

Respiration, dissolution, and the lysocline

Burke Hales

College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA

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[1] Here I synthesize the results of several types of measurements of organic carbon respiration and calcium carbonate dissolution rates in pelagic seafloor sediments. Measurements of pore water oxygen demonstrate that most of the respiration takes place very near the sediment-water interface, with a scale depth of a few millimeters. The remainder of the oxic respiration occurs much deeper in the sediments, with a scale depth of several centimeters. All measures of respiration from locations as disparate as the tropical Pacific and Atlantic, and the subtropical North Atlantic agree that pelagic seafloor rates of oxic respiration of organic carbon are relatively independent of depth and location, with the exception of sediments beneath the Pacific eastern equatorial upwelling zone. Calcite dissolution in seafloor sediments requires forcing by respiration-produced CO_2 , and rates are consistent with a first-order dependence on pore water undersaturation, solubility as determined by Mucci [1983] at atmospheric pressure, and locally variable mass-specific dissolution rate constants. Respiration-driven calcite dissolution fluxes predicted by this combination of respiration and dissolution rate expressions are significantly lower than many previous estimates. Comparison of dissolution fluxes in the oligotrophic open ocean measured by other researchers with benthic chamber incubation techniques with those predicted by this combination of rate expressions is, within stated uncertainties, in agreement in all but one case, questioning the need for complicated mechanisms such as surface buffering or authigenic precipitation to explain seafloor calcite diagenesis. Applying these kinetics to a simple one-dimensional, steady state model of the bulk calcite content and sediment accumulation rates of the sediment mixed layer yields results consistent with observations of the seafloor lysocline, the region of transition from high calcite to low-calcite sediments, on the Ceara Rise in the western tropical North Atlantic and the Ontong-Java Plateau in the western equatorial Pacific. Scenarios ignoring dissolution driven by respiration-produced CO_2 in pore waters and using the high-order dependence on undersaturation and very large dissolution rate constants implied by some earlier laboratory studies do not simulate these observations. While the scheme represented here does, in fact, imply a strong shift in the locus of carbonate dissolution toward the sediment water interface as bottom-water saturation decreases, as implied by the observations of Martin *et al.* [2000], no simple combination of sediment transport coefficients and reaction kinetics can reproduce the observation of increasing ^{14}C age as dissolution progresses. These results emphasize the importance of accurate knowledge of the kinetics of respiration and dissolution to interpretation of either the present-day or paleolysocline. *INDEX TERMS:* 1050 Geochemistry: Marine geochemistry (4835, 4850); 4267 Oceanography: General: Paleoceanography; 4804 Oceanography: Biological and Chemical: Benthic processes/benthos; 4806 Oceanography: Biological and Chemical: Carbon cycling; 4825 Oceanography: Biological and Chemical: Geochemistry; *KEYWORDS:* CaCO_3 dissolution

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1. Introduction and Background

[2] Calcite makes up a significant fraction of deep seafloor sediments, and is one of the most reactive common minerals on the Earth's surface [Morse and Mackenzie, 1990]. The balance between the influx of alkalinity from rivers and the loss by oceanic burial of calcium carbonate can determine the CO_2 partial pressure (P_{CO_2}) of the surface waters and hence of the atmosphere on glacial timescales [Archer and Maier-Reimer, 1994; Emerson and Archer, 1992; Broecker, 1989; Boyle, 1988; Broecker and Peng, 1987]. Archer and Maier-Reimer [1994] argued that dissolution in pelagic sediments forced

by respiration-produced CO_2 can drive observed atmospheric CO_2 differences between glacial and interglacial periods if the ratio of the supply rates of organic carbon and calcite to the sediments changed over those timescales. It is clear that calcium carbonate accumulation in the sediments is linked to glacial cycles [Farrell and Prell, 1989]; however, separating the effects of dissolution (either due to bottom-water saturation state changes or increased supply of organic matter to the sediments) from changes in productivity is difficult without quantification of the kinetics of dissolution [Archer, 1991b]. While seafloor diagenetic reactions are of obvious importance to the bulk calcite composition of the sediments, more recently it has been shown that trace metal and isotopic signatures also reflect dissolution, often well before bulk sediment properties show strong changes [McCorkle *et al.*, 1995;

Lohmann, 1995]. Thus, for any interpretation of these historical records or inference of past climatic conditions, an understanding of the mechanisms and magnitudes of seafloor diagenetic reactions is critical.

[3] Seafloor calcite is formed primarily in the surface ocean by planktonic coccolithophoridae and foraminifera. When these organisms die, their shells sink to the seafloor where they are either buried in the sediments or dissolved. Whether or not shells dissolve is determined by the saturation state Ω_C of the water in contact with the calcite, defined by

$$\Omega_C \equiv \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K'_{sp,C}}, \quad (1)$$

where $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ are the concentrations of dissolved calcium and carbonate ions, respectively, and $K'_{sp,C}$ is the stoichiometric calcite solubility product. When the water is undersaturated ($\Omega_C < 1$), calcite can dissolve; when it is supersaturated ($\Omega_C > 1$) dissolution does not occur.

[4] Two types of undersaturation can drive dissolution on the seafloor: bottom-water undersaturation, $\Omega_{C,BW}$, and pore water undersaturation driven by oxic respiration of organic carbon. Since calcium concentrations are very nearly constant in the ocean, variations in carbonate concentration and $K'_{sp,C}$ drive oceanic variations in $\Omega_{C,BW}$. Carbonate ion typically decreases weakly (due to depth distributions of alkalinity and total CO_2) and $K'_{sp,C}$ increases (due to increasing pressure) with depth in the ocean, making $\Omega_{C,BW}$ a strong function of depth. The distribution of calcite on the seafloor reflects this—sediments in shallower regions of the ocean basins contain higher calcite fractions than deeper sediments [e.g., *Biscaye et al.*, 1976; *Kolla et al.*, 1976; *Berger et al.*, 1976]. The second factor, respiration-driven pore water undersaturation, can also cause significant dissolution. Respiration of organic carbon within the sediments produces CO_2 , which in turn consumes CO_3^{2-} and drives down the saturation state of the pore waters, causing dissolution even in sediments overlain by supersaturated bottom-waters. *Emerson and Bender* [1981] first quantified the amount of calcite that could dissolve in sediments in response to metabolically produced CO_2 . Subsequent in situ pH electrode measurements in pore waters of sediments both above and below the saturation horizon could not be explained without respiration-driven dissolution [*Archer et al.*, 1989; *Hales and Emerson*, 1996, 1997a; *Hales et al.*, 1994; *Cai et al.*, 1995]. Studies of pore water chemistry, sampled with in situ samplers, also implicate respiration-driven dissolution [*Sayles*, 1980, 1985; *Sayles and Curry*, 1988; *Martin and Sayles*, 1996; *Martin et al.*, 2000]. Most benthic flux chamber experiments [*Berelson et al.*, 1990; *Jahnke et al.*, 1997; *Jahnke and Jahnke*, 2003] require respiratory dissolution to explain observed alkalinity and calcium fluxes.

[5] The significance of respiratory dissolution is not universally accepted, particularly in calcite-preserving sediments in the oligotrophic open ocean. Bulk sediment calcite content and sediment dissolution indices based on

foraminiferal assemblages often do not show significant changes above the depth of the saturation horizon [*Berger et al.*, 1982; *Broecker and Clark*, 2003]. *Jahnke et al.* [1994] found detectable alkalinity and calcium fluxes out of sediments at water-column depths below the saturation horizon but none from depths near or above the saturation horizon—fluxes predicted with respiration and dissolution rate models used previously [*Emerson and Bender*, 1981; *Archer et al.*, 1989; *Archer and Maier-Reimer*, 1994] were significantly greater than the benthic chamber measurements, while models including dissolution driven only by bottom-water undersaturation were in agreement with these observations. Recently, *Jahnke and Jahnke* [2003] synthesized several suites of in situ benthic chamber incubations and showed that despite their many observations of respiration-driven dissolution, this process may be retarded in calcite-rich sediments overlain by supersaturated bottom-waters. This indicates that metabolic dissolution may have variability due to factors such as buffering by calcite surfaces or in situ precipitation in addition to the organic carbon rain rate and bottom-water saturation state.

2. Seafloor Respiration

[6] Organic carbon raining to the seafloor is probably made up of a huge variety of organic compounds. Their degradation reactions, even if limited to a single oxidant (e.g., O_2), are likely quite complex and characterization of these reactions is certainly beyond the scope of this paper. Respiration in sediments near ocean margins is complicated by very high surface productivity, and the high organic matter rain to the seafloor and the consequent utilization of oxidants other than oxygen, in addition to high bioturbation and irrigation rates and downslope transport of mineral and organic matter. Nonetheless, pooling measurements of pore water oxygen from pelagic sediments [*Hales and Emerson*, 1996, 1997a; *Hales et al.*, 1994; *Hammond et al.*, 1996] yields some conclusions about the rate of oxic metabolism of organic carbon. First, pore water oxygen profiles are adequately reproduced by models that include a rate of O_2 consumption R_{O_2} ($\mu\text{mol cm}^{-3} \text{ yr}^{-1}$) with an empirical dependence on depth given by:

$$R_{\text{O}_2} = r_f \exp\left(\frac{-z}{z_f^*}\right) + r_s \exp\left(\frac{-z}{z_s^*}\right), \quad (2)$$

where z (cm) is depth below the sediment-water interface, the r ($\mu\text{mol cm}^{-3} \text{ yr}^{-1}$) and z^* (cm) terms are empirical coefficients, and the subscripts f and s refer to “fast” and “slow” degrading fractions of organic carbon. While this may not represent the true reaction mechanism, it can be thought of conceptually as the depth dependence that would result from an organic carbon rain consisting of a highly labile (“fast”) fraction and a more recalcitrant (“slow”) fraction. (Note that this formulation is essentially the same as that given by *Hales and Emerson* [1996, 1997a], except I have not explicitly included the porosity here, to facilitate the comparison between scale depths at different locations). Simpler formulations (such as a single

Table 1. Ocean Basin Respiration Kinetics

Location	Water Depth, m	Sediment O ₂ Consumption, $\mu\text{mol cm}^{-2} \text{yr}^{-1}$	% fast ^a	z_f^* , cm	z_s^* , cm
Western North Atlantic (n = 1)	4501	21	53	0.42	6.9
Ceara Rise, W. tropical Atlantic (n = 5)	3280	20 ± 6	62 ± 15	0.33 ± 0.05	4.3 ± 0.5
Ceara Rise, W. tropical Atlantic (n = 1)	4000	28	74	0.35	6.6
Ceara Rise, W. tropical Atlantic (n = 4)	4685	18 ± 5	65 ± 8	0.34 ± 0.09	6.9 ± 0.2
Ontong-Java Plateau, W. equatorial Pacific (n = 4)	2330	17 ± 5	55 ± 19	0.39 ± 0.05	3.8 ± 1
Ontong-Java Plateau, W. equatorial Pacific (n = 2)	2963	23 ± 5	76 ± 5	0.25 ± 0.05	5.3 ± 0.3
Average of above (n = 18)		20 ± 6	63 ± 15	0.34 ± .07	4.9 ± 1
E. equatorial Pacific (JGOFS [Hammond <i>et al.</i> , 1996] (n = 7))		32 ± 10	83 ± 9	0.44 ± .2	4.4 ± 0.4

^aPercentage of the total flux due to the fast degrading (more labile) organic carbon fraction.

exponential term) do not fit the observations [Hales and Emerson, 1996, 1997a; Hammond *et al.*, 1996]. The results (Table 1) indicate that the “fast” term accounts for a majority of the total respiration, and has an average scale depth z_f^* of 0.34 ± 0.07 cm; the scale depth of the second term z_s^* is equal to 4.9 ± 1 cm. This is remarkably consistent with the results of Hammond *et al.* [1996] who reported reaction scale depths of 0.4 ± 0.1 cm and 4.4 ± 0.4 cm using models of O₂ profiles measured in pore waters extracted from retrieved cores in the equatorial Pacific. The depth scale of the fast term is significantly shallower than that of respiration reactions using single-exponential formulations. For example, the respiration reaction used in the sediment models of Jahnke *et al.* [1994], Archer and Maier-Reimer [1994] and Archer [1996a, 1996b] has a scale depth of about 2 cm (when the interfacial decrease in porosity is considered). This difference has significant impact on the sensitivity of the lysocline to bottom-water saturation and organic carbon rain rate.

[7] These results also show that with the exception of sediments underlying the region of high-productivity in the eastern equatorial Pacific [Hammond *et al.*, 1996], there is little consistent variability in the total oxygen fluxes as a function of depth or ocean basin. This lack of dependence on depth and location is supported by other types of measurements of seafloor respiration, whether performed by benthic chamber incubation, or inferred from sediment-trap estimates of deep carbon fluxes to the seafloor (Figure 1). The magnitude of the oxygen consumption is also largely consistent with Jahnke’s [1996] synthesis of global ocean sedimentary oxygen consumption, which shows large areas of benthic O₂ fluxes of $\sim 20 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ in the oligotrophic open ocean, although his maps do show depth dependence as a result of his application of Berger *et al.*’s [1987] empirical carbon flux decrease with depth. The apparent lack of depth dependence shown in the seafloor oxygen fluxes here is supported by the notion that the vast majority of organic matter reaching the seafloor does so in close association with fast-sinking, low-lability mineral phases such as calcite and clay [Francois *et al.*, 2002; Armstrong *et al.*, 2002; Klaas and Archer, 2002]. Examination of the variability that is present in the total oxygen flux shows a positive correlation with the “% fast,” which implies that large, possibly episodic, fluxes of highly labile

organic carbon determine the spatial and temporal variability of seafloor respiration rates (Figure 2).

3. Seafloor Dissolution

3.1. Kinetics

[8] Most representations of dissolution in marine sediments assume a dependence on the undersaturation $(1 - \Omega_C)$ of the surrounding waters with respect to calcite, e.g.,

$$R_{d,C} \propto (1 - \Omega_C)^n, \quad (3)$$

where $R_{d,C}$ is the dissolution rate of calcite and n is the “order” of the reaction. Authigenic precipitation of calcite in deep-sea sediments is generally ignored, although Jahnke and Jahnke [2003] have recently examined those effects. Recently, Morse and Arvidson [2002] published an exhaustive synthesis of the laboratory dissolution and precipitation kinetics of carbonate minerals, showing that in most cases the kinetics are nonlinear with respect to the solution chemistry of the surrounding waters, due largely to the complexities of reactions at the solid-solution interface. In the laboratory study most often cited by researchers studying calcite diagenesis in the field, Keir [1980] proposed a kinetic representation of dissolution that was proportional to $(1 - \Omega_C)^{4.5}$. Arakaki and Mucci [1995], however, with a thorough and mechanistic representation of all the processes determining calcite precipitation and dissolution rates, showed only a first-order dependence on $(1 - \Omega_C)$ for the range of pH and carbonate ion concentrations experienced in most of the ocean. Hales and Emerson [1997b] demonstrated that near-saturation calcite dissolution kinetics in sediments on the seafloor, and in Keir’s laboratory results themselves, may be better described by a first-order dependence on undersaturation than by a higher-order dependence when the most modern estimates of calcite solubility [Mucci, 1983] are used to calculate Ω_C . Further, Hales and Emerson [1997b] showed that the dissolution rate constant may vary between seafloor locations by up to an order of magnitude, ostensibly due to variability in size distributions of bulk sedimentary calcite.

3.2. Respiration-Driven Dissolution

[9] Undersaturation can be driven by both increases in calcite solubility ($K_{sp,C}$), e.g., as a function of increasing

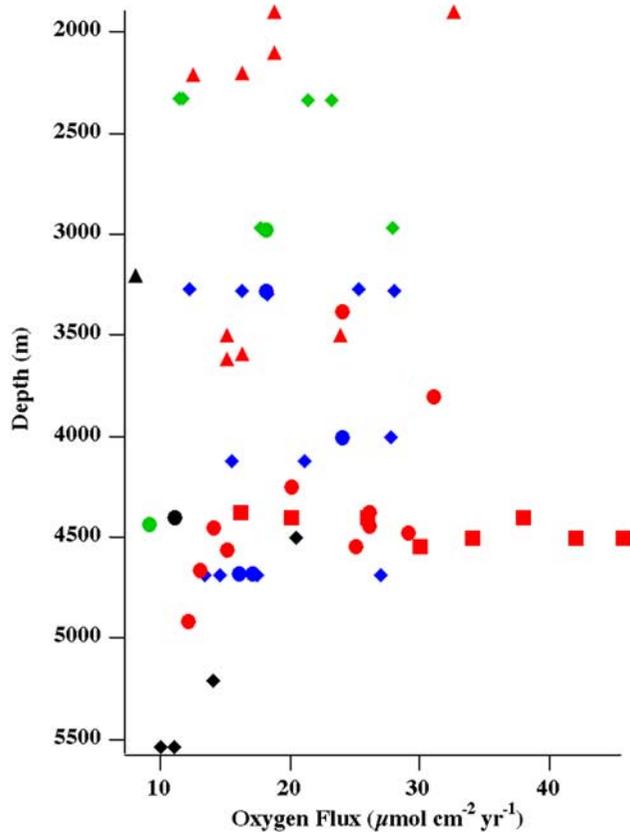


Figure 1. O_2 flux as a function of water column depth for a variety of open-ocean locations and estimated by a variety of measurement techniques, as follows: diamonds, fluxes based on in situ O_2 electrodes profiles; circles, fluxes estimated by benthic chamber incubation experiments; squares, fluxes based on shipboard whole-core squeezer O_2 profiles; triangles, fluxes based on sediment trap organic carbon rain rates multiplied by a C: O_2 stoichiometry of 1/0.65; green symbols, Ontong-Java Plateau; blue symbols, Ceara Rise; black symbols, western North Atlantic; solid red symbols, eastern equatorial Pacific; red half-filled symbols, off-equator eastern equatorial Pacific. While there appear to be higher fluxes to the sediments of the eastern equatorial Pacific, variability within repeat measurements at other locations appears to be comparable to the variability between those locations or to the variability at any one location as a function of depth. Data compiled from Hales and Emerson [1996, 1997a], Hales et al. [1994], Martin and Sayles [1996], Jahnke et al. [1994], Jahnke and Jahnke [2003], Berelson et al. [1994], Hammond et al. [1996], Sayles et al. [1994], Honjo et al. [1995].

pressure in the deep ocean, and by decreases in the carbonate ion concentration of the ambient fluid. Carbonate ion concentration can be driven down in bottom waters and pore waters alike by the addition of respiratory CO_2 released during the oxidation of organic matter. Because transport within pore waters is limited to molecular diffusion, and because much of the degradation of organic matter that takes place in the deep ocean takes place in the

sediments [Jahnke and Jackson, 1987; Jahnke, 1996], the effect of respiratory CO_2 on Ω_C can be pronounced in pore waters. As first suggested by Emerson and Bender [1981], it is possible for respiratory CO_2 to drive pore water carbonate ion concentrations below saturation values even in sediments overlain by supersaturated bottom-waters.

[10] Respiration-driven dissolution is of course sensitive to the magnitude and form of the rate of respiratory CO_2 production. The degree to which that respiratory CO_2 drives calcite dissolution is dependent on both the saturation state of the overlying water and the calcite dissolution rate constant. Dissolution driven by the two parts of the respiration reaction (equation (2)) respond to these factors quite differently. The “slow” respiration term takes place at such great depths in the sediment that respiration-induced undersaturation cannot be effectively moderated by diffusion of bottom waters into the sediments. This is illustrated in Figure 3, which shows the difference in dissolution rates as a function of bottom-water saturation ($\Omega_{C,bw}$) for a variety of scenarios.

[11] The calcite dissolution driven by the CO_2 produced in stoichiometric proportion to these oxygen consumption

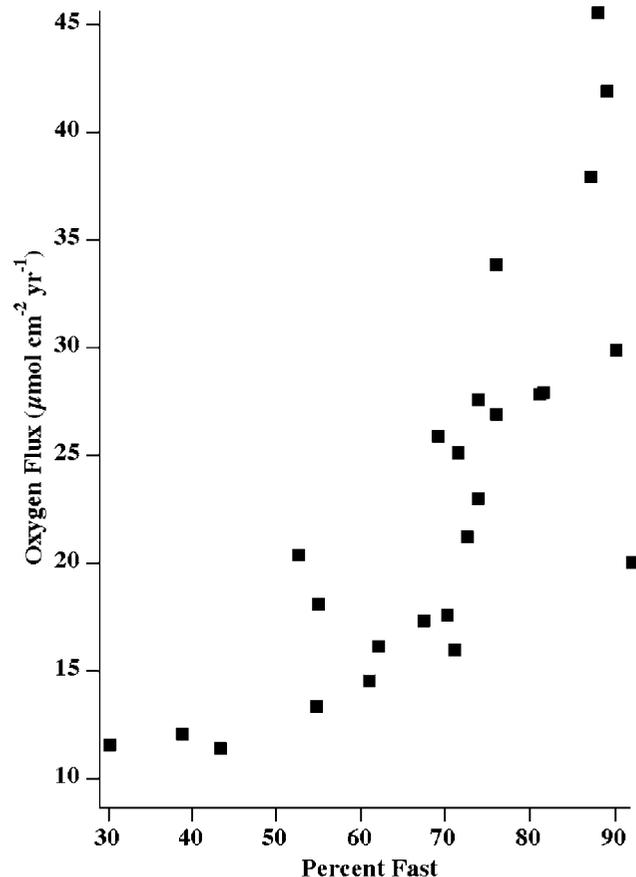


Figure 2. Total O_2 flux to the sediments versus the “% fast,” or the part of the total due to the first exponential term in equation (2), showing the positive relationship between the two. Data are from Hales and Emerson [1996, 1997a], Hales et al. [1994], and Hammond et al. [1996], as summarized in Table 1.

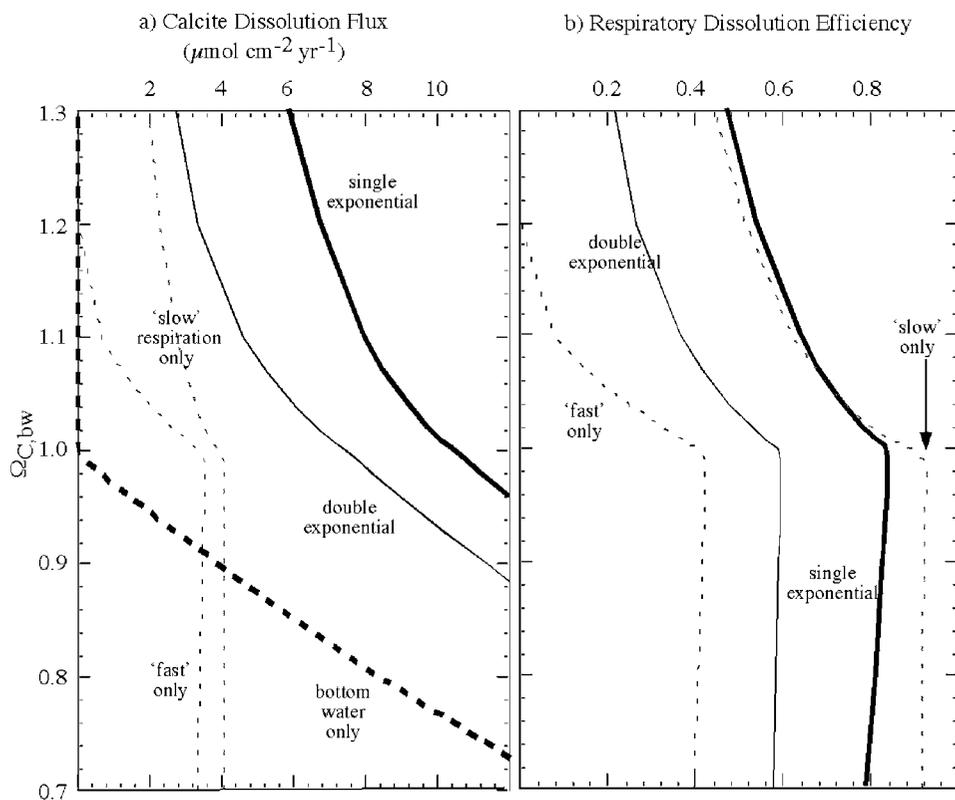


Figure 3. Hypothetical dissolution as a function of bottom-water saturation Ω_{bw} for oligotrophic ocean-basin sediments with a mixed-layer calcite content of 50%, a first-order dissolution reaction with a dissolution rate constant of 0.0365 year^{-1} , and an organic carbon respiration rate of $13 \mu\text{mol cm}^{-2} \text{yr}^{-1}$. Figure 3a shows the dissolution driven by various forcing components. The heavy dashed line represents the dissolution that would occur due to bottom-water undersaturation only, in the absence of any metabolic CO_2 . The light solid line is the total calcite dissolution (bottom-water + metabolic CO_2) for the average ocean-basin respiration rate (Table 1). The two light dashed lines show the dissolution driven by each component (fast or slow, as labeled) of that reaction. Note that the dissolution driven by the slow term is fairly constant above the saturation horizon ($\Omega_{bw} = 100\%$) in comparison to that driven by the fast term, which is near zero until a bottom-water saturation of about 110% and then rises rapidly until the saturation horizon is reached. The heavy solid line shows, for comparison, the dissolution driven by a respiration formulation with a single exponential term with a scale depth of 2 cm. This respiration rate drives more dissolution for the same organic carbon rain than the two-exponential formulation in all saturation cases, particularly above the saturation horizon. Figure 3b shows the dissolution efficiency of each respiration term, defined as the dissolution driven by each term (Figure 3a) divided by the metabolic CO_2 produced by that term. Note that the efficiency of the two-exponential respiration (light solid line) is only about 0.2 above the saturation horizon, implying very small dissolution fluxes for typical ocean-basin organic carbon rain rates.

rates (I will assume a stoichiometric ratio of 0.65 mole metabolic CO_2 produced per mol of O_2 consumed, and thus a carbon rain rate of $13 \mu\text{mol cm}^{-2} \text{yr}^{-1}$. This lower-than-Redfield C:O₂ stoichiometry is consistent with that suggested by *Anderson and Sarmiento* [1994] and *Hedges et al.* [2002]) is illustrated in Figure 3, and is perhaps best summarized by the following statement: The “fast” part of the respiration reaction, while accounting for most of the total respiration, happens so near the interface that its ability to dissolve calcite is very sensitive to the saturation state of the overlying water with respect to calcite. In contrast, the “slow” part of the reaction happens at such great depth in

the sediment that it dissolves calcite with much less sensitivity to bottom-water chemistry. Figure 3a illustrates this effect, for the simple case of a sediment column that has a fixed calcite composition of 50% (by mass) and a wide range of Ω_C . The dissolution driven by the first respiration term is zero until the saturation horizon is approached, where it rapidly rises to its maximum, and nearly constant, value. The dissolution driven by the second term, however, is much less dependent on the bottom-water saturation state, showing only a gradual increase with decreasing saturation. The efficiency with which each term dissolves calcite (defined as the dissolution driven by each term divided by the

metabolic CO_2 produced by that term) is shown in Figure 3b. For comparison, both figures include the dissolution driven by a single-exponential respiration rate with a scale depth of 2 cm and the same overall organic carbon rain rate to the sediments as the two-exponential case. Note that the two-exponential respiration reaction drives calcite dissolution rates that are only 50–70% of those driven by the single exponential formulation, and that the “dissolution efficiency” (moles calcite dissolved per mole of respiration CO_2 produced) of the two exponential respiration is only about 20% at high degrees of bottom-water supersaturation. This, combined with the low organic carbon fluxes to the sediments in these settings, means that the dissolution rates above the saturation horizon are very near the detection limit of the benthic chamber incubation (R. Jahnke, Skidaway Institute of Oceanography, personal communication), and may not always be detectable by that method.

[12] Finally, I demonstrate the general applicability of this combination of respiration and dissolution kinetic formulations by simulating other, independent, seafloor observations of calcite dissolution. Figure 4a demonstrates that, within uncertainties, this combination of respiration and dissolution kinetic formulations agrees reasonably well with all observations of open-ocean seafloor calcite dissolution. For the sake of comparison, I have prepared a figure that shows the relationship between predicted and measured fluxes, when the same independent measurements are simulated with a scenario including dissolution forced by a more traditional representation of respiration kinetics. In this case, oxygen is consumed by a single exponential term, which decays below the sediment water interface with a characteristic depth of 2 cm. Respiratory CO_2 is produced in classical Redfield proportion to the oxygen consumption (e.g., $\Delta\text{CO}_2: -\Delta\text{O}_2 = 106:138 = 0.77$). The combination of the deeper release of respiratory CO_2 and the higher CO_2 production stoichiometry significantly increases the estimated dissolution. In contrast to Figure 4a, most of the estimated dissolution fluxes are greater than the measured fluxes. The relative effect is most pronounced at the super- and near-saturated sites (open squares and triangles labeled “Jahnkes...”; see later discussion) where there is little, if any, bottom-water driven dissolution. In these situations, the traditional representation of sedimentary respiration drives at least twice as much dissolution as the forcing described above.

4. Lysocline

[13] In the above paragraphs I demonstrated that seafloor respiration shows a similar dependence on depth within the sediments in the deep pelagic ocean, and that the oxygen flux is relatively insensitive to water column depth or location. I also showed that the observations of seafloor dissolution are consistent with respiration-driven dissolution, and dissolution with a first-order dependence on undersaturation. Now the task is to determine if these results are consistent with observed distributions of calcite on the seafloor. It is important to note here that my goal is not to simulate the global distributions of seafloor calcite, but rather to apply a simple model to a few well-constrained case study regions to assess the importance of the respira-

tion and dissolution kinetics in determining the shape of the lysocline.

[14] I have chosen two such regions to use as case studies: the Ontong-Java Plateau and the Ceara Rise. I chose these for several reasons. They span a wide saturation range with little variation in surface-ocean productivity. They are pelagic sites far from the complications of input of organic or terrigenous matter by down-slope transport from adjacent margins (as shown, e.g., by *Biscaye et al.* [1988]). They have been widely studied from the perspectives of pore water distributions, benthic fluxes, and sediment preservation history. They are bathed by well-oxygenated bottom-waters, and the complexities of sub- and an-oxic diagenesis can be ignored in the mixed layer. High-quality data constraining the deep-water carbonate chemistry are available from these locations from the researchers who have studied sediment diagenesis there and from the WOCE and TTO programs.

[15] Despite the similarities in terms of applicability for this kind of study, the two locations do have some notable differences. Bottom waters on the Ontong-Java Plateau are undersaturated at depths well shallower than 3000 m, while the saturation horizon on the Ceara Rise is not reached until a depth of over 4000 m. Sediments on the Ontong-Java Plateau show increases in several dissolution indices [*Broecker et al.*, 1999; *Broecker and Clark*, 1999a, 1999b; *McCorkle et al.*, 1995; *Lohmann*, 1995] at depths shallower even than 2000 m; similar indices on the Ceara Rise do not show strong dissolution signatures until 4000 m or deeper [*Broecker and Clark*, 2003]. Additionally, calcite content in the two locations is markedly different: the shallowest sediments on the Ceara rise are only about 65% calcite; by a depth of 4700 m (and a bottom-water saturation of about 0.85), that has dropped to about 40%. In contrast, shallow (but still undersaturated!) sediments on the Ontong-Java Plateau approach 90% calcite, and deeper sediments (with bottom-water saturations of about 0.7) drop only to about 70%. These differences at otherwise similar locations will prove to be valuable tests of the simple model described below.

[16] This is of course not the first attempt to model the calcite lysocline using kinetics based on in situ pore water diagenesis studies. *Archer* [1996a, 1996b, 1991a], *Emerson and Archer* [1990], and *Mekik et al.* [2002] have all undertaken much more ambitious modeling efforts. None, however, have used the two-exponential respiration rate (equation (2); Table 1) or first-order dissolution rate kinetics suggested here. My goal is only to demonstrate that this combination of kinetics yields good approximation of sediment distributions at two open ocean sites that have been studied extensively by the sediment diagenesis and paleoceanographic communities.

4.1. Model

[17] The model I have constructed to simulate the lysocline is simple. The pore waters are described by the model used by *Hales and Emerson* [1996, 1997a]. The solid phase consists of three particulate fractions with varying degrees of reactivity: organic carbon, which is entirely consumed by oxid degradation and does not contribute to the preserved sediment make-up or mass accumulation rates; calcite,

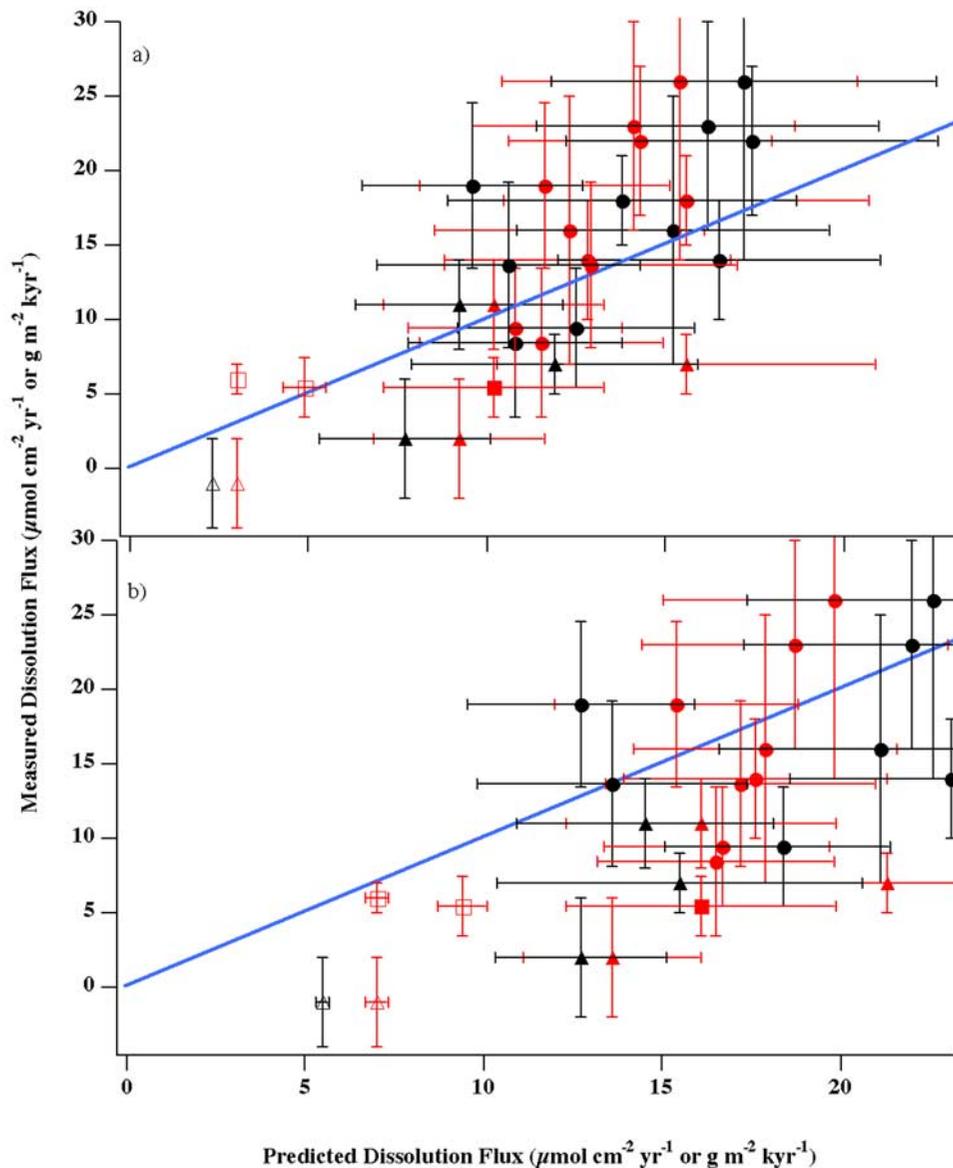


Figure 4. (a) Measured dissolution as a function of that predicted by the simple respiration and dissolution reactions discussed in the text for deep, pelagic locations. The solid blue line represents the 1:1 relationship between measured and predicted fluxes. Red symbols represent dissolution predicted by the model assuming a constant flux of $20 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ and the sediment respiration depth dependence shown in Table 1; black symbols represent dissolution predicted using O_2 fluxes reported specifically for given sites, forced to have the depth dependence from Table 1. Circles represent dissolution fluxes calculated from measured alkalinity fluxes during the benthic chamber experiments of *Berelson et al.* [1994] triangles are dissolution fluxes calculated from measured alkalinity fluxes during the benthic chamber experiments of *Jahnke et al.* [1994] and *Jahnke and Jahnke* [2003]; squares are dissolution fluxes calculated from pore water profiles of calcium sampled by in situ whole core squeezing [*Martin and Sayles*, 1996]. Solid symbols represent fluxes from locations where the bottom waters are undersaturated with respect to calcite; open symbols represent fluxes from locations where bottom waters are supersaturated with respect to calcite. Vertical error bars are taken from the stated analytical uncertainties of the measurements; horizontal error bars cover the range of dissolution predictions resulting from dissolution rate constants ($k_{d,C}$) between 0.00365 and 0.0365 year^{-1} . The two pairs of triangles in the lower left corner of the plot are the oligotrophic open ocean sites where *Jahnke and Jahnke* [2003] have identified a lack of respiration-driven dissolution. (b) As Figure 4a, except the predicted dissolution is generated using classical Redfield ($-\Delta\text{O}_2:\text{CO}_2 = 138:106$) respiration stoichiometry, and a depth dependence described by a single exponential function that decays with increasing depth below the interface with a scale depth of 2 cm.

which is partially dissolved by the combined effects of respiration CO_2 and bottom-water undersaturation; and “clay,” broadly defined as an inert fraction that does not dissolve at all. Sediments are transported by advection (sediment accumulation); mixing (bioturbation) is assumed to be fast enough that mixed-layer sediment composition is constant with depth. Sediment accumulation is determined at the base of the mixed layer by the input of solids to the sediments, the dissolution integrated to that depth, and the sediment porosity. Calcite dissolves in response to undersaturation of pore waters driven both by production of respiratory CO_2 and by bottom-water undersaturation. The flux of organic carbon is determined by the oxygen flux, assumed to equal the pelagic average shown in Table 1. The rain rates of calcite and clay to the sediment, and the calcite dissolution rate constant, are treated as adjustable parameters at the two locations; these three are optimized to find the best reproduction of the observed lysocline at each of the two sites using a numerical optimization method (Powell’s method [Press *et al.*, 1989]). Model results thus give not only the mixed-layer calcite distribution as a function of depth, but also the necessary input fluxes of calcite and clay, and dissolution rate constants.

[18] The model is steady state. Several authors have questioned whether or not the mixed layer, which likely has a mean age of a few thousand years, can be considered in steady state, especially at the Ontong-Java Plateau [Archer, 1996a, 1996b; Oxburgh, 1998; Matsumoto *et al.*, 2001]. This is a much larger issue than I can hope to address in this paper, and I will not attempt to. My goal in this effort is to simulate, with the simplest model possible, the distributions of calcium carbonate in two areas of diagenetic and paleoceanographic interest. Successful reproduction of the distributions in these two areas will only bolster the veracity of the simple model.

4.1.1. Input Fluxes

[19] Much effort has been made in demonstrating a depth-dependence for fluxes of particles raining through the water column that takes into account decay and dissolution during this transit to the sediments [e.g., Berger *et al.*, 1987]). While there are strong decreases in flux between the surface ocean and the bottom of the thermocline, the decrease from there to the seafloor is equivocal [see, e.g., Armstrong *et al.*, 2002; Francois *et al.*, 2002]. The respiration fluxes in Figure 1 show no strong decrease in flux with depth. Sediment trap data sometimes show weak decreases in particle fluxes with depth but often they show increases as well. Sediment burial of clay particles often increases with depth, implying that total particle flux to the sediments may increase as well [Curry and Lohmann, 1990; Francois *et al.*, 1990]. Comparison of seafloor oxygen fluxes with carbon rain to sediment traps over 1000 m above shows that the seafloor degradation of organic matter is at least as large as the flux of particles through the water column [Sayles *et al.*, 1994]. Given the uncertain nature of even the sign of the depth dependence of the particle rain, I have chosen to use depth-independent inputs of calcite, organic carbon, and inert clay particles to the sediment water interface.

4.1.2. Lysocline Data

[20] Observed lysoclines were constructed from literature data relating sediment mixed layer calcite content, depth, and

bottom-water saturation; these are cited in the corresponding figure captions. Mixed layer calcite content was defined as the average over the surficial 8–10 cm. Bottom-water saturation was calculated by pooling measurements of alkalinity (ALK) and total CO_2 (T_{CO_2}) made by researchers involved in benthic diagenesis research in the two case study areas, and from nearby stations occupied during the WOCE, TTO, and GEOSECS programs. Bottom-water carbonate ion concentrations were calculated from these values and the carbonic acid dissociation constants and their pressure dependences given by UNESCO [1987]; Mucci’s [1983] 1-atm solubility product corrected by the pressure dependence of Millero [1983] yielded the in situ estimate of $K'_{\text{sp,C}}$. Bottom-water saturations calculated in this way using the WOCE data (Carbon Dioxide Information and Analysis Center, <http://cdiac.ornl.gov/home.html> [see also Feely *et al.*, 2002]) were about 10% higher than values constrained by the in situ pore water pH profiles at undersaturated stations (see Hales and Emerson [1996, 1997a, 1997b] for discussion), so the WOCE-based saturation was corrected downward as a result of this. I make no attempt to decide if this correction is due to uncertainty in calculation of carbonate ion from ALK and T_{CO_2} data or to uncertainties in the calcite solubility product, but note that the bottom-water saturation states implied by Mucci’s [1983] solubility and carbonate ion concentrations calculated from the ALK and T_{CO_2} measurements made by S. R. Emerson [Hales and Emerson, 1996], C. E. Reimers (unpublished data), and the TTO project are mutually consistent with the saturation states constrained by the pore water pH data, and that a +10% error in calculated carbonate ion concentration is easily explained by a $+15\mu\text{eq kg}^{-1}$ offset in the WOCE ALK data, which is of similar magnitude to suggested ALK corrections for the WOCE data listed by Lamb *et al.* [2002].

4.2. Results

[21] Results of this exercise are presented in Figure 5. Clearly, the simple model with the average oxygen consumption rate from Table 1, and calcite dissolution proportional to $(1 - \Omega_c)$, and respiration-driven dissolution can reproduce the observed distributions of surficial sediment calcite content (light solid lines) at both locations. The extreme case of dissolution driven by kinetics as suggested by Keir [1980] without a contribution by respiratory CO_2 (heavy dashed lines in Figure 5) does not explain the distribution in either case. Model parameters corresponding to the best simulations of the two lysoclines are summarized in Table 2. Calcite rain rates to the seafloor at the two locations are similar, in accordance with close coupling between calcite and organic carbon rain rates [Klaas and Archer, 2002], which appear to be similar at the two sites as well.

[22] The differences between the lysoclines at the two locations appear to be driven by two factors: (1) the dissolution rate constant necessary to explain the lysocline data at the Ontong-Java plateau is several-fold lower than that required to explain the data at the Ceara Rise; and (2) the rain rate of inert clay at the Ceara Rise appears to be several-fold higher than that at the Ontong-Java Plateau. The first of these is consistent with the conclusions of Hales and Emerson [1997b], who found that pore water

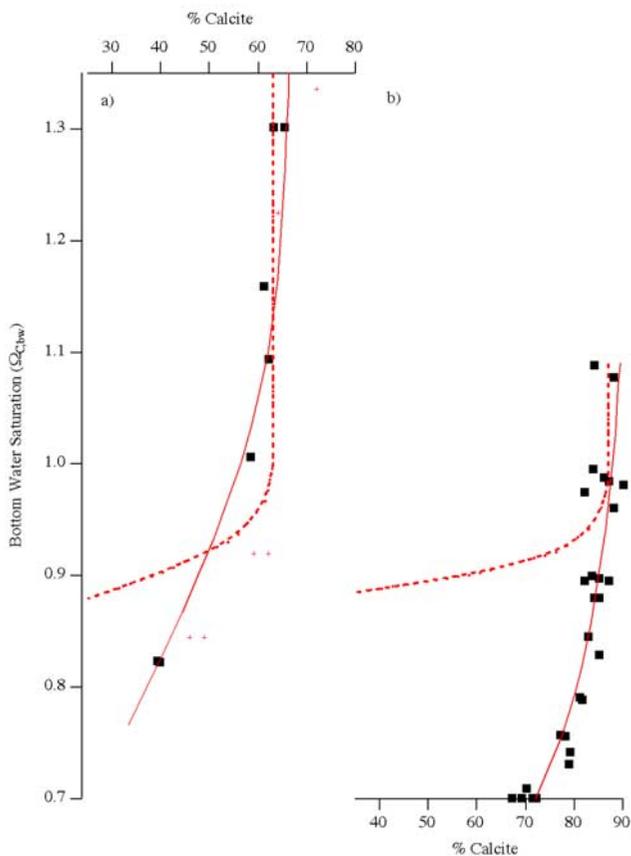


Figure 5. Modeled and observed lysocline for the (a) Ceara Rise, and (b) Ontong Java Plateau. Observations at the Ontong-Java Plateau (solid squares) taken from *Berger and Killingley* [1982], *Jahnke et al.* [1994], *Hales and Emerson* [1996], *McCorkle et al.* [1995], and *Broecker et al.* [1999]. Observations at the Ceara Rise (solid squares taken from *Hales and Emerson* [1997a] and *Martin and Sayles* [1996]). Calcite content data from *Francois et al.* [1990] and *Curry and Lohmann* [1990] seem to have a positive offset from the others (calcite content nearly 10% higher at ~ 3000 m, and several percent higher at 4300 m than *Martin and Sayles*' [1996] data at 4100 m) and were not used to constrain the model. They are shown as small crosses for comparison only. Model lysoclines, constructed at the two sites using the simple model and input fluxes and dissolution rate constants given in Table 2 are shown in both figures as light, solid lines. For contrast, the lysocline predicted by *Keir's* [1980] kinetics ($n_C = 4.5$ and $k_{d,C} = 3650 \text{ year}^{-1}$) without respiration-driven dissolution is shown as the heavy dashed line.

profiles at the two sites required dissolution rate constants nearly an order of magnitude higher at the Ceara Rise. It is also consistent with the findings of *Jahnke et al.* [1994] and *Jahnke and Jahnke* [2003], who report much higher dissolution rates at the Ceara Rise than the Ontong-Java Plateau for similar degrees of bottom-water saturation. The second is consistent with reported accumulation rates of noncalcitic material at the two locations as reported by

Berger and Killingley [1982] for the Ontong-Java Plateau ($\sim 2 \text{ g m}^{-2} \text{ yr}^{-1}$) and *Curry and Lohmann* [1990] and *Francois et al.* [1990] for the Ceara Rise ($4\text{--}9 \text{ g m}^{-2} \text{ yr}^{-1}$). It is not surprising that the clay accumulation rates are different in these two locations far from terrigenous inputs; atmospheric dust deposition is thought to be several-fold higher over the tropical Atlantic than over the tropical Pacific [e.g., *Duce et al.*, 1991]. Thus the simple model contains enough flexibility to accurately represent two distinctly different lysoclines in the oligotrophic open ocean.

5. Discussion

[23] One of the reasons for undertaking this synthesis and modeling effort was to address some issues that have been raised in recent literature regarding the significance (and even the existence) of respiration-driven dissolution in sediments above the saturation horizon. Two key pieces of evidence have been offered in opposition to respiration-driven dissolution: (1) the apparent lack of trend in bulk solid-phase dissolution indices in sediments above the saturation horizon followed by marked decreases in these below the saturation horizon; and (2) the apparent lack of agreement between pore water and benthic chamber-based estimates of dissolution in sediments overlain by supersaturated bottom-waters.

[24] The first of these has recently been highlighted by *Broecker and Clark* [2003]. Indicators of dissolution in sediments above the saturation horizon are relatively constant, while they change rapidly with depth below the saturation horizon. As seen in Figure 3, the combination of kinetic expressions for respiration and dissolution suggested in sections 2 and 3 leads to low dissolution rates above the saturation horizon, which only increase slowly as saturation decreases above the saturation horizon. Obviously, differentiating between no dissolution above the saturation horizon and low, near-constant dissolution above the saturation horizon will be difficult. The consistency of dissolution above the saturation horizon with observed bulk sediment calcite content was demonstrated in the previous section (Figure 5); the question now is whether dissolution indices such as calcite size fraction are consistent with this model as well. The calcite dissolution flux is shown in Figure 6 for the two locations. At the Ontong-Java Plateau, which is mostly overlain by undersaturated bottom-waters, and where the dissolution rate constant is low, the dissolution flux increases with depth in a near-linear fashion. At the Ceara Rise, which is overlain by supersaturated bottom waters over much of its shallower depths and where the dissolution rate constant is large, the dissolution flux is low and changes slowly in sediments overlain by supersaturated bottom-waters, and

Table 2. Summary of Lysocline Model Parameters

	Ceara Rise	Ontong-Java Plateau
Calcite rain rate, $\text{g m}^{-2} \text{ yr}^{-1}$ or $\mu\text{mol cm}^{-2} \text{ yr}^{-1}$	16.4	16.0
Clay rain rate, $\text{g m}^{-2} \text{ yr}^{-1}$	1.3	6.7
Dissolution rate constant, yr^{-1}	0.022	0.007

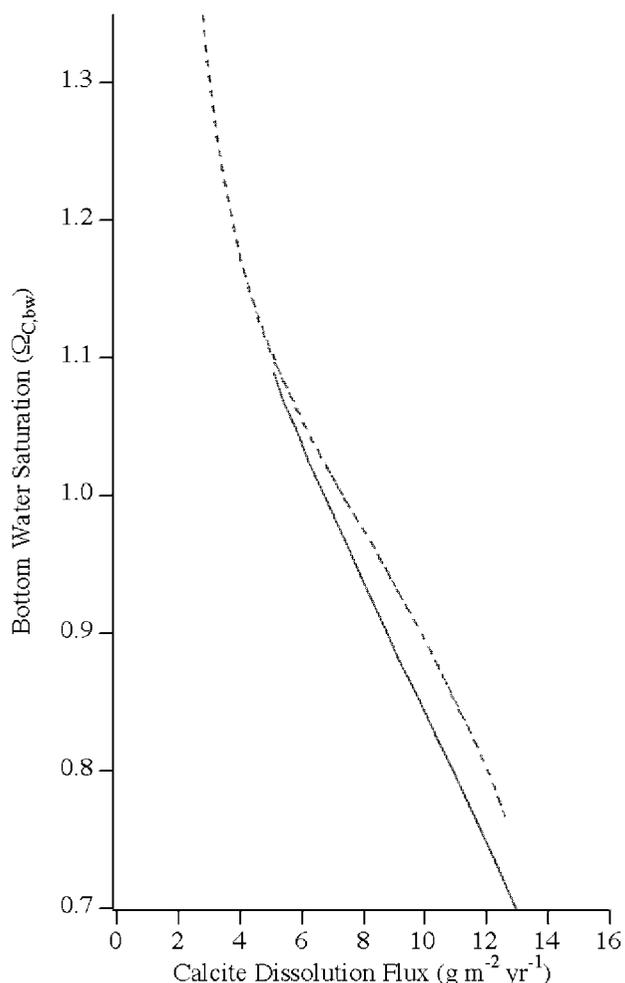


Figure 6. Modeled dissolution rates as a function of bottom-water saturation for the Ontong-Java Plateau (solid line) and Ceara Rise (dashed line) lysoclines. Note that the dissolution above the saturation horizon on the Ceara Rise does not increase strongly until the saturation horizon is closely approached.

increases rapidly as bottom waters become ever more undersaturated. These functionalities track the observed depth-dependences in calcite particle size distribution, which has been put forth as a dissolution proxy at the two locations [Broecker and Clark, 1999a, 1999b, 2003]. At the Ontong-Java Plateau, calcite particle size distributions grow finer in a linear fashion as depth (and undersaturation) increases; at the Ceara Rise calcite size distributions are largely invariant at shallow depths but grow rapidly finer as the saturation horizon is crossed and undersaturation increases.

[25] The second line of reasoning against respiratory dissolution in these high calcite pelagic settings has been widely discussed and recently summarized by Jahnke and Jahnke [2003]. Briefly, they conclude that respiration-driven dissolution is a major factor in all sediments except those consisting of over 60% (by weight) calcite and overlain by supersaturated bottom-waters. They support this conclusion

with benthic chamber observations from three sites: the Cape Verde Plateau, an extremely high-productivity ocean margin location, the likes of which I have excluded from the prior discussion; and the Ceara Rise and Ontong-Java Plateau, both case studies presented earlier. Jahnke and Jahnke suggest two possible mechanisms to reconcile these observations: surface buffering, and authigenic reprecipitation. In both cases, abundant calcite particles are rapidly mixed throughout the sediment mixed layer. While in supersaturated, near-interfacial pore waters, the calcite particles “collect” buffering capacity from the water, either through adsorption on the mineral surface or by actual precipitation of a mineral calcite layer. When these particles are mixed into deeper, corrosive pore waters, they release this buffering capacity either through dissolution or desorption. If the adsorption/precipitation is largely balanced by the desorption/dissolution, then there will be no net flux across the sediment-water interface.

[26] The results presented in prior sections provide a different mechanism for resolving this discrepancy in the pelagic ocean. Jahnke and Jahnke’s [2003] estimated respiration-driven dissolution fluxes were based on respiratory CO_2 generated in sediments with a more traditional single-exponential respiration rate depth-dependence, and Redfield C: O_2 respiration stoichiometry [Jahnke et al., 1994; Jahnke and Jahnke, 2003]. The respiratory dissolution efficiency of such respiration is over a factor of 2 greater than the two-exponential respiration presented here at high degrees of bottom-water supersaturation, and Redfield respiration stoichiometry releases nearly 20% more CO_2 than the lower C: O_2 stoichiometry used here. These factors combine to predict nearly a third less dissolution, for the same oxic respiration flux, than the estimates used by Jahnke et al. [1994] and Jahnke and Jahnke [2003]. I will show below that these lower respiratory dissolution fluxes are within the stated uncertainties of chamber-based fluxes in these high-calcite locations in almost every case.

[27] At the Ontong-Java Plateau, Jahnke et al.’s [1994] shallowest station (at a depth of ca 3000 m) is probably not overlain by supersaturated bottom-waters. Models of the pore water pH data [Hales and Emerson, 1996, 1997b] imply a bottom-water saturation of about 0.9; even in the most extreme case of carbonate ion calculated from WOCE ALK and T_{CO_2} and Mucci’s [1983] calcite solubility, bottom waters are still minimally undersaturated with respect to calcite [Feely et al., 2002]. In this case, neither the surface buffering nor the reprecipitation hypotheses, which both rely on transport of alkalinity from supersaturated interfacial pore waters to depth in the sediment, can work. Whatever the bottom-water saturation state, Jahnke et al.’s alkalinity-based dissolution flux at that station is $2 \pm 3 \mu\text{mol cm}^{-2} \text{yr}^{-1}$, while Hales and Emerson report an estimated range of 4–6 $\mu\text{mol cm}^{-2} \text{yr}^{-1}$ at that same station when using oxygen consumption rates measured there, comfortably within Jahnke et al.’s error bars. Even dissolution estimated by application of the average pelagic oxygen consumption rate (Table 1) to the conditions of that location predicts a dissolution flux of about 7 $\mu\text{mol cm}^{-2} \text{yr}^{-1}$ (Figure 4) for the low dissolution rate constants appropriate to that area, only marginally larger than Jahnke et al.’s measurements.

[28] At the Ceara Rise, *Jahnke and Jahnke* [2003] report flux estimates from two sites that meet their criteria of supersaturated bottom waters and high sediment calcite content. One of these sites, at 4000 m depth, has a large discrepancy between the calcium-based and alkalinity-based dissolution estimates of -6 and $29 \mu\text{mol cm}^{-2} \text{yr}^{-1}$, respectively, which are far lower and far higher, respectively, than pore water-based estimates of $6-9 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ [*Hales and Emerson, 1997a; Martin and Sayles, 1996*]. Following *Jahnke and Jahnke's* [2003] suggestion, I have excluded that station from the comparison. What is left is one site on the Ceara Rise at a depth of ~ 3300 m where *Jahnke and Jahnke* report an alkalinity-based dissolution flux of $-1 \pm 1 \mu\text{mol cm}^{-2} \text{yr}^{-1}$. At this location, *Hales and Emerson* report a range of pore water pH-based dissolution fluxes of $3-12 \mu\text{mol cm}^{-2} \text{yr}^{-1}$; *Martin and Sayles* report a range of $5-7 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ based on pore water calcium profiles. At this location, these pore water-based estimates do appear to be statistically significantly different than *Jahnke and Jahnke's* chamber based dissolution estimates. Thus the entire “disagreement” between benthic chamber and pore water-based dissolution fluxes in the oligotrophic open ocean rides on a single benthic chamber deployment.

[29] While I have gone to great lengths to exclude locations where surface productivity is extremely high and the potential for lateral supply of organic and terrigenous matter to the seafloor is great, I will finally, and briefly, address the *Jahnke and Jahnke* [2003] chamber results from the Cape Verde Plateau. They report fluxes from four benthic chamber incubation experiments at a site about 3100 m deep where the sediments consist of about 65% (by mass) calcium carbonate. Bottom waters saturation there is about 1.3. This site apparently receives a tremendously high rain of labile organic carbon from the productive overlying waters, as evidenced by the oxygen fluxes of $70-100 \mu\text{mol cm}^{-2} \text{yr}^{-1}$. Dissolution fluxes, however, are equivocal as to even their sign. Further complicating the interpretation of these dissolution fluxes are two factors: (1) reported precision of calcium and alkalinity fluxes for all four experiments are large relative to the fluxes themselves; and (2) one of the experiments (which coincidentally has the largest oxygen flux) has an alkalinity-based dissolution flux of $3 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ while the calcium-based flux is $-28 \mu\text{mol cm}^{-2} \text{yr}^{-1}$, a discrepancy that appears to exceed the uncertainty of the measurements. I address the first of these problems by discussing average fluxes from the four experiments, and reporting error bars for the alkalinity and calcium-based fluxes as those propagated from the reported analytical precision of each. I address the second problem by reporting the averages and uncertainties for only the other three experiments, followed by the same for all four experiments in parentheses. The summary is as follows: oxygen flux to the sediments there is 70 ± 3 (78 ± 14) $\mu\text{mol cm}^{-2} \text{yr}^{-1}$; alkalinity-based dissolution flux from the sediments is 4 ± 13 (4 ± 10) $\mu\text{mol cm}^{-2} \text{yr}^{-1}$; and calcium-based dissolution flux from the sediments is 1 ± 10 (-6 ± 12) $\mu\text{mol cm}^{-2} \text{yr}^{-1}$.

[30] Direct comparison between these fluxes and those based on the simple models of respiration and dissolution discussed above is tenuous at best. In any interpretation the

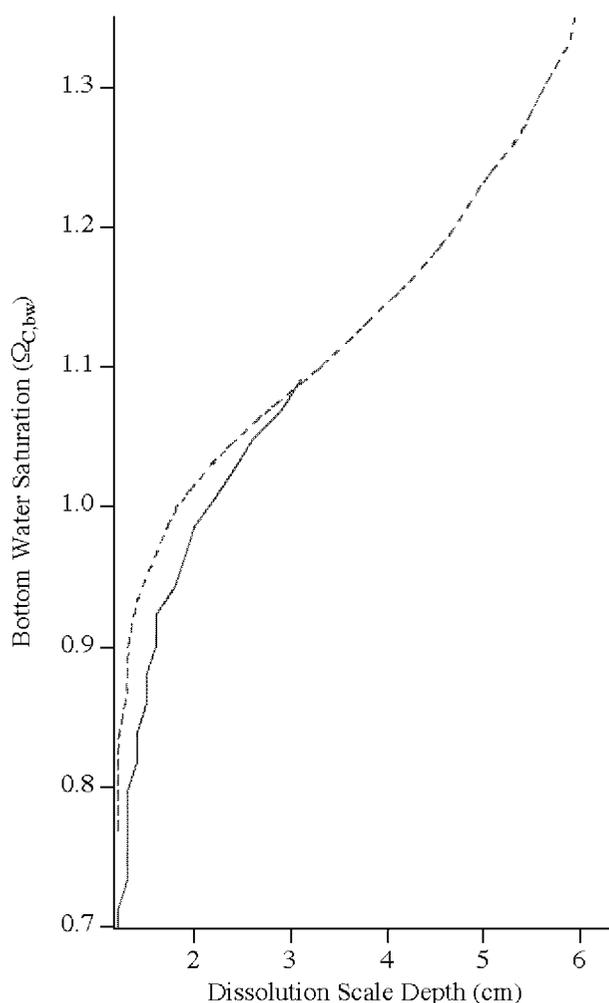


Figure 7. Depth at which dissolution is 50% complete as a function of bottom-water saturation at the Ontong-Java Plateau (solid line) and Ceara Rise (dashed line). These results show the strong shoaling of the locus of dissolution toward the sediment-water interface.

oxygen fluxes at this site are dramatically higher than any seen in the pelagic sites shown in Figure 2, and simply applying the depth dependence shown in Table 1 to a scaled-up total flux should be done with caution. Extrapolation of the results of Section 3 to higher fluxes might tempt one to assign a greater “percent fast” to such a high total flux (see Figure 2); however, what little pore water oxygen data exists for this site (*J.-F. Gaillard, The diagenesis and recycling of biogenic particles in the surficial sediments of the tropical North Atlantic under oligotrophic to eutrophic conditions, unpublished manuscript, 1993*) is not well suited for a rigorous respiration rate depth-dependence determination of the form of equation (2). Throwing caution aside, however, I will make a crude estimate of the dissolution flux that the simple respiration and dissolution model would predict for this site: assuming an $\text{O}_2:\text{C}$ stoichiometry of 0.65, as I have throughout this paper;

and taking the “respiratory dissolution efficiency” of 0.2 at $\Omega_{bw,C} = 1.3$, as shown in Figure 3, I estimate that the dissolution flux at this site should be $9 \mu\text{mol cm}^{-2} \text{yr}^{-1}$, or nearly 20% of the calcite rain to the sediments there if the molar rain ratio between calcite and organic carbon implied by the model lysoclines at the Ontong-Java Plateau and the Ceara Rise can be assumed. Once again, this estimate, while geochemically significant, is well within the reported uncertainty of *Jahnke and Jahnke*'s [2003] chamber-based fluxes, and it seems that no further explanation of a discrepancy is required.

[31] It should be made clear here that the *Jahnke and Jahnke* [2003] scenarios to reconcile their wealth of chamber-based flux data span the open ocean and high-flux, near-margin regions that I have specifically excluded in the previous discussion. The respiration reaction described by equation (2) and Table 1 probably does not describe metabolic processes in these settings well at all. Certainly in settings like those described by *Jahnke et al.* [1997] where pore water oxygen is entirely depleted within a couple centimeters of the sediment-water interface, an oxic reaction term with a scale depth of 5 cm, such as the “slow” part of equation (2), has no validity. I will say that the more traditional representation of respiratory CO_2 release at depths of a few cm below the sediment-water interface can drive significantly greater dissolution, as shown in Figure 4b. If there were some mechanism to cause this in the low-calcite, high rain-rate settings described by *Jahnke et al.* [1997], that might explain their observations simply there as well. I am unaware of any such mechanism.

[32] Finally, I will feebly, and ultimately unsuccessfully, address the “ ^{14}C age problem.” It has been well documented that calcite in surficial sediments has a ^{14}C age that is well approximated by the integrated calcite content of the mixed layer divided by the preservation rate (equivalently the mixed layer depth divided by the linear sediment accumulation rate), and, as a result, the ^{14}C age increases as dissolution increases with increasing depth [e.g., *Broecker et al.*, 1999; *Matsumoto et al.*, 2001; *Keir and Michel*, 1993]. Models of dissolution where calcite dissolves within the sediments, and the dissolving calcite is treated the same as the bulk calcite (e.g., “homogeneous dissolution” [*Broecker et al.*, 1999, 1991] show a mixed layer age that reflects more closely the integrated calcite content of the mixed layer divided by the particulate rain rate, and this age increases with depth as older calcite is preferentially dissolved in the mixed layer. *Martin et al.* [2000] recently showed definitively, with profiles of pore water ^{14}C , that calcite is in fact dissolving in the sediments, but that younger calcite is preferentially dissolved at locations with undersaturated bottom-waters.

[33] The simple model presented here, cannot, of course, simulate such selective dissolution—the mixed layer calcite is defined to be homogeneous and of fixed composition. There is faint initial hope for resolving this problem, however, when the depth at which dissolution occurs within the sediments is shown (Figure 7). Sediments above the saturation horizon dissolve far below the sediment-water interface, but as bottom-water saturation is approached, the dissolution depth rapidly shoals. This gives rise to the possibility that, if more recently deposited sediments were in fact strongly concentrated at shallower depths in the sediments, younger calcite would be dissolved preferentially. Unfortunately, in an attempt to simulate this with a model that allowed calcite and its ^{14}C to have depth-dependence, there was no scenario that would allow selective dissolution of young calcite and, simultaneously, the lack of variability generally observed in mixed-layer calcite content and ^{14}C age. Resolving this question requires a new understanding of age-dependent calcite transport and reactivity.

6. Summary and Conclusions

[34] The preceding discussion demonstrated the consistency of a simple model of oxic respiration of organic carbon and dissolution of calcium carbonate in sediments on the deep pelagic seafloor with independent observations of the interfacial fluxes as a result of these reactions and with the patterns of preservation of calcium carbonate on the seafloor. It also showed the importance of both respiration and dissolution kinetics in determining the rates of dissolution on the seafloor, and the dissolution response to variations in both organic carbon rain rates and bottom-water saturation with respect to calcite. While these simple models are consistent with all the observations, scenarios that rely on high-order dependence of dissolution on undersaturation with respect to calcite and very large dissolution rate constants while neglecting dissolution driven by respiration-produced CO_2 are not. Because of the low respiratory dissolution predicted by this combination of kinetics above the saturation horizon, a much discussed and recently published disagreement between benthic chamber-based dissolution fluxes has been reduced to a small discrepancy at one low-flux site on the Ceara Rise. Complicated mechanisms to explain this seem unjustified without further confirmation of its existence.

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B. Hales, College of Oceanic and Atmospheric Sciences, Oregon State University, 104 Ocean Administration Building, Corvallis, OR 97331, USA. (bhales@coas.oregonstate.edu)