux of dissolved carbonate to the ocean that overlies carbonate rich sediments is greater than previously assumed and carries an alkalinity:DIC ratio less than the value of two for inorganically driven $CaCO_3$ dissolution. Since sediment trap studies indicate that most $CaCO_3$ dissolution in the ocean occurs on the bottom and most organic matter degradation above a depth of 1000 m, the process of metabolically driven calcite dissolution on the sea floor may be the origin of the nearly equal alkalinity:DIC trend observed in the carbonate chemistry of the deep ocean waters from the Atlantic to Pacific Ocean (Broecker & Peng 1982).

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