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Carbon fluxes at the sediment-water interface of the deep-sea: calcium carbonate preservation

by Steven Emerson[1] and Michael Bender[2]

ABSTRACT

The degradation of organic matter at the seawater-sediment interface plays an important role in the pattern of calcium carbonate preservation in the deep sea. A model developed to quantify this effect shows that the amount of calcium carbonate dissolved by metabolic CO_2 at the sediment-water interface is dependent upon the rain ratio of organic carbon and calcium carbonate, and the rates of organic matter degradation and calcite dissolution. Using the best estimates presently available for these parameters, we show that the onset of $CaCO_3$ dissolution in deep sea sediments should begin at a depth which is up to one kilometer above the calcite saturation horizon in the water column. The model predicts that 40-80% of the calcium carbonate rain from surface waters should dissolve near the sediment-water interface at the depth of the saturation horizon.

Recent estimates of the depth dependence of the calcite solubility product and data for the percent calcium carbonate as a function of depth in the Northwest Atlantic Ocean are used as evidence to support the model. These data suggest that the onset of calcium carbonate dissolution in deep sea sediment lies above the water column saturation horizon in this region.

1. Introduction

The role of metabolic CO_2 in determining the global distribution of calcium carbonate is recognized (Berger, 1970; Broecker, 1971; Bender and Graham, 1978), however its effect in regulating the preservation of $CaCO_3$ in sediments has been neglected. Models used to explain the relationship between calcite saturation in the oceans and the preservation of $CaCO_3$ in the sediments have not considered the effect of metabolic CO_2 generated at the sediment water interface. In this paper, we show that experimental evidence supports this mechanism for $CaCO_3$ dissolution; and we present a model which quantifies the effect of particulate organic carbon deposition on calcium carbonate preservation.

To illustrate the effect of metabolic CO_2 production in sediments on the depth dependence of $CaCO_3$ abundance, we present the following hypothetical arguments: (1) First, let us assume that the rain of particulate organic carbon to the sediment

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water interface is much less than the rain of $CaCO_3$, and that calcite dissolution is instantaneous (i.e., $CaCO_3$ dissolves infinitely rapidly in undersaturated pore waters until saturation is attained). In this case, the calcite accumulation rate will be equal to the rain rate above the water column saturation horizon and zero below the saturation horizon. The onset of dissolution of $CaCO_3$ in the sediments and the point where the percent calcium carbonate goes to zero (the carbonate compensation depth, CCD) are both at the depth of the saturation horizon. If the dissolution rate is not infinitely rapid, the onset of $CaCO_3$ dissolution in the sediments would lie at the saturation horizon and the CCD below. This case is conceptually similar to that discussed by Takahashi and Broecker, 1977; Schink and Guinasso, 1977; and Keir, 1979. (2) In the second hypothetical argument, we assume that the rain rate of organic carbon (abbreviated here as CHOH) is 106/124 times the rain rate of calcium carbonate, the organic carbon is bacterially degraded by oxygen reduction immediately after incorporation into the sediments, and calcium carbonate dissolution into an undersaturated solution is infinitely rapid. Carbonic, nitric, and phosphoric acids are produced during organic matter degradation according to the reaction:

$$(CHOH)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 \rightarrow 106CO_2 + 16NO_3^- \\ + HPO_4^= + 18H^+ + 122H_2O.$$

The metabolic acids will titrate "excess" $CO_3^=$ (*defined* here as $([CO_3^=]_{\text{bottom water}} - [CO_3^=]_{\text{saturation}})$) and cause pore waters at and above the saturation horizon to be undersaturated, thereby driving $CaCO_3$ dissolution according to the overall equation:

$$(CHOH)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 + 124CaCO_3 \rightarrow 16H_2O + 16NO_3^- \\ + HPO_4^= + 124Ca^{++} + 230HCO_3^-.$$

In this case, the onset of dissolution of $CaCO_3$ in the sediments will lie above the saturation horizon, at a depth where the input of metabolic acid is exactly sufficient to titrate excess CO_3^{2-}. The CCD will lie at the saturation horizon where the production of metabolic acids is just sufficient to dissolve all the sedimenting $CaCO_3$. At depths between the onset of dissolution and the CCD, some $CaCO_3$ will be preserved because a fraction of the metabolic acids are required to titrate the excess CO_3^{2-}. (3) Finally, if the $CHOH/CaCO_3$ rain rate is $>106/124$ (and with the other stated assumptions obtaining), the onset of calcium carbonate dissolution and the compensation depth will both lie above the saturation horizon.

In the following sections we present the experimental evidence which suggests that the processes involved in the latter two cases are occurring in the pore waters of the surface sediments of the deep sea. A model is then presented from which we calculate the calcium carbonate accumulation rate in sediments as a function of the $CHOH/CaCO_3$ rain ratio, the degree of bottom water saturation with respect to calcite, and the calcium carbonate dissolution and organic matter degradation rates.

Table 1. Carbonate and carbon fluxes from near bottom sediment traps.

Location	Trap Depth (m)	Fluxes Organic C.	 $CaCO_3$	$\frac{F_{Org.C}}{F_{CaCO_3}}$	Reference
		($\times 10^{6}$m/cm^2 yr)			
N. Atlantic 31N 55W (5581 m)	4000	4.9	7.9	0.6	Brewer *et al.* (1980)
Sub. Trop. Atlantic 13N 54W (5288 m)	5086	7.6	11.1	0.7	
Sub. Trop. Pacific 15N 150W (5792 m)	5582	2.0	2.4	0.8	Honjo (1980)
N. Atlantic 38N 69W (3520 m)	~3470	18.7*	12.2	1.5	Hinga *et al.* (1979)
N. Atlantic 38N 69-72W					Rowe and Gardner (1979)
(3577 m)	3059	35.	30.7	1.1	
(2816 m)	2316	19.2	15.7	1.2	
(2815 m)	2795	32.8	31.2	1.1	
(2192 m)	2162	52.5	67.7	0.8	
Eg. Pacific 0°N 86°W (2670)	2570	13.6	24.9	0.6	Cobler and Dymond (1980)

* Table 6 of Hinga *et al.* (1979) should read "organic matter" instead of "organic carbon". (Hinga, pers. Comm.).

2. Experimental evidence

In order for metabolic CO_2 released in surface sediments to have an effect on the preservation of calcium carbonate, the organic matter rain to the sediment-water interface must be of the same magnitude (on a molar basis) as the calcium carbonate rain, and a significant fraction must be oxidized within the sediments rather than *at* the sediment water interface. Recent deep sea sediment trap and pore water studies provide the evidence necessary to evaluate these criteria.

If one assumes a bulk sedimentation rate of 2 cm/10^3 yrs and an organic carbon concentration of 1% by weight in the sediment, a burial rate of 2×10^{-6} mC/cm^2 yr is calculated. Near-bottom fluxes of carbon and calcium carbonate reported from several recent independent sediment trap studies are presented in Table 1. The sediment trap fluxes of carbon are much greater than the calculated burial rate (with the exception of the results from the sub-tropical Pacific where the organic carbon concentrations and sedimentation rate are both much lower than the values used in the above calculation, Heath *et al.*, 1977). Far more organic carbon is raining to the sea floor than is preserved, and the molar ratio of the rain rate of organic carbon to calcium carbonate is close to unity. The near equal magnitude of these rates points out the potential influence of the degradation of organic matter on the preservation of calcium carbonate.

Smith and co-workers (Smith, 1978; Smith *et al.*, 1978; and Smith *et al.*, 1979)

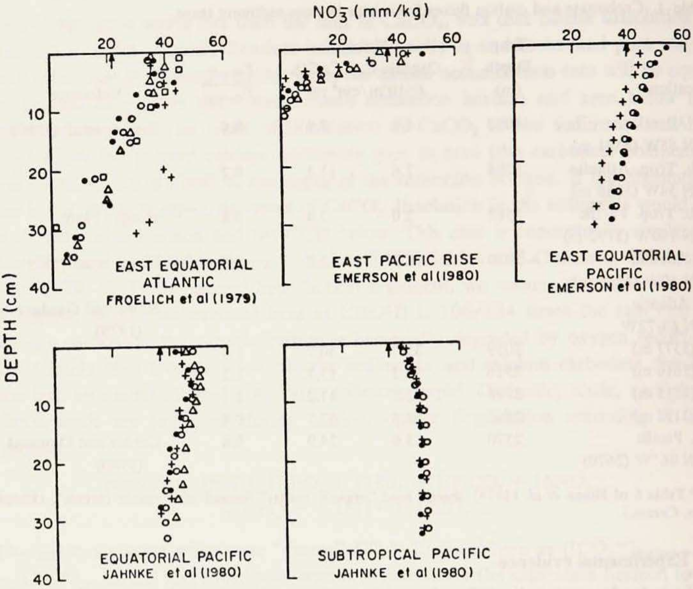


Figure 1. Pore water nitrate data from five different locations in the ocean. Arrows indicate the bottom water values. The minimum sample depth interval is 2 cm.

have shown the functionality of benthic oxygen utilization with depth in the sea. Hinga *et al.* (1979, Fig. 5) compiled these data along with their own to show a nearly log linear relationship between benthic oxygen flux and depth. Values at 3000 and 5000 meters were 40-20 μm cm^{-2} yr^{-1} and 0.7-4.0 μm cm^{-2} yr^{-1}, respectively. Murray and Grundmanis (1980) calculate, from their pore water data for oxygen, an O_2 flux into equatorial Pacific sediments of about ~2 μm/cm^2 yr. The measured and calculated oxygen fluxes are in the same range as the organic carbon rain rates in Table 1.

The agreement between sediment trap organic carbon flux and benthic respirometer measurements indicates that the rain of organic carbon is sufficient to fuel respiration at the sediment-water interface (Hinga *et al.*, 1979). Whether the bacterial degradation occurs *at* the interface or within the sediments is uncertain based on the oxygen flux measurements, but can be resolved from existing data on the chemistry of interstitial waters. Since measurements of oxygen in pore water are limited (Murray and Grundmanis, 1980), we will base our arguments on the more abundant nitrate data. Figure 1 shows nitrate profiles from sediments of the sub-

Table 2. Estimate of the minimum oxygen flux into deep sea sediments from pore water nitrate data and comparison of this flux with integrated organic matter degredation from 2 cm to 50 cm depth.

	Bottom Water		Pore Water, 0-2cm		F_{O_2}min+	*J*‡carbon, 2-30cm
	O_2	NO_3^-	NO_3^-	$O_{2,calc*}$		
Location	($\times 10^6$ m/kg)				($\times 10^6$ m/cm^2 yr)	
Eq. Atlantic[a] 0-4N, 6-16W (4000-5000 m)	250	22	35-45	86-158	10-18	3.0
Eq. Pacific[b]						
8N 104W[b] (3100 m)	110	39	45-55	0-60	5-13	0.15
6N 92W[b] (3500 m)	110	38	40-50	0†	12	1.2
1N 138W[c] (4400 m)	160	37	42-49	74-124	8-14	0.7
11N 140W[c] (4895 m)	160	36	41-43	110-125	4-5.5	1.5

a. Froelich *et al.* (1979).
b. Emerson *et al.* (1980).
c. MANOP Pore Water Group (Unpublished results).
* $O_{2,0\text{-}2cm} = O_{2,BW} - D_{NO_3-}/D_{O_2}\{(138/16)\ (NO_{3,BW} - NO_{3,0\text{-}2})\}$ See text
\+ Minimum oxygen flux $F_{O_2,min} = D_{O_2}/2cm\ (O_{2,BW} - O_{2,0\text{-}2cm})$
‡ Estimate of organic carbon degredation below 2 cm based on nitrate profiles.
† O_2 estimated to be near zero because of significant dentrification in the O-2 cm interval.

tropical and equatorial Atlantic and Pacific. The oxygen concentration in the 0-2 cm interval can be calculated from the observed nitrate excess ($NO_3^-{}_{,\ 0\text{-}2cm} - NO_3^-{}_{,\ bottom\ water}$), the diffusion coefficients for O_2 and NO_3, and a ratio of 138/16 for the stoichiometry of the nitrification reaction (see Bender *et al.*, 1977; Froelich *et al.*, 1979; and Emerson *et al.*, 1980). Suess and Muller (1980) suggested that the C:N ratio of organic matter at the sediment-water interface is greater than twice the Redfield ratio (106:16), however, Grundmanis and Murray (1980) calculated a C:N ratio of 7.7 for organic matter decomposition in the equatorial Pacific. Since the calculated oxygen concentration is inversely proportional to this ratio, a higher C:N ratio in the organic matter will result in a lower calculated oxygen value. The estimates presented here (Table 2, column 5) represent upper limits because we assume Redfield stoichiometry. A minimum value for the flux of oxygen into the pore water is calculated using the flux equation and assuming a linear gradient of O_2 between zero and two centimeters (Table 2, column 6). Values calculated in this way are of the same magnitude as those measured directly by the benthic respirometer for similar water depths and inferred from the sediment trap organic carbon fluxes. The pore water data thus indicate that the degradation of organic matter which reaches the sediment water interface occurs, to a great extent, *within* the sediments, causing oxygen depletion and the release of metabolic CO_2 into the surficial interstitial waters.

In the final column of Table 2, the integrated degradation of organic matter between 2 cm and 30 cm is estimated using the curvature of the nitrate profiles shown in Figure 1. This calculation is made to illustrate (by comparison with the minimum oxygen flux estimate) that the bulk of organic matter respiration in deep sea sediments occurs near the sediment-water interface.

3. The model

To model the effect of organic matter degradation on the preservation of calcium carbonate, we begin by defining a region at the sediment surface which is relatively rich in organic matter. A schematic representation and the equations which govern the distribution of organic carbon and calcium carbonate are presented in Figure 2. It is assumed that the important reactions which govern the preservation of organic carbon and calcium carbonate in the sediments occur within this region. Thus, in this model the decomposable organic carbon rain (R_C in Fig. 2) is oxidized very near the sediment-water interface. The solid carbonate mass balance across the layer is

$$R_{CaCO_3} - P_{CaCO_3} = F_{Ca^{2+}} \tag{1}$$

where R_{CaCO_3} and P_{CaCO_3} are the rain rate and preservation rate of calcium carbonate, and $F_{Ca^{2+}}$ is the flux of dissolved calcium out of the sediments (here defined as a positive value).

The flux of calcium is a measure of depth-integrated dissolution rate of calcium carbonate. The dissolution rate is a function of the degree of undersaturation of calcium carbonate in the interstitial waters (we assume that sediments which contain calcium carbonate are saturated with respect to calcite below a few mm depth; see Sayles, 1980; and Emerson *et al.*, 1980). Since the CO_3^{2-} ion concentration in the pore waters near the interface is more sensitive to change (on a percentage of the total basis) than the Ca^{2+} ion concentration, the degree of saturation will be formulated as a function only of the former.

The three reactions which control the concentration of CO_3^{2-} are shown in Figure 2. During organic matter degradation, CO_2 is released into the interstitial waters. The carbon dioxide reacts with dissolved carbonate ion to form bicarbonate; this reaction is fast and may be considered instantaneous for our purposes. Consumption of CO_3^{2-} by this reaction requires a replenishment of this ion by either diffusion from the overlying waters or dissolution of calcium carbonate. If the degradation rate of organic matter is much faster than calcium carbonate dissolution, CO_2 will be neutralized (reaction b of Fig. 2) by the flux of carbonate from the bottom water. If, on the other hand, the dissolution of calcium carbonate is relatively rapid, 124/

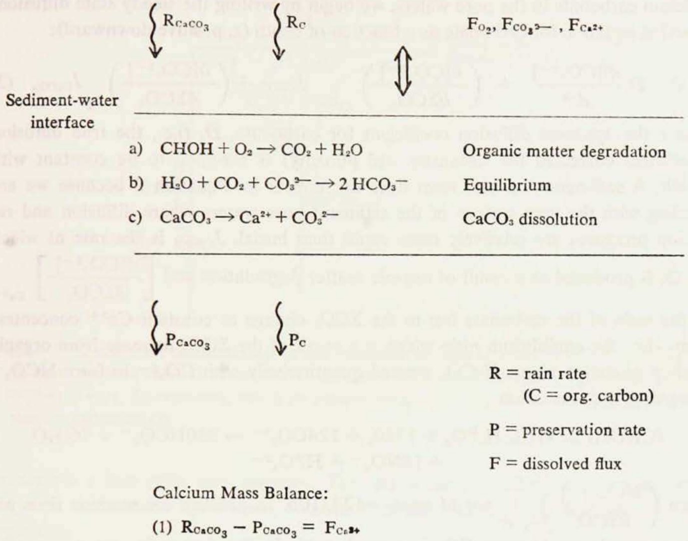


Figure 2. A schematic representation of the organic matter rich sediment surface of the deep sea. The particulate fluxes are indicated by wavy lines, the dissolved fluxes by an arrow. Abbreviated forms of the important organic carbon and calcium carbonate reactions are indicated. (CHOH is used to represent organic matter for brevity.)

106 moles of $CaCO_3$ will dissolve for each mole of organic carbon oxidized. These competing kinetics control the preservation of calcium carbonate and hence the flux of Ca^{2+} and alkalinity out of the sediments.

A schematic representation of the profile of CO_3^{2-} in the sediment pore waters is presented in Figure 3. For cases in which the bottom waters are supersaturated with respect to calcite and the organic carbon rain is sufficient to neutralize the pore water excess carbonate ion (case c in Fig. 3), the pore waters are supersaturated to some depth defined as Z and undersaturated or saturated below Z. In the following derivation we assume that calcium carbonate does not precipitate in the region of pore water supersaturation. Later, in the discussion of the results, we show the effect of allowing precipitation in the region above Z.

To quantify the processes outlined in Figures 2 and 3, one must define the dissolved calcium flux (F_{Ca}) from the sediments as a function of the rain rate of organic matter, the degradation rate of organic matter, and the dissolution rate of $CaCO_3$. Since at steady state the calcium flux is equal to the integrated dissolution rate of calcium carbonate in the pore waters, we begin by writing the steady state diffusion-reaction equation for carbonate as a function of depth (z, positive downward):

$$0 = D\frac{d^2[CO_3{}^{2-}]}{dz^2} + \left(\frac{\partial[CO_3{}^{2-}]}{\partial\Sigma CO_2}\right)_{Ca^{2+}} J_{CHOH} + \left(\frac{\partial[CO_3{}^{2-}]}{\partial\Sigma CO_2}\right)_{O_2} J_{CaCO_3} \quad (2)$$

where the apparent diffusion coefficient for carbonate, D, (i.e., the true diffusion coefficient corrected for tortousity and porosity) is assumed to be constant with depth. A sedimentation rate term does not appear in Equation 2 because we are dealing with the very surface of the sediment pore waters where diffusion and reaction processes are relatively more rapid than burial. J_{CHOH} is the rate at which ΣCO_2 is produced as a result of organic matter degradation and $\left[\frac{\partial[CO_3{}^{2-}]}{\partial\Sigma CO_2}\right]_{Ca^{2+}}$ is the ratio of the carbonate ion to the ΣCO_2 change at constant Ca^{2+} concentration—i.e., the equilibrium ratio which is a result of the ΣCO_2 increase from organic carbon oxidation alone. If CO_2 reacted quantitatively with $CO_3{}^{2-}$ to form $HCO_3{}^-$ according to the reaction

$$(CHOH)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 + 124CO_3{}^{2-} \rightarrow 230HCO_3{}^- + 16H_2O$$
$$+ 16NO_3{}^- + HPO_4{}^{2-}$$

then $\left(\frac{\partial[CO_3{}^{2-}]}{\partial\Sigma CO_2}\right)_{Ca^{2+}}$ would equal $-124/106$. In practice the reaction does not go to completion because CO_2 is a weak acid. In the Appendix, we present the derivation of $\left(\frac{\partial[CO_3]^{2-}}{\Sigma\partial CO_2}\right)_{Ca^{2+}}$ and show that it has a value of approximately -0.6 in the pore waters of this study.

J_{CaCO_3} is the rate at which ΣCO_2 increases due to $CaCO_3$ dissolution and $\left(\frac{\partial[CO_3{}^{2-}]}{\partial\Sigma CO_2}\right)_{O_2}$ is the ratio of the $CO_3{}^{2-}$ to ΣCO_2 increase during calcium carbonate dissolution. The subscript, depicting constant O_2, indicates that the ratio is independent of organic matter degradation. Since some of the $CO_3{}^{2-}$ released to the pore waters during $CaCO_3$ dissolution reacts with CO_2 to form $HCO_3{}^-$ via the reaction

$$CO_3{}^{2-} + CO_2 + H_2O = \rightarrow 2HCO_3{}^-$$

$\left(\frac{\partial[CO_3{}^{2-}]}{\partial\Sigma CO_2}\right)_{O_2}$ is less than one. The term is evaluated in the Appendix to be about $+0.7$ in the pore waters.

The rates, J, can be cast in terms of the concentrations of solid organic matter and carbonate ion. The rate of total CO_2 production during organic matter degradation, J_{CHOH}, is assumed to be first order with respect to the degradable organic carbon concentration, C (Berner, 1974):

$$J_{CHOH} = jC \quad (3)$$

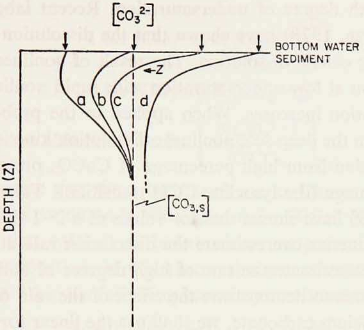


Figure 3. A schematic representation of the carbonate ion concentration [CO_3^{2-}] as a function of depth for four cases of bottom water saturation with respect to calcite: (a) undersaturated bottom waters, (b) saturated, and (c,d) supersaturated. [CO_3^{2-}]$_s$ is the saturation concentration for carbonate ion.

where *j* is a first order rate constant. The steady state distribution of carbon with depth is determined by a mass balance between "mixing" by bioturbation and oxidation

$$K\frac{d^2C}{dz^2} = jC \tag{4}$$

in which K is the "effective mixing rate." Using the boundary condition that the organic carbon concentrations at $z = 0$ equals C_o, Equation (4) has the solution:

$$C = C_o\, e^{(-\sqrt{j/K})z} \tag{5}$$

Since the organic matter degradation rate integrated over the entire sediment column is equal to the flux, R_C:

$$C_o = R_C/\sqrt{jK}$$

The ratio, $1/\sqrt{j/K}$, represents the scale depth for the organic carbon profile. In a continuous model which assumes oxygen is the only electron acceptor for bacterial oxidation, this ratio also represents the scale depth for the oxygen profile.

The carbonate dissolution rate term, J_{CaCO_3}, is a function of the degree of undersaturation of $CaCO_3$ in the pore waters.

$$J_{CaCO_3} = k([CO_3{}^{2-}]_s - [CO_3{}^{2-}])^n \quad \text{for } [CO_3{}^{2-}]_s > [CO_3{}^{2-}] \tag{6}$$

where $[CO_3]_s$ is the carbonate ion saturation value, k is a rate constant, and n represents the functionality between the degree of undersaturation and the dissolution rate. If $n = 1$ in Equation (6) there is a linear increase in the rate of dissolution of calcium carbonate with degree of undersaturation. Recent laboratory experiments (Keir, 1979; and Morse, 1978) have shown that the dissolution rate is in fact nonlinear and $n = 4.5$ for calcite dissolution. The result of nonlinear kinetics is a very slow rate of dissolution at low undersaturation with rapid nonlinear increase as the degree of undersaturation increases. When applied to the problem of preservation of calcium carbonate in the deep sea, nonlinear dissolution kinetics result in a change in shape of the transition from high percentage of $CaCO_3$ preservation in the sediments to a low percentage (the lysocline-CCD transition). Takahashi and Broecker (1977) and Keir (1979) have shown that for values of $n > 1$ the transition becomes sharper. (The linear kinetics overestimate the dissolution rate at low degrees of undersaturation and underestimate the rate of high degrees of undersaturation.) Since our main purpose here is to demonstrate the effect of the rain of organic matter on the preservation of calcium carbonate, we shall use the linear form of the dissolution rate equation ($n = 1$) for simplicity.

The rate of calcium carbonate dissolution in sediments is proportional to the $CaCO_3$ surface area exposed to the pore waters. Although it has been shown (Keir, 1979) that the surface area of dissolving particles is not linearly proportional to the weight percent of $CaCO_3$, we adopt this assumption as a first approximation. Following Takahashi and Broecker (1977), the rate constant, k, is related to the rate constant in 100% $CaCO_3$ sediments, k^*, by:

$$k = Xk^* \tag{7}$$

X represents the fraction of the sediment which is calcium carbonate and is a function of the particulate carbonate rain, R_{CaCO_3}, and preservation, P_{CaCO_3}, rates:

$$X = P_{CaCO_3}/[(R_{CaCO_3}/X_o) - R_{CaCO_3} + P_{CaCO_3}] \tag{8}$$

where the subscript (o) indicates the fraction of $CaCO_3$ in the region of no dissolution. In the following treatment we assume that the percent $CaCO_3$, X, and the rate constant, k, are not a function of depth, z, in the sediments. The relationship expressed in Equation 7 is used only to require that the rate constant k is proportional to the fraction of calcium carbonate remaining in the sediments after it has passed through the organic matter degradation layer. This is a simplification of the true case in which there is a depth gradient in percent $CaCO_3$, X, between the sediment-water interface and the bottom of the reaction layer. The consequences of this simplification, however, are very slight since nearly 90% of the particulate carbonate rain must dissolve to reduce the fraction of calcium carbonate in the sediments to one half its original value, X_o.

The diffusion-reaction equation for CO_3^{2-} may be written as:

$$0 = D_{CO_3^{2-}} \frac{d^2[CO_3^{2-}]}{dz^2} + f_{CO_3}\, j\, C_o e^{-(\sqrt{j/K})z} + \theta f_{CaCO_3}\, k([CO_3^{2-}]_s - [CO_3^{2-}]) \tag{9}$$

where θ is defined as

$$\theta = \begin{cases} 1 \text{ for } [CO_3{}^{2-}] < [CO_3{}^{2-}]_s \\ 0 \text{ for } [CO_3{}^{2-}] \geqslant [CO_3{}^{2-}]_s \end{cases}$$

and f_{CO_3} and f_{CaCO_3} are abbreviations for $\left[\frac{\partial[CO_3{}^{2-}]}{\partial\Sigma CO_2}\right]_{Ca^{2+}}$ and $\left[\frac{\partial[CO_3{}^{2-}]}{\partial\Sigma CO_2}\right]_{O_2}$ respectively. We assume that these two terms are constant over the depth interval of the calculation. The condition in which $\theta = 0$ for $[CO_3{}^{2-}] \geqslant [CO_3{}^{2-}]_s$ is a result of our assumption that calcium carbonate does not precipitate in supersaturated pore waters. The ramifications of this assumption are examined in the discussion of the results. Equation 9 has the following boundary conditions:

$$\begin{aligned} z = 0 &: [CO_3{}^{2-}] = [CO_3{}^{2-}]^* \\ z \to \infty &: [CO_3{}^{2-}] = [CO_3{}^{2-}]_s \end{aligned} \tag{10}$$

where $[CO_3{}^{2-}]^*$ is the carbonate concentration in the bottom water. To simplify the notation in the solution we introduce the following variables: $\Delta CO_3 = [CO_3{}^{2-}] - [CO_3{}^{2-}]_s$, the excess carbonate concentration; $\alpha_C = \sqrt{j/K}$, the inverse sale depth for organic carbon degradation; and $\alpha_{Ca} = \sqrt{kf_{CaCO_3}/D}$, the inverse scale depth for the change in carbonate ion concentration due to calcium carbonate dissolution.

If the bottom waters are undersaturated or saturated with respect to calcium carbonate ($\Delta CO_3{}^* \leqslant 0$), the pore waters never attain a supersaturated state (see Fig. 3, cases a and b). The solution to Equation 9 for this condition is:

$$\Delta CO_3 = \Delta CO_3{}^* \, e^{-\alpha_{Ca} z} + \frac{f_{CO_3} R_C \alpha_C}{D(\alpha_C{}^2 - \alpha_{Ca}{}^2)} \left(e^{-\alpha_{Ca} z} - e^{-\alpha_C z}\right) \tag{11}$$

If the bottom waters are supersaturated with respect to carbonate ($\Delta CO_3{}^* > 0$, cases c and d in Fig. 3), the solution to Equation 9 is (for $\Delta CO_3 > 0$):

$$\Delta CO_3 = \Delta CO_3{}^* + \frac{f_{CO_3} R_C}{\alpha_C D} \left(1 - e^{-\alpha_C z}\right) + Gz \tag{12}$$

where G is an integration constant. If the degree of supersaturation in the bottom waters is large enough, i.e., if $\Delta CO_3{}^* \geqslant \left|\frac{f_{CO_3} R_C}{\alpha_C D}\right|$, ΔCO_3 will never go to zero (case *d* in Fig. 3). In this case $G = 0$ and the boundary condition ΔCO_3 $(z \to \infty) = 0$ cannot be fulfilled because we have not allowed the authigenic precipitation of $CaCO_3$ in the model. In actual fact the pore waters may return to saturation over a long time period, but we argue later that this process is not rapid (i.e., does not occur on the time scale of the processes described in this model).

If $\Delta CO_3{}^*$ is not larger than $\left|\frac{f_{CO_3} R_C}{\alpha_C D}\right|$, there exists a depth Z where ΔC

changes sign due to the degradation of organic matter (case c, Fig. 3). Below Z ΔCO_3^{2-} returns to the equilibrium value, $\Delta CO_3^{2-} = 0$, due to calcium carbonate dissolution and diffusion of carbonate from the bottom waters. The integration constant in this case can be expressed as a function of the depth Z.

For $0 \leqslant z \leqslant Z$ (layer 1):

$$\Delta CO_{3_1} = \Delta CO_3{}^* \left(1 - \frac{z}{Z} \right) + \frac{f_{CO_3} R_C}{\alpha_C D} \{(1 - e^{-\alpha_C z}) - \frac{z}{Z} (1 - e^{-\alpha_C Z})\} \tag{13}$$

For $z > Z$ (layer 2)

$$\Delta CO_3 = \frac{f_{CO_3} R_C \alpha_C}{D(\alpha_C{}^2 - \alpha_{Ca}{}^2)} e^{-\alpha_C Z} (e^{-\alpha_{Ca}(z-Z)} - e^{-\alpha_C(z-Z)}) \tag{14}$$

The relationship between the degree of saturation of the bottom waters, $\Delta CO_3{}^*$, and the depth, Z, is derived by combining Equations (13) and (14) and the boundary condition:

$$\left.\frac{d\Delta CO_{3_1}}{dz}\right]_{z=Z} = \left.\frac{d\Delta CO_{3_2}}{dz}\right]_{z=Z} \tag{15}$$

which results in the relationship:

$$-f_{CO_3} R_C(Z\alpha_C\alpha_{Ca} + \alpha_C + \alpha_{Ca})\, e{-\alpha_C z} = (-f_{CO_3} R_C - \Delta CO_3{}^* D\alpha_C)(\alpha_C + \alpha_{Ca}) \tag{16}$$

Note that f_{CO_3} is negative and Equation (16) has a solution as long as $\Delta CO_3{}^* < \left| \frac{f_{CO_3} R_C}{\alpha_C D} \right|$.

Equations (11) to (16) describe the distribution of carbonate ion in the sediments as a function of the degree of bottom water saturation, $\Delta CO_3{}^{2-*}$, the rain rate of organic carbon, R_C, the scale depth for organic matter degradation, α_C, and the calcite dissolution rate, k.

The flux of calcium at Z (and hence out of the sediments at $z = 0$, since no dissolution of $CaCO_3$ occurs above Z) is equal to the integral of Equation (6) between Z and ∞:

$$F_{Ca} = -k \int_{z=Z}^{z=\infty} \Delta CO_3 \, dz \tag{17}$$

If the bottom waters are undersaturated, Z is zero and ΔCO_3^{2-} is given by Equation (11). Thus:

$$F_{Ca} = -k \left[\frac{\Delta CO_3{}^*}{\alpha_{Ca}} + \frac{f_{CO_3} R_C}{D(\alpha_C + \alpha_{Ca})\alpha_{Ca}} \right] \tag{18}$$

F_{Ca} is larger than zero since both $\Delta CO_3{}^*$ and f_{CO_3} are negative. If the bottom waters are saturated or supersaturated, but $\Delta CO_3{}^* < \left| \frac{f_{CO_3} R_C}{\alpha_C D} \right|$, ΔCO_3 is given by Equation (14) which when combined with (17) gives:

$$F_{\mathrm{Ca}} = -\frac{k f_{\mathrm{CO}_3} R_{\mathrm{C}} e^{-\alpha_{\mathrm{C}} z}}{D \alpha_{\mathrm{Ca}(\alpha_{\mathrm{C}}+\alpha_{\mathrm{Ca}})}} \qquad (19)$$

where the saturation depth Z is given by Equation (16). Finally, if the initial supersaturation is very high, such that $\Delta\mathrm{CO}_3{}^* \geqslant \frac{R_{\mathrm{C}} f_{\mathrm{CO}_3}}{\alpha_{\mathrm{C}} D}$ no CaCO_3 dissolution occurs:

$$F_{\mathrm{Ca}} = 0 \qquad (20)$$

We will use the equations derived in this section to calculate the percent calcite, X, in the sediments as a function of organic carbon rain, R_{C}, the organic matter degradation rate, α_{C}, and CaCO_3 dissolution rate, k. The expressions in (18) (for $Z = 0$) or (19) (for $Z > 0$) are solved simultaneously with Equations (1), (7), and (8) to derive P_{CaCO_3} and X. Equation (1) relates the CaCO_3 rain and preservation rates to the dissolved calcium flux, and Equations (7) and (8) define the relationship between the rate constant, k, and the fraction of calcium carbonate preserved in the sediments. This set of equations is nonlinear and was solved by an iteration method.

4. Evaluation of the model parameters

The magnitude of the effect of the degradation of organic matter on CaCO_3 preservation is determined by the value of the organic carbon rain and the rate parameters. The utility of the model is entirely dependent upon our ability to quantify these terms. In this section we evaluate, to the extent presently possible in deep sea sediments, the organic carbon:calcium carbonate rain rate, $R_{\mathrm{C}}/R_{\mathrm{CaCO}_3}$: the scale depth for organic matter degradation, $1/\sqrt{j/K}$; and the scale depth for calcium carbonate dissolution, $1/\sqrt{k/D}$.

a. R_C/R_{CaCO_3}. For this ratio we rely on the near bottom sediment trap data presented in Table 1 and discussed in the introduction. A value of 0.5-1.0 is adopted as a best estimate for this term.

b. $1/\sqrt{k/D}$. The depth interval between the level of the onset of rapid dissolution and the CCD in the ocean is dependent upon the rain rate of calcium carbonate and the rate of dissolution (Takahashi and Broecker, 1977; Schink and Guinasso, 1977; and Keir, 1979). The rain rate of organic carbon contributes to the control of the relationship between this depth interval and the saturation horizon, but, as we will see later, plays only a small role in determining its magnitude. The functionality among the rain rate of CaCO_3, R_{CaCO_3}, the dissolution rate constant, k, and the degree of undersaturation, $\Delta\mathrm{CO}_3$ (for $R_{\mathrm{C}} = 0$), are presented in Figure 4. The depth dependence of $\Delta\mathrm{CO}_3$ in the oceans has been well defined by the GEOSECS program (Broecker and Takahashi, 1978) and is included on the ordinate of the Figure. A maximum value for k is that which has been observed by *in situ* saturometer experiments; ~1/(7 min) (Ben-Yaakov, *et al.*, 1974, reported in Takahashi and Broecker, 1977).

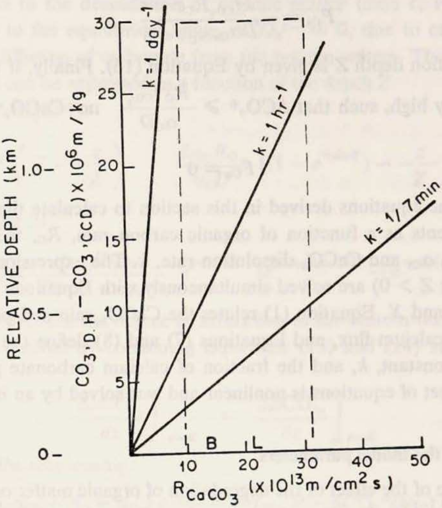


Figure 4. The difference between the carbonate ion concentration at the onset of $CaCO_3$ dissolution, dissolution horizon = *DH*, and at the CCD ($CO_{3,DH} - CO_{3,CCD}$) as a function of the particulate carbonate rain rate, R_{CaCO_3}. The depth scale is calculated using the relationship between the $[CO_3^{2-}]$ in seawater and depth presented by Broecker and Takahashi (1978). Lines represent different values for the calcium carbonate dissolution rate constant (*k*). The dotted lines enclose a range of $CaCO_3$ rain rate and depth which is observed in the ocean (*B* = Biscaye *et al.*, 1972; *L* = Li *et al.*, 1969).

Given the available estimates for the calcium carbonate rain rate and the distance between the onset of rapid $CaCO_3$ disappearance and the CCD in the oceans (0.5-1.5 km; Berger, 1977), one sees from Figure 4 that the dissolution rate constant must lie in the interval of a few reciprocal minutes to a few reciprocal hours. Takahashi and Broecker (1977) estimate a value in the higher range; ~1/(9 min). Since the effective diffusion coefficient for carbonate in sediments at 4°C is $\sim 1 \times 10^{-6}$ cm^2 s^{-1}, the scale depth for carbonate dissolution, $1/\sqrt{k/D}$, must lie in the range of 0.1-1.0 millimeters. We adopt 1/(7 min) to 1/(60 min) as the best estimate of *k*, with greater confidence in the values at the high end.

c. $1/\sqrt{j/K}$. The characteristic depth for organic carbon degradation (or oxygen consumption) at the sediment surface is less well known than the scale depth for $CaCO_3$ dissolution. A crude estimate of this depth, however, can be assessed by considering a mass balance for oxygen at the sediment-water interface. The flux of oxygen F_{O_2}, is proportional to the integrated organic carbon degradation rate (or, in our model, the rain rate of carbon, R_C):

$$F_{O_2} = \alpha\, r\, R_C$$

where α is the stoichiometric coefficient for the oxidation reaction $\left(\alpha = \frac{\Delta O_2}{\Delta C} = 138/106\right)$ and r is the respiratory coefficient of the sedimenting organic carbon ($r = 0.9$; Wiebe *et al.*, 1976). Assuming a linear oxygen gradient in the organic carbon-rich layer, ΔZ:

$$\left(D_{O_2}\Big/_{\Delta Z}\right)(O_{2,BW} - O_2) = \alpha\, r\, R_C$$

where D_{O_2} in sediments at 4°C ~5×10^{-6} cm^2 s^{-1}. The value of ΔZ in the above equation is a crude calculation of the scale depth for organic matter oxidation. Using a value for R_C of 10×10^{-6} m cm^{-2} yr (Table 1) and an oxygen gradient of 10×10^{-9} m cm^{-3} (i.e., an estimate of the minimum measurable difference using nitrate data) a minimum value for ΔZ is about 1.5 millimeters. Thus, in order for the surface pore waters to become measurably depleted in O_2, the depth of active organic matter degradation must be greater than a few millimeters. We adopt 0.2-2.0 cm (the latter being the pore water sampling interval) as the best estimate for the range of $1/\sqrt{j/K}$.

d. The influence of the reaction rate terms on $CaCO_3$ preservation. With estimates of the magnitude of the reaction rate terms, we can assess their effect on the preservation of calcium carbonate. The ratio of the flux of bottom water $CO_3{}^{2-}$ across the sediment-water interface, F_{CO_3}, to the integrated dissolution rate of $CaCO_3$ (or the calcium flux, F_{Ca}) is a measure of the source of the carbonate ion which neutralizes metabolic CO_2 created during organic matter degradation. If organic matter degradation is very fast with respect to $CaCO_3$ dissolution, the ratio will be greater than one. If the inverse is true, then the ratio will be much less than one.

The F_{CO_3} term is derived by substituting Equation (11) into the flux equation, and the calcium flux is given by Equation (19). Assuming $f_{CaCO_3} = 1$ and $\Delta CO_3{}^* = 0$ thus $Z = 0$):

$$\frac{F_{CO_3}}{F_{Ca}} = \frac{D(\sqrt{j/K} + \sqrt{k/D})}{k(\sqrt{K/j} - \sqrt{D/k})} \tag{21}$$

Equation (21) is evaluated for various values of k and $1/\sqrt{j/K}$ in Table 3. For a given $CaCO_3$ dissolution rate constant, the ratio decreases with decreasing rate of organic matter degradation (increasing $1/\sqrt{j/K}$). The flux of $CO_3{}^{2-}$ from bottom waters plays an increasingly smaller role in the reaction with metabolic CO_2 as the organic matter degradation rate becomes relatively slower. For the appropriate range of $CaCO_3$ dissolution rate constants, 1/7 to 1/(60 min), the flux of carbonate

Table 3. The ratio F_{CO_3}/F_{Ca} as a function of the scale depth for organic matter degradation (or oxygen consumption), $1/\sqrt{j/K}$, and the rate constant for $CaCO_3$ dissolution, k.

$1/\sqrt{j/K}$ (cm)	(F_{CO_3}/F_{Ca}) $k = 1/(7\ \text{min.})$	 $k = 1/(60\ \text{min.})$
0.01	2.0	6
0.05	0.4	1.8
0.10	0.2	0.6
0.20	0.1	0.3
0.50	0.04	0.1
1.00	0.02	0.06

F_{CO_3} is unimportant for $1/\sqrt{j/k}$ greater than 2 and 5 mm, respectively. Since we determined above that the scale depth for organic matter degradation must be greater than a few millimeters to explain the oxygen depletion in pore waters, the precise value of $1/\sqrt{j/K}$ will play only a small role in the preservation of calcium carbonate at and below the saturation horizon for k values near 1/(7 min), but may become significant if k is smaller than 1/(60 min).

Above the saturation horizon where Z is >0 the above arguments no longer hold. The value of Z is dependent mainly on the degree of supersaturation of bottom water. For the ranges of the other parameters determined above, $Z \sim 0.1$ cm for $\Delta CO_3^* = 1 \times 10^{-9}$ m/cm^3 and ~ 1.0 cm for $\Delta CO_3^* = 10 \times 10^{-9}$ m/cm^3. Thus, depending upon the degree of supersaturation and the scale depth for organic matter degradation, the horizon marking the onset of $CaCO_3$ dissolution in the sediments (Z) could be above or below the depth of the maximum organic matter degradation. If $Z = 1.0$ cm and $1/\sqrt{j/K} = 2.0$ cm, the effect of the organic matter degradation on $CaCO_3$ preservation will be large since it occurs in a region which is significantly removed from the sediment water interface (hence F_{CO_3} is small) and within the zone where $CaCO_3$ precipitation is active ($k \neq 0$). If, on the other hand, $1/\sqrt{j/K} = 0.2$ cm, calcium carbonate dissolution will be much less since the bulk of the organic matter degradation occurs near the interface and in a region where $k = 0$.

5. Results and discussion

Predictions for the preservation rate of calcite as a function of depth are presented in Figures 5 and 6. Each of the figures includes both the $CaCO_3$ preservation:rain rate ratio and percent $CaCO_3$ in the sediments as a function of depth. The relationship between these two is given in Equation 8. These figures illustrate the insensitivity of the percent $CaCO_3$ plot to preservation. An increase in the particulate carbon to carbonate rain ratio (Figs. 5a, b, and c) displaces the onset of calcium carbonate dissolution and the CCD upward with respect to the water column saturation horizon. If the rain of particulate organic carbon is equal to that of calcium carbonate

($R_C/R_{CaCO_3} = 1$, Fig. 5c), the model predicts that the carbonate compensation depth should lie near the saturation horizon. Also, there is a tendency to preserve less $CaCO_3$ above the saturation horizon as the organic carbon:calcium carbonate rain ratio increases.

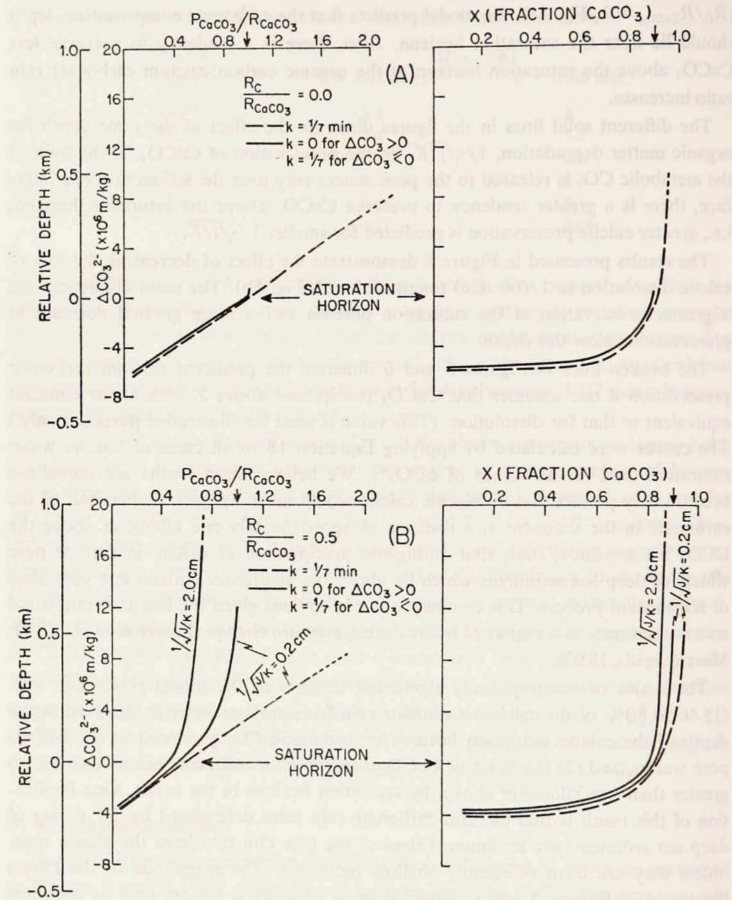
The different solid lines in the figures illustrate the effect of the scale depth for organic matter degradation, $1/\sqrt{j/K}$, on the preservation of $CaCO_3$. If the bulk of the metabolic CO_2 is released to the pore waters very near the sediment-water interface, there is a greater tendency to preserve $CaCO_3$ above the saturation horizon; i.e., greater calcite preservation is predicted for smaller $1/\sqrt{j/K}$.

The results presented in Figure 6 demonstrate the effect of decreasing the rate of calcite dissolution to 1/(60 min) (compared with Fig. 5b). The main differences are a greater preservation at the saturation horizon and a more gradual decrease in preservation below this depth.

The broken lines in Figures 5 and 6 illustrate the predicted calcium carbonate preservation if one assumes that $CaCO_3$ precipitates above Z with a rate constant equivalent to that for dissolution. (This value is used for illustrative purposes only.) The curves were calculated by applying Equation 18 to all cases of bottom water saturation (i.e., for all values of $\Delta CO_3{}^*$). We believe these results are unrealistic because they predict that authigenic calcite would make up greater than half of the carbonate in the sediment at a distance of approximately one kilometer above the CCD. We conclude, thus, that authigenic precipitation of calcite in surface pore waters of deep sea sediments which lie above the saturation horizon is a very slow or nonexistent process. This conclusion is not obvious given the fact that interstitial waters resaturate in a matter of hours during pressure change (Emerson *et al.*, 1980; Murray *et al.*, 1980).

The major oceanographically significant features of the model predictions are: (1) 40 to 80% of the calcium carbonate rain from surface water is dissolved at the depth of the calcite saturation horizon by metabolic CO_2 produced in the surface pore waters, and (2) the onset of $CaCO_3$ dissolution in sediments occurs one half to greater than one kilometer above the saturation horizon in the ocean. One implication of this result is that calcium carbonate rain rates determined by C^{14} dating of deep sea sediments are minimum values of the true rain rate from the photic zone, unless they are from sufficiently shallow sediments. The magnitude of the effects illustrated in Figures 5 and 6 should depend upon local factors such as sediment depth (the amount of organic carbon reaching the sediment-water interface is depth dependent, Hinga *et al.*, 1979) and the productivity of surface waters.

a. Tests for the validity of the model. The logical test for the model is the relationship between the saturation horizon in the ocean and the preservation of calcite in adjacent sediments. Qualitative evidence of this type is based on the observations of the abundance of delicate calcite tests in sediments. Berger (see review in Berger,



1977) used this method to define the lysocline depth in the oceans. Using these criteria he showed that calcite tests from the fertile coastal area off of Africa revealed signs of dissolution well above the depth where there was a rapid decrease in the percent calcium carbonate in the sediments, and that the lysocline surfaces slope upwards as the coastal regions are approached. Berger (1977) attributed these ob-

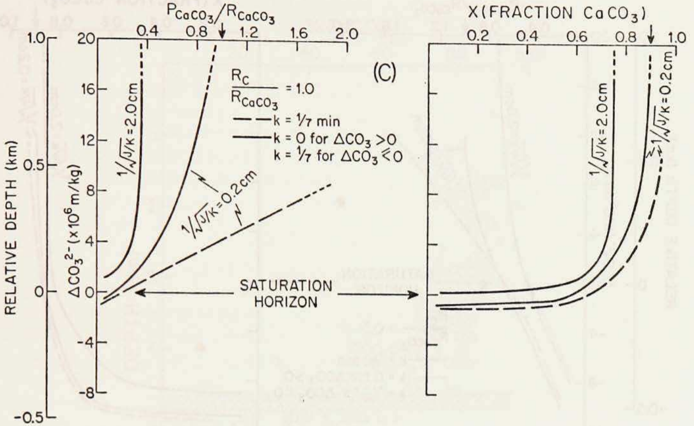


Figure 5. The preservation:rain ratio (P_{CaCO_3}/R_{CaCO_3}) and the equivalent fraction (X) of $CaCO_3$ in sediments as a function of depth for three different molar ratios of the particulate carbon to particulate carbonate rain rate (R_C/R_{CaCO_3}). The relationship between X and P_{CaCO_3}/R_{CaCO_3} is given in Equation (8). The relative depth scale is described in the caption to Figure 4. **(A) $R_C/R_{CaCO_3} = 0.0$, (B) $R_C/R_{CaCO_3} = 0.5$, and (C) $R_C/R_{CaCO_3} = 1.0$. The solid lines are for** different organic matter degradation rates $1/\sqrt{j/K}$. The broken line shows the results for authigenic precipitation of $CaCO_3$ above Z. (See text for explanations.)

servations to the fact that relatively more organic material reaches the sediment water interface in these regions, thus causing greater $CaCO_3$ dissolution by metabolic CO_2 in the surface pore waters. The model results in Figure 5 show the trend for greater $CaCO_3$ dissolution with an increasing ratio of organic carbon to calcium carbonate reaching the sediments.

A more quantitative test of the model is the comparison of the relationship between the percent calcite in deep sea sediments and the location of the water column saturation horizon. Although this argument is not totally satisfactory because of the uncertainties in the depth of the saturation horizon and the possible contribution of aragonite tests to the $CaCO_3$ in the shallower sediments (<2500 m in the Atlantic, Berner, 1977), it provides some interesting observations in light of our predictions. Broecker and Takahashi (1978) pointed out that the *in situ* saturometer experiments of Ben-Yaakov *et al.* (1974) predict saturation depths which are consistent with the calcite solubility product of Ingle *et al.* (1974) at one atmosphere and 25°C if a partial molar volume for calcite of −37 cc/mole (which is in the range of measured values) is assumed. The corroboration of these data from independent

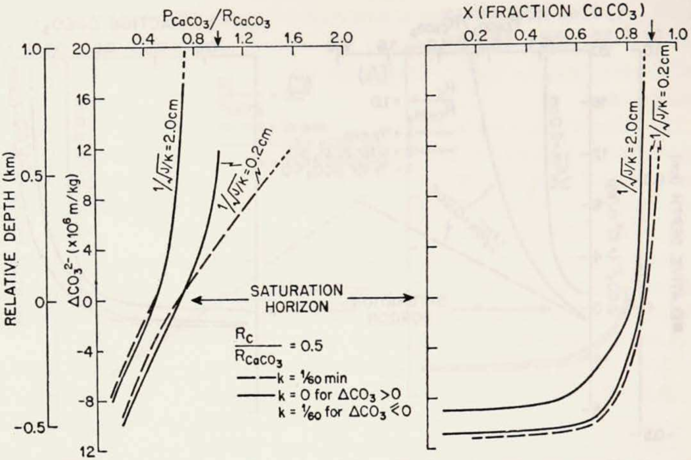


Figure 6. The same as Figure 5b except that the rate constant for calcium carbonate dissolution (k) is 1/(60 min.).

sources is convincing and probably the best present estimate of the saturation horizon in the ocean. In Figure 7 we show the percent calcite as a function of depth in the northwestern Atlantic taken from Biscaye *et al.* (1976). The "critical carbonate ion" concentration of Broecker and Takahashi (1978) is also plotted in the figure. Clearly, the saturation horizon (using the criteria defined above) is below the region of the onset of $CaCO_3$ dissolution. Broecker and Takahashi (1978) show that the foraminiferal lysocline is defined by Kipp (1976) in this region lies at a depth of about 4750 ± 100 meters. The data in Figure 7 indicate that onset of bulk $CaCO_3$ dissolution occurs before the evidence for dissolution indicated by foraminifera tests.[3]

The evidence for $CaCO_3$ depletion from the sediments at the saturation horizon and the gradual increase in percent $CaCO_3$ with decreasing depth (below 2.5 km), as illustrated in Figure 7, may be the result of the corrosive effect of metabolic CO_2 in the surface pore waters of the sediments. Many of the calcium carbonate data for the Atlantic (Biscaye *et al.*, 1976; areas 1, 3, 4, 6, 7, and 10) and Pacific (Berger *et al.*, 1976, areas 7 and 15) reveal the same trend indicating that the phenomenon is widespread.

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[3] Recent estimates of the apparent solubility product of calcite and its pressure dependence may raise the saturation horizon in the North Atlantic ocean to near 4 km (John Morse, personal communication). Although this would decrease the magnitude of the effect indicated by the data in Figure 7, there is still a clear indication of an increase in $\% CaCO_3$ in the sediments between 3 and 4 km.

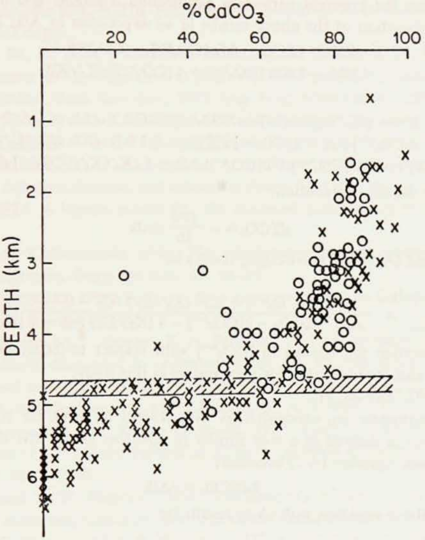

Figure 7. The percent calcium carbonate in sediments of the north equatorial Atlantic as a function of depth. (From Biscaye *et al.*, 1976, as presented in Keir, 1979; (o) represent the data from area 1 and (*x*) are for area 3). The dashed region indicates the depth of the "critical carbonate ion concentration" from Broecker and Takahashi (1978).

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Appendix

The ratio, $\partial CO_3/\partial \Sigma CO_2$, during organic matter degradation, f_{co_3};
and calcium carbonate dissolution, f_{CaCO_3}

$f_{co_3} \equiv \partial CO_3/\partial \Sigma CO_2)_{org.deg.}$

To derive the time rate of change of CO_3^{2-} with respect to the CO_2 change, we begin with the carbonate mass balance and equilibrium relationships:

$$\Sigma CO_2 = HCO_3^- + CO_3^{2-} + CO_2 \qquad (A\text{-}1)$$

$$Alk = HCO_3^- + 2\,CO_3^{2-} \qquad (A\text{-}2)$$

$$K_1' = \frac{[HCO_3^-][H^+]}{[CO_2]} \qquad (A\text{-}3)$$

$$K_2' = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \qquad (A\text{-}4)$$

where K_1' andK_2' are the apparent carbonate equilibrium constants and brackets [ ] indicate concentration. Combination of the above results in an expression in Alk, $\Sigma\mathrm{CO_2}$ and $[\mathrm{CO_3^{2-}}]$

$$\begin{aligned}[\mathrm{CO_3^{2-}}]\,\Sigma\mathrm{CO_2} = {}&\mathrm{Alk}\,[\mathrm{CO_3^{2-}}] - [\mathrm{CO_3^{2-}}]^2 + \\ &(\mathrm{Alk}^2 - 4\,\mathrm{Alk}\,[\mathrm{CO_3^{2-}}] + 4\,[\mathrm{CO_3^{2-}}]^2)(K_2'/K_1')\end{aligned} \tag{A-5}$$

Differentiating (A-5):

$$\begin{aligned}0 = {}&-(d\Sigma\mathrm{CO_2}[\mathrm{CO_3^{2-}}] + d[\mathrm{CO_3^{2-}}]\,\Sigma\mathrm{CO_2}) + d\mathrm{Alk}\,[\mathrm{CO_3^{2-}}] + \\ &d[\mathrm{CO_3^{2-}}]\,\mathrm{Alk} - 2[\mathrm{CO_3^{2-}}]\,d[\mathrm{CO_3^{2-}} + 2\,\mathrm{Alk}\,d\mathrm{Alk}\,(K_2'/K_1') - \\ &4(K_2'/K_1')\,(d\mathrm{Alk}\,[\mathrm{CO_3^{2-}}] + d[\mathrm{CO_3^{2-}}]\,\mathrm{Alk} + 8\,(K_2'/K_1')\,[\mathrm{CO_3^{2-}}]\,d[\mathrm{CO_3^{2-}}]\end{aligned} \tag{A-6}$$

But, during organic matter degradation:

$$d\Sigma\mathrm{CO_2} = -\frac{106}{16}\,d\mathrm{Alk} \tag{A-7}$$

Combining (A-6) and (A-7) and rearranging results in:

$$\left.\frac{d[\mathrm{CO_3}]}{d\Sigma\mathrm{CO_2}}\right)_{\mathrm{org.deg.}} = \frac{(1.15\,[\mathrm{CO_3^{2-}}] + 0.30\,(K_2'/K_1')\,\mathrm{Alk} - 0.6\,(K_2'/K_1')\,[\mathrm{CO_3^{2-}}])}{\mathrm{Alk} - \Sigma\mathrm{CO_2} - 2[\mathrm{CO_3^{2-}}] - 4\,(K_2'/K_1')\,\mathrm{Alk} + 8\,(K_2'/K_1')\,[\mathrm{CO_3^{2-}}]} \tag{A-8}$$

Equation (A-8) describes the change in $[\mathrm{CO_3^{2-}}]$ with respect to $\Sigma\mathrm{CO_2}$ during organic matter degradation. The value is about −0.6 for pore waters in this study.

$f_{CaCO_3} \equiv \partial[CO_3^{2-}]/\partial\Sigma CO_2)_{CaCO_3\ Diss.}$

The change in carbonate ion concentration with respect to $\Sigma\mathrm{CO_2}$ (or $[\mathrm{Ca^{2+}}]$) during calcium carbonate dissolution is derived in a way similar to equation (A-8). The difference is that during $\mathrm{CaCO_3}$ dissolution equation (A-7) becomes:

$$2d\Sigma\mathrm{CO_2} = d\mathrm{Alk} \tag{A-9}$$

Combining the above equation with (A-6) results in:

$$\left.\frac{d[\mathrm{CO_3^{2-}}]}{d\Sigma\mathrm{CO_2}}\right)_{\mathrm{CaCO_3 Diss.}} = \frac{-[\mathrm{CO_3^{2-}}] - 4(K_2'/K_1')\,\mathrm{Alk} + 8\,(K_2'/K_1')\,[\mathrm{CO_3^{2-}}]}{\mathrm{Alk} - \Sigma\mathrm{CO_2} - 2[\mathrm{CO_3^{2-}}] - 4(K_2'/K_1')\,\mathrm{Alk} + 8(K_2'/K_1')\,[\mathrm{CO_3}]} \tag{A-10}$$

At the pore water conditions of this problem

$$d[\mathrm{CO_3^{2-}}]/d\Sigma\mathrm{CO_2})_{\mathrm{CaCO_3 Diss.}} \sim 0.7.$$

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