6.19
The Oceanic CaCO₃ Cycle

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6.19.1 INTRODUCTION

Along with the silicate debris carried to the sea by rivers and wind, the calcitic hard parts manufactured by marine organisms constitute the most prominent constituent of deep-sea sediments. On high-standing open-ocean ridges and plateaus, these calcitic remains dominate. Only in the deepest portions of the ocean floor, where dissolution takes its toll, are sediments calcite-free. The foraminifera shells preserved in marine sediments are the primary carriers of paleoceanographic information. Mg/Ca ratios in these shells record past surface water temperatures; temperature corrected ¹⁸O/¹⁶O ratios record the volume of continental ice; ¹³C/¹²C ratios yield information about the strength of the ocean’s biological pump and the amount of carbon stored as terrestrial biomass; the cadmium and zinc concentrations serve, respectively, as proxies for the distribution of dissolved phosphate and dissolved silica in the sea. While these isotopic ratios and trace element concentrations constitute the workhorses of the field of paleoceanography, the state of preservation of the calcitic material itself has an important story to tell. It is this story with which this chapter is concerned.

In all regions of the ocean, plots of sediment composition against water depth have a characteristic shape. Sediments from mid-depth are rich in CaCO₃ and those from abyssal depths are devoid of CaCO₃. These two realms are separated by a transition zone spanning several hundreds of meters in water depth over which the CaCO₃ content drops toward zero from the 85–95% values which characterize mid-depth sediment. The upper bound of this transition zone has been termed the “lysocline” and signifies the depth at which dissolution impacts become noticeable. The lower bound is termed the “compensation depth” and signifies the depth at which the CaCO₃ content is reduced to 10%. While widely used (and misused), both of these terms suffer from ambiguities. My recommendation is that they be abandoned in favor of the term
“transition zone.” Where quantification is appropriate, the depth of the mid-point of CaCO₃ decline should be given. While the width of the zone is also of interest, its definition suffers from the same problems associated with the use of the terms “lysocline” and “compensation depth,” namely, the boundaries are gradual rather than sharp.

While determinations of sediment CaCO₃ content as a function of water depth in today’s ocean or at any specific time in the past constitute a potentially useful index of the extent of dissolution, it must be kept in mind that this relationship is highly nonlinear. Consider, for example, an area where the rain rate of calcite to the seafloor is 9 times that of noncarbonate material. In such a situation, were 50% of the calcite to be dissolved, the CaCO₃ content would drop only from 90% to only 82%, and were 75% dissolved away, it would drop only to 69% (see Figure 1). One might counter by saying that as the CaCO₃ content can be measured to an accuracy of ±0.5% or better, one could still use CaCO₃ content as a dissolution index. The problem is that in order to obtain a set of sediment samples covering an appreciable range of water depth, topographic gradients dictate that the cores would have to be collected over an area covering several degrees. It is unlikely that the ratio of the rain rate of calcite to that of noncalcite would be exactly the same at all the coring sites. Hence, higher accuracy is not the answer.

### 6.19.2 DEPTH OF TRANSITION ZONE

As in most parts of today’s deep ocean the concentrations of Ca²⁺ and of CO₃²⁻ are nearly constant with water depth, profiles of CaCO₃ content with depth reflect mainly the increase in the solubility of the mineral calcite with pressure (see Figure 2). This increase occurs because the volume occupied by the Ca²⁺ and CO₃²⁻ ions dissolved in seawater is smaller than when they are combined in the mineral calcite. Unfortunately, a sizable uncertainty exists in the magnitude of this volume difference. The mid-depth waters in the ocean are everywhere supersaturated with respect to calcite. Because of the pressure dependence of solubility, the extent of supersaturation decreases with depth until the saturation horizon is reached. Below this depth, the waters are undersaturated with respect to calcite. While it is tempting to conclude that the saturation horizon corresponds to the top of the transition zone, as we shall see, respiration CO₂ released to the pore waters complicates the situation by inducing calcite dissolution above the saturation horizon.

One might ask what controls the depth of the transition zone. The answer lies in chemical economics. In today’s ocean, marine organisms manufacture calcitic hard parts at a rate several times faster than CO₂ is being added to the ocean–atmosphere system (via planetary outgassing and weathering of continental rocks) (see Figure 3). While the state of saturation in the ocean is set by

![Figure 1](image_url)  
**Figure 1** A diagrammatic view of how the extent of dissolution impacts the percent calcite in the sediment. In each example, the right-hand vertical arrows give the rain rate and accumulation rate of non-CaCO₃ debris and the left-hand vertical arrows the rain rate and accumulation rate of calcite. The wavy arrows represent the dissolution rates of calcite. As can be seen from the graph on the lower right, the percent of calcite in the sediment gives a misleading view of the fraction of the raining calcite which has dissolved, for large amounts of dissolution are required before the calcite content of the sediment drops significantly.
the product of the Ca\(^{2+}\) and CO\(_3^{2-}\) concentrations, calcium has such a long residence (10\(^6\) yr) that, at least on the timescale of a single glacial cycle (10\(^5\) yr), its concentration can be assumed to have remained unchanged. Further, its concentration in seawater is so high that CaCO\(_3\) cycling within the sea does not create significant gradients. In contrast, the dissolved inorganic carbon (i.e., CO\(_2\), HCO\(_3^−\), and CO\(_3^{2−}\)) in the ocean is replaced on a timescale roughly equal to that of the major glacial to interglacial cycle (10\(^5\) yr). But, since in the deep sea CO\(_3^{2−}\) ion makes up only ~5% of the total dissolved inorganic carbon, its adjustment time turns out to be only about one-twentieth that for dissolved inorganic carbon or ~5,000 yr. Hence, the concentration of CO\(_3^{2−}\) has gradients within the sea and likely has undergone climate-induced changes.

Hence, at least on glacial to interglacial timescales, attention is focused on distribution of CO\(_3^{2−}\) concentration in the deep sea for it alone sets the depth of the transition zone. Thus, it is temporal changes in the concentration of carbonate ion which have captured the attention of those paleoceanographers interested in glacial to interglacial changes in ocean operation. These changes involve both the carbonate ion concentration averaged over the entire deep ocean and its distribution with respect to water depth and geographic location. Of course, it is the global average carbonate ion concentration in the deep sea that adjusts in order to assure that burial of CaCO\(_3\) in the sediments matches the input of CO\(_2\) to the ocean atmosphere system (or, more precisely, the input minus the fraction destined to be buried as organic residues). For example, were some anomaly to cause the burial of CaCO\(_3\) in seafloor sediments to exceed supply, then the CO\(_3^{2−}\) concentration would be drawn down. This drawdown would continue until a balance between removal and supply was restored. As already mentioned, the time constant for this adjustment is on the order of 5,000 yr.

### 6.19.3 DISTRIBUTION OF CO\(_3^{2−}\) ION IN TODAY’S DEEP OCEAN

As part of the GEOSECS, TTO, SAVE and WOCE ocean surveys, \(\Sigma\text{CO}_2\) and alkalinity
measurements were made on water samples captured at various water depths in Niskin bottles. Given the depth, temperature and salinity for these samples, it is possible to compute the in situ carbonate ion concentrations. LDEO’s Taro Takahashi played a key role not only in the measurement programs, but also in converting the measurements to in situ carbonate ion concentrations. Because of his efforts and, of course, those of many others involved in these expeditions, we now have a complete picture of the distribution of CO$_3^{2-}$ ion concentrations in the deep sea.

Below 1,500 m in the world ocean, the distribution of carbonate ion concentration is remarkably simple (see Broecker and Sutherland, 2000 for summary). For the most part, waters in the Pacific, Indian, and Southern Oceans have concentrations confined to the range $83 \pm 8 \mu$mol kg$^{-1}$. The exception is the northern Pacific, where the values drop to as low as $60 \mu$mol kg$^{-1}$. In contrast, much of the deep water in the Atlantic has concentrations in the range $112 \pm 5 \mu$mol kg$^{-1}$. The principal exception is the deepest portion of the western basin where Antarctic bottom water (AABW) intrudes.

As shown by Broecker et al., the deep waters of the ocean can be characterized as a mixture of two end members, i.e., deep water formed in the northern Atlantic and deep water formed in the Southern Ocean. These end members are characterized by quite different values of a quasi-conservative property, PO$_4^+$ (i.e., PO$_4 - 1.95 + \frac{O_2}{175}$). Although these two deep-water sources have similar initial O$_2$ contents, those formed in the northern Atlantic have only roughly half the PO$_4$ concentration of the deep waters descending in the Southern Ocean. Thus, the northern end member is characterized by a PO$_4^+$ value of $0.73 \pm 0.03$, while the southern end member is characterized by a value of $1.95 \pm 0.05 \mu$mol kg$^{-1}$. In Figure 4 is shown a plot of carbonate ion concentration for waters deeper than 1,700 m as a function of PO$_4^+$. The points are color coded according to O$_2$ content. As can be seen, the high O$_2$ waters with northern Atlantic PO$_4^+$ values have carbonate ion concentrations of $\approx 120 \mu$mol kg$^{-1}$, while those formed in Weddell Sea and Ross Sea have values closer to $90 \mu$mol kg$^{-1}$.

The sense of the between-ocean difference in carbonate ion concentration is consistent with the PO$_4^+$-based estimate that Atlantic deep water (i.e., North Atlantic deep water (NADW)) is a mixture of about 85% deep water formed in the northern Atlantic and 15% deep water formed in Southern Ocean, while the remainder of the deep ocean is flooded with a roughly 50–50 mixture of these two source waters (Broecker, 1991). The interocean difference in carbonate ion concentration relates to the fact that deep
water formed in the northern Atlantic has a higher CO$_3^{2-}$ concentration than that produced in the Southern Ocean. The transition zone between NADW and the remainder of the deep ocean is centered in the western South Atlantic and extends around Africa into the Indian Ocean (fading out as NADW mixes into the ambient circumpolar deep water).

The difference in carbonate ion concentration between NADW and the rest of the deep ocean is related to the difference in PO$_4$ concentration. NADW has only about half the concentration of PO$_4$ as does, for example, deep water in equatorial Pacific. This is important because, for each mole of phosphorus released during respiration, $\sim 120$ mol of CO$_2$ are also produced. This excess CO$_2$ reacts with CO$_3^{2-}$ ion to form two HCO$_3^-$ ions. Were PO$_4$ content the only factor influencing the interocean difference in carbonate ion concentration, then it would be expected to be more like 90 $\mu$mol kg$^{-1}$ rather than the observed 30 $\mu$mol kg$^{-1}$. So, something else must be involved.

This something is CO$_2$ transfer through the atmosphere (Broecker and Peng, 1993). The high-phosphate-content waters upwelling in the Southern Ocean lose part of their excess CO$_2$ to the atmosphere. This results in an increase in their CO$_3^{2-}$ ion content. In contrast, the low-PO$_4$-content waters reaching in the northern Atlantic have CO$_2$ partial pressures well below that in the atmosphere and hence they absorb CO$_2$. This reduces their CO$_3^{2-}$ concentration. Hence, it is the transfer of CO$_2$ from surface waters in the Southern Ocean to surface waters in the northern Atlantic reduces the contrast in carbonate ion concentration between deep waters in the deep Atlantic and those in the remainder of the deep ocean.

One other factor expected to have an impact on the carbonate ion concentration in deep Pacific Ocean and Indian Ocean turns out to be less important. Much of the floor of these two oceans lies below the transition zone. Hence, most of the CaCO$_3$ falling into the deep Pacific Ocean and Indian Ocean dissolves. One would expect then that the older the water (as indicated by lower $^{14}C$/C ratios), the higher its CO$_3^{2-}$ ion concentration would be. While to some extent this is true, the trend is much smaller than expected. The reason is that in the South Pacific Ocean and South Indian Ocean an almost perfect chemical titration is being conducted, i.e., for each mole of respiration CO$_2$ released to the deep ocean, roughly one mole of CaCO$_3$ dissolves (Broecker and Sutherland, 2000). So indeed, the older the water, the higher its $\Sigma$CO$_2$ content. But, due to CaCO$_3$ dissolution, there is a compensating increase in alkalinity such that the carbonate ion concentration remains largely unchanged. Only in the northern reaches of these oceans does the release of metabolic CO$_2$ overwhelm the supply of CaCO$_3$ allowing the CO$_3$ concentration to drop.

As in the depth range of transition zone, the solubility of CaCO$_3$ increases by $\sim 14$ $\mu$mol kg$^{-1}$ km$^{-1}$ increase in water depth, the 30 $\mu$mol kg$^{-1}$ higher CO$_3^{2-}$ concentration in NADW should (other things being equal) lead to a 2 km deeper transition zone in the Atlantic than in the Pacific Ocean and the Indian Ocean. In fact, this is more or less what is observed.

### 6.19.4 DEPTH OF SATURATION HORIZON

A number of attempts have been made to establish the exact depth of the calcite saturation horizon. The most direct way to do this is to suspend preweighed calcite entities at various water depths on a deep-sea mooring, then months later, recover the mooring and determine the extent of weight loss (see Figure 5). Peterson (1966) performed such an experiment at 19$^\circ$N in the Pacific Ocean using polished calcite spheres and observed a pronounced depth-dependent increase in weight loss that commenced at ~3,900 m. Honjo and Erez (1978) performed a similar experiment at 32$^\circ$N in the Atlantic and found that coccoliths, foraminifera shells and reagent calcite experienced a 25–60% weight loss at 5,500 m but no measurable weight loss at 4,900 m. Thus the North Atlantic–North Pacific depth difference in the depth of the onset of dissolution is more or less consistent with expectation. Broecker and Takahashi (1978) used a combination of the depth of the onset of sedimentary CaCO$_3$ content decline and the results of a technique referred to as in situ saturationmetry (Ben-Yaakov and Kaplan, 1971) to define the depth dependence of solubility. While fraught with caveats, these results are broadly consistent with those from the mooring experiment. By measuring the composition of pore waters extracted in situ from sediments at various water depths, Sayles (1985) was able to calculate what he assumed to be saturation CO$_3^{2-}$ concentrations. Finally, several investigators have performed laboratory equilibrations of calcite and seawater as a function of confining pressure. But, as each approach is subject to biases, more research is needed before the exact pressure dependence of the solubility of calcite can be pinned down.

### 6.19.5 DISSOLUTION MECHANISMS

Three possible dissolution processes come to mind. The first of these is termed water column dissolution. As foraminifera shells fall quite rapidly and as they encounter calcite undersaturated water only at great depth, it might be concluded that dissolution during fall is unimportant. But it has been suggested that
organisms feeding on falling debris ingest and partially dissolve calcite entities (Milliman et al., 1999). Because of their small size, coccoliths are presumed to be the most vulnerable in this regard. But little quantitative information is available to permit quantification of this mode of dissolution.

The other two processes involve dissolution of calcite after it reaches the seafloor. A distinction is made between dissolution that occurs before burial (i.e., interface dissolution) and dissolution that takes place after burial (i.e., pore-water dissolution). The former presumably occurs only at water depths greater than that of the saturation horizon. But the latter has been documented to occur above the calcite saturation horizon. It is driven by respiration CO2 released to the pore waters.

Following the suggestion of Emerson and Bender (1981) that the release of respiration CO2 in pore waters likely drives calcite dissolution above the saturation horizon, a number of investigators took the bait and set out to explore this possibility. David Archer, as part of his PhD thesis research with Emerson, developed pH microelectrodes that could be slowly ratcheted into the upper few centimeters of the sediment from a bottom lander. He deployed these pH microelectrodes along with the O2 microelectrodes and was able to show that the release of respiration CO2 (as indicated by a reduction in pore-water O2) was accompanied by a drop in pH (and hence also of CO32- ion concentration). Through modeling the combined results, Archer et al. (1989) showed that much of the CO2 released by respiration reacted with CaCO3 before it had a chance to escape (by molecular diffusion) into the overlying bottom water. As part of his PhD research, Burke Hales, a second Emerson student, improved Archer’s electrode system and made measurements on the Ceara Rise in the western equatorial Atlantic (Hales and Emerson, 1997) and on the Ontong–Java Plateau in the western equatorial Pacific (Hales and Emerson, 1996) (see Figure 6). Taken together, these two studies strongly support the proposal that dissolution in pore waters of sediments leads to substantial dissolution of calcite. This approach has been improved upon by the addition of an LIX electrode to measure CO2 itself and a micro-optode to measure Ca2+ (Wenzhöfer et al., 2001).

In another study designed to confirm that most of the CO2 released into the upper few centimeters of the sediments reacts with CaCO3 before escaping to the overlying bottom water, Martin and Sayles (1996) deployed a very clever device that permitted the in situ collection of closely spaced pore-water samples in the upper few centimeters of the sediment column. Measurements of $\Sigma$CO2 and alkalinity on these pore-water samples revealed that the gradient of $\Sigma$CO2 ($\mu$mol km$^{-1}$) with depth is close to that of alkalinity ($\mu$equiv. kg$^{-1}$). This can only be the case if much of the respiration CO2 reacts with CaCO3 to form a Ca2+ and two HCO3- ions.

Dan McCorkle of Woods Hole Oceanographic Institution conceived of yet another way to confirm that pore-water respiration CO2 was largely neutralized by reaction with CaCO3. As summarized in Figure 7, he made $^{13}$C/$^{12}$C ratio measurements on $\Sigma$CO2 from pore-water profiles and found that the trend of $\delta^{13}$C with

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**Figure 5** Results of in situ dissolution experiments. Peterson (1966) re-weighed polished calcite spheres after a 250 d deployment on a mooring in the North Pacific. Honjo and Erez (1978) observed the weight loss for calcitic samples (coccoliths, foraminifera and reagent calcite) and an aragonitic sample (pteropods) held at depth for a period of 79 d. While Peterson hung his spheres directly in seawater, the Honjo–Erez samples were held in containers through which water was pumped. The results suggest that the calcite saturation horizon lies at 4,800 ± 200 m in the North Atlantic and at about 3,800 ± 200 m in the North Pacific. For aragonite, which is 1.4 times more soluble than calcite, the saturation horizon in the North Atlantic is estimated to be in the range 3,400 ± 200 m.
excess $\Sigma CO_2$ is consistent with a 50–50 mixture of carbon derived from marine organic matter ($-20\%$) and that derived from marine calcite ($+1\%$) (Martin et al., 2000). Again, these results require that a large fraction of the metabolic $CO_2$ reacts with $CaCO_3$.

There is, however, a fly in the ointment. Benthic flux measurements made by deploying chambers...
on the seafloor reveal a curious pattern (see Figure 8). R. A. Jahnke and D. B. Jahnke (2002) found that alkalinity and calcium fluxes from sediments (both high and low in CaCO₃ content) below the calcite saturation horizon and on low-CaCO₃-content sediments from above the saturation horizon yield more or less the expected fluxes. However, chambers deployed on high-CaCO₃-content sediments from above the saturation horizon yield no measurable alkalinity flux. Yet pore-water profiles and electrode measurements for these same sediments suggest that calcite is dissolving. Whole foraminifera shell weight and CaCO₃ size index measurements (see below) agree with conclusion of these authors that calcite dissolution is not taking place. R. A. Jahnke and D. B. Jahnke (2002) propose that impure CaCO₃ coatings formed on the surfaces of calcite grains are redissolved in contact with respiration CO₂-rich pore waters and that the products of this dissolution diffuse back to sediment–water interface. Based on this scenario, the reason that these authors record no calcium or alkalinity flux is that the ingredients for upward diffusion of calcium and alkalinity are being advected downward bound to the surfaces of calcite grains. Hence, there is no net flux of either property into their benthic chamber. Yet pore-water profiles and electrode measurements for these same sediments suggest that calcite is dissolving. Whole foraminifera shell weight and CaCO₃ size index measurements (see below) agree with conclusion of these authors that calcite dissolution is not taking place. R. A. Jahnke and D. B. Jahnke (2002) propose that impure CaCO₃ coatings formed on the surfaces of calcite grains are redissolved in contact with respiration CO₂-rich pore waters and that the products of this dissolution diffuse back to sediment–water interface. Based on this scenario, the reason that these authors record no calcium or alkalinity flux is that the ingredients for upward diffusion of calcium and alkalinity are being advected downward bound to the surfaces of calcite grains. Hence, there is no net flux of either property into their benthic chamber. That such coatings form was demonstrated long ago by Weyl (1965), who showed that when exposed in the laboratory to supersaturated seawater it was the calcite crystal surfaces that achieved saturation equilibrium with seawater rather than vice versa.

Berelson et al. (1994) report chamber-based alkalinity fluxes from high-calcite sediment, the sites at which their studies were performed are very likely bathed in calcite-undersaturated bottom water. If so, coatings would not be expected to form.

One other observation, i.e., core-top radiocarbon ages, appears to be at odds with pore-water dissolution. The problem is as follows. To the extent that respiration CO₂-driven dissolution occurring in the core-top bioturbated zone is homogeneous (i.e., all calcite entities lose the same fraction of their weight in a unit of time), then the core-top radiocarbon age should decrease slowly with increasing extent of dissolution. The reason is that dissolution reduces the time of residence of CaCO₃ entities in the core-top mixed layer, and hence also their apparent ¹⁴C age. But, as shown by Broecker et al. (1999), core-top radiocarbon ages on Ontong–Java Plateau cores from a range of water depths reveal an increase rather than a decrease with water depth (see Figure 10). This increase is likely the result of dissolution that occurs on the seafloor in calcite-undersaturated bottom waters before the calcite is incorporated into the core-top mixed layer. In this case, the reduction of CaCO₃ input to the sediment leads to an increase in the average residence time itself that dissolve. As shown in Figure 9, while on the Ontong–Java Plateau, there is a progressive decrease in shell weight and CaCO₃ size index with water depth; on the Ceara Rise, neither of these indices shows a significant decrease above a water depth of 4,100 m. This is consistent with the conclusion that no significant dissolution occurs at the depth of 3,270 m where the pore-water and chamber measurements were made.

Although Broecker and Clark (2003) fortify the mechanism proposed by R.A. Jahnke and D. B. Jahnke, providing additional evidence by proposing that it must be coatings rather than the biogenic calcite
of calcite in the bioturbated layer. It may be that competition between pore-water dissolution and seafloor dissolution changes with depth. As shown in Figure 3, down to about 3 km pore-water dissolution appears to have the upper hand (and hence the ¹⁴C ages becomes progressively younger with water depth). Below 3 km, the situation switches and seafloor dissolution dominates (hence, the ¹⁴C ages become progressively older with increasing water depth).

6.19.6 DISSOLUTION IN THE PAST

One of the consequences of dissolution of CaCO₃ in pore waters is that it creates an ambiguity in all of the sediment-based methods for reconstructing past carbonate ion distributions in the deep sea. By “sediment-based” methods, one means methods involving some measure of the preservation of the CaCO₃ contained in deep-sea sediments. The ambiguity involves the magnitude of the offset between the bottom-water and the pore-water carbonate ion concentrations. The results obtained using any such methods can be applied to time trends in bottom-water carbonate ion concentration only if the pore-water–bottom-water offset is assumed to have remained nearly constant.

Fortunately, two methods have been proposed for which this ambiguity does not exist. One

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**Figure 9** The upper panel shows shell weight and CaCO₃ size fraction results from core top covering a range of water depth on the Ontong–Java Plateau. The lower panel shows shell weight results from Ceara Rise and CaCO₃ size fraction results from the equatorial Atlantic.
6.19.7 SEDIMENT-BASED PROXIES

A number of schemes have been proposed by which changes in the carbonate ion concentration in the deep sea might be reconstructed. The most obvious of these is the record of the CaCO₃ content of the sediment. Unfortunately, as already discussed, the CaCO₃ content depends on the ratio of the rain rate of CaCO₃ to that of silicate debris as well as on the extent of dissolution of the calcite. Unless quite large, changes in the extent of dissolution cannot be reliably isolated from changes in the composition of the raining debris. Other schemes focus on the state of preservation of the calcite entities. One involves the ratio of dissolution-prone to dissolution-resistant planktonic foraminifera shells (Ruddiman and Heezen, 1967; Berger, 1970). The idea is that the lower this ratio, the greater the extent of dissolution. A variant on this approach is to measure the ratio of foraminifera fragments to whole shells (Peterson and Prell, 1985; Wu and Berger, 1989). The idea behind both approaches is that as dissolution proceeds, the foraminifera shells break into pieces. These methods suffer, however, from two important drawbacks. First, any method involving entity counting is highly labor-intensive. Second, the results depend on the initial makeup of the foraminifera population in the sediment.

Figure 10 ¹⁴C ages (reservoir corrected by 400 yr) as a function of water depth for core-top samples from the Ontong–Java Plateau (Broecker et al., 1999). As can be seen, the ages for cores taken on the equator are systematically younger than those for cores taken a degree or so off the equator. The reason is that the sedimentation rates are twice as high on, than off the equator, while the depth of bioturbation is roughly the same. The onset of the increase in core-top age occurs at a depth of ~3 km. If this onset can be assumed to represent the depth of the saturation horizon (see text), then these results suggest a value ΔV of ~45 cm³ mol⁻¹ for the reaction \( \text{CO}_2^+ + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 \) (calcite). On the other hand, this depth may represent the horizon where interface dissolution just matches pore-water dissolution.

involves measurements of boron isotope ratios in benthic foraminifera (Sanyal et al., 1995) and the other Zn/Cd ratios in benthic foraminifera (Marchitto et al., 2000). Unfortunately, as of early 2003, neither of these methods has received wide enough application to allow its utility to be proven (see below). Until this has been done, we are left with the ambiguity as to whether sediment-based methods reflect mainly changes in bottom-water CO₂⁻⁻⁻ or as proposed by Archer and Maier-Reimer (1994) in the pore-water-bottomwater CO₂⁻⁻⁻ offset.

Despite their drawbacks, these methods have led to several important findings. First, it was clearly demonstrated that during glacial time the mean depth of the transition zone did not differ greatly from today’s. This finding is important because it eliminates one of the hypotheses which have been put forward to explain the lower glacial atmospheric CO₂ content, namely, the coral reef hypothesis (Berger, 1982). According to this idea, shallow-water carbonates (mainly coral and coraline algae) formed during the high-sea stands of periods of interglaciation would be eroded and subsequently dissolved during the low-sea stands of periods of glaciation, alternately reducing and increasing the sea’s CO₂⁻⁻⁻ concentration. But in order for this hypothesis to be viable, the transition zone would have to have been displaced downward by several kilometers during glacial time. Rather, the reconstructions suggest that...
the displacement was no more than a few hundred meters.

Two other findings stand out. First, as shown by Farrell and Prell (1989), at water depths in the 4 km range in the eastern equatorial Pacific, the impact of dissolution was greater during interglacials than during glacials (i.e., the transition zone was deeper during glacial time). Second, fragment-to-whole foraminifera ratios measured on a series of cores from various depths in the Caribbean Sea clearly demonstrate better preservation during glacials than interglacials (Imbrie, 1992). These findings have been confirmed by several investigators using a range of methods. Taken together, these findings gave rise to the conclusion that the difference between the depth of the transition zone in the Atlantic from that in the Pacific was somewhat smaller than now during glacial time. In addition, the existence of a pronounced dissolution event in the Atlantic Ocean at the onset of the last glacial cycle has been documented (Curry and Lohmann, 1986).

6.19.8 SHELL WEIGHTS

An ingenious approach to the reconstruction of the carbonate ion concentration in the deep sea was developed by WHOI’s Pat Lohmann (1995). Instead of focusing on ratios of one entity to another, he developed a way to assess the extent of dissolution experienced by shells of a given species of planktonic foraminifera. He did this by carefully cleaning and sonification of the greater than 63 \( \mu m \) material sieved from a sediment sample. He then picked and weighed 75 whole shells of a given species isolated in a narrow size fraction range (usually 355–420 \( \mu m \)). In so doing, he obtained a measure of the average shell wall thickness. By obtaining shell weights for a given species from core-top samples spanning a range in water depth, Lohmann was able to show that the lower the pressure-normalized carbonate ion concentration, the smaller the whole shell weight (and hence the thinner the shell walls) (see Figure 11).

Lohmann’s method seemingly has the advantage over those used previously in that no assumptions need to be made about the initial composition of the sediment. However, Barker and Elderfield (2002) make a strong case that the thickness of the foraminifera shell walls varies with growth conditions. They did so by weighing shells of temperate foraminifera from core tops from a number of locales in the North Atlantic. They found strong correlations between shell weight and both water temperature and carbonate ion concentration, the warmer the water and the higher its carbonate ion concentration, the thicker the shells. If, as Barker and Elderfield (2002) contend, it is the carbonate ion concentration that drives the change in initial wall thickness, then glacial-age shells should have formed with thicker shells than do their Late Holocene counterparts. Fortunately, the ice-core-based atmospheric CO2 record allows the carbonate ion concentration in the glacial surface waters to be reconstructed and hence presumably also the growth weight of glacial foraminifera. At this point, however, several questions remain unanswered. For example, does the dependence of shell weight on surface water carbonate ion concentration established for temperate species apply to tropical species? Perhaps the shell weight dependence flattens as the high carbonate ion concentrations characteristic of tropical surface waters are approached. Is carbonate ion concentration the only environmental parameter on which initial shell weights depends? As discussed below, there
Table 1 The calcite-saturation carbonate ion concentration in cold seawater and the slope of this solubility as a function of water depth based on a 1 atm solubility of 45 \( \mu \text{mol CO}_2^-/\text{kg} \) and a \( \Delta V \) of 40 cm\(^3\) mol\(^{-1}\).

<table>
<thead>
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<th>Water depth (km)</th>
<th>Calcite sat. (( \mu \text{mol CO}_2^-/\text{kg} ))</th>
<th>Sol. slope (( \mu \text{mol kg}^{-1} \text{ km}^{-1} ))</th>
<th>CO(^2-) versus shell wt. (( \mu \text{mol kg}^{-1} \text{ \mu g}^{-1} ))</th>
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</tr>
<tr>
<td>4.5</td>
<td>100.1</td>
<td>17.9</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Also shown is the slope of the shell-weight loss–carbonate ion concentration relationship for various water depths. The 0.7 \( \mu \text{mol kg}^{-1} \text{ km}^{-1} \) increase in carbonate ion concentration in the Ontong–Java Plateau deep-water column is taken into account.

is reason to believe that the situation is perhaps more complicated.

Lohmann’s method has other drawbacks. Along with all sediment-based approaches, it suffers from an inability to distinguish changes in bottom-water carbonate ion concentration from changes in bottom-water to pore-water concentration offset. Shell thickness may also depend on growth rate and hence nutrient availability. Finally, a bias is likely introduced when dissolution becomes sufficiently intense to cause shell breakup, in which case the shells with the thickest walls are likely to be the last to break up. Nevertheless, Lohmann’s method opens up a realm of new opportunities.

The sensitivity of shell-weight to pressure-normalized carbonate ion concentration (i.e., after correction for the increase in the solubility of calcite with water depth) was explored by determining the weight of Late Holocene shells from various water depths in the western equatorial Atlantic (Ceara Rise) and western equatorial Pacific (Ontong–Java Plateau). This strategy takes advantage of the contrast in carbonate ion concentration between the Atlantic and Pacific deep waters. As shown in Figure 9, shell weights for Ontong–Java Plateau samples do decrease with water depth and hence with decreasing pressure-normalized carbonate ion concentrations (Broecker and Clark, 2001a). However, the surprise is that there is no evidence of either weight loss or shell break at depths less than 4,200 m for Ceara Rise core-top samples. Rather, weight loss and shell breakup is evident only for samples from deeper than 4,200 m. This observation is in agreement with the benthic chamber results of R. A. Jahnke and D. B. Jahnke and hence supports the hypothesis that above the calcite saturation horizon the gradients in pore-water composition are fueled primarily by the dissolution of “Weyl” (1965) coatings rather than of the biogenic calcite itself.

The Ontong–Java results yield a weight loss of \( \sim 8 \mu \text{g} \) for each kilometer increase in water depth. In order to convert this to a dependence on pressure-normalized carbonate ion concentration, it is necessary to take into account the change in in situ carbonate ion concentration in the water column over the Ontong–Java Plateau water column (i.e., \( \text{CO}_2^- = 72 + 3(z - 2) \mu \text{mol kg}^{-1} \)), where \( z \) is the water depth in km) and the pressure dependence of the saturation carbonate ion concentration. The latter depends on the difference in volume between \( \text{Ca}^{2+} \) and \( \text{CO}_3^{2-} \) ions when in solution and when they are bound into calcite. The relationship is as follows:

\[
(\text{CO}_3^{2-})_{z}^2 = (\text{CO}_3^{2-})_{z}^0 e^{\frac{PV}{RT}}
\]

where the units of \( z \) are km, of \( \Delta V \), L mol\(^{-1}\), of \( R \), L atm, and \( T \), K. If \( \Delta V \) is re-expressed as cm\(^3\) mol\(^{-1}\), the relationship becomes

\[
(\text{CO}_3^{2-})_{z}^2 = (\text{CO}_3^{2-})_{z}^0 e^{\frac{z PV}{225}}
\]

where \( \Delta V \) is the volume of the ions when bound into calcite minus that when they are dissolved in seawater. \( (\text{CO}_3^{2-})^0 \) is 45 mol kg\(^{-1}\) and while the exact value of \( \Delta V \) remains uncertain, 40 cm\(^3\) mol\(^{-1}\) fits most ocean observations (Peterson, 1966; Honjo and Erez, 1978; Ben-Yaakov and Kaplan, 1971; Ben-Yaakov et al., 1974). Listed in Table 1 are the saturation concentrations based on this \( \Delta V \) and the slope of the solubility as a function of water depth. Also given are estimates of the weight loss for foraminifera shells per unit decrease in carbonate ion concentration.

6.19.9 THE BORON ISOTOPE PALEO pH METHOD

Theoretical calculations by Kakinaka et al. (1977) suggested that the uncharged species of dissolved borate (\( \text{B(OH)}_3^- \)) should have a 21 per mil higher \(^{11}\text{B}/^{10}\text{B} \) ratio than that for the charged species (\( \text{B(OH)}_4^- \)). Hemming and Hanson (1992) demonstrated that this offset might be harnessed as a paleo pH proxy. Their reasoning was as follows. As the residence time of borate in seawater is tens of millions of years, on the
timescale of glacial cycles the isotope composition of oceanic borate could not have changed. They further reasoned that it must be the charged borate species that is incorporated into marine CaCO₃ and hence marine calcite should have an isotope composition close to that of the charged species in seawater. This is important because as shown in Figure 12 the isotopic composition of the charged species must depend on the pH of the seawater. The higher the pH, the larger the fraction of the borate in the charged form and hence the closer its isotopic composition will be to that for bulk seawater borate. In contrast, for pH values the isotopic composition of the residual amount of charged borate must approach a value 21 per mil lower than that for bulk seawater borate. Working with a graduate student, Abhijit Sanyal, Hemming applied his method to foraminifera shells and demonstrated that indeed foraminifera shells record pH (Sanyal et al., 1995). Benthic foraminifera had the expected offset from planktonics. Glacial age G. sacculifer, as dictated by the lower glacial atmospheric CO₂ content, recorded a pH about 0.15 units higher than that for Holocene shells. Sanyal went on to grow planktonic foraminifera shells at a range of pH values (Sanyal et al., 1996, 2001). He also precipitated inorganic CaCO₃ at a range of pH values (Sanyal et al., 2000). These results yielded the expected pH dependence of boron isotope composition. However, they also revealed sizable species-to-species offsets (as do the carbon and oxygen isotopic compositions).

The waterloo of this method came when glacial-age benthic foraminifera were analyzed. The results suggested that the pH of the glacial deep ocean was 0.3 units greater than today (Sanyal et al., 1995). This corresponds to a whopping 90 μmol kg⁻¹ increase in carbonate ion concentration. The result was exciting because, if correct, the lowering of the CO₂ content of the glacial atmosphere would be explained by a whole ocean carbonate ion concentration change. But this result was clearly at odds with reconstructions of the depth of the glacial transition zone. Such a large increase in deep-water carbonate ion concentration would require that it deepened by several kilometers. Clearly, it did not. Archer and Maier-Reimer (1994) proposed a means by which this apparent disagreement might be explained. They postulated that if during glacial time the release of metabolic CO₂ to sediment pore waters (relative to the input of CaCO₃) was larger than today’s, this would have caused a shoaling of the transition zone and thereby thrown the ocean’s CaCO₃ budget out of kilter. Far too little CaCO₃ would have been buried relative to the ingredient input. The result would be a steady increase in the ocean’s carbonate ion inventory (see Figure 13) and a consequent progressive deepening of the transition zone. This deepening would have continued until a balance between input and loss was once again achieved. In so doing, a several kilometer offset between the depth of the saturation horizon and the depth of the transition zone would have been created. However, this explanation raised three problems so serious that the boron isotope-based deep-water pH change has fallen into disrepute. First, it required that the change in glacial ecology responsible for the increase in the rain of organic matter be globally uniform. Otherwise, there would have been very large "wrinkles" in the depth of the glacial transition zone. No such wrinkles have been documented. Second, at the close of each glacial period when the flux of excess organic matter was shut down, there must have been a prominent global preservation event. In order to restore the saturation horizon to its interglacial position, an excess over ambient CaCO₃ accumulation of ~3 g cm⁻² would have to have occurred over the entire seafloor. It would be surprising if some residue from this layer were not to be found in sediments lining the abyssal plains. It has not. These sediments have no more than 0.2% by weight CaCO₃. In other words, of the 3 g cm⁻² deposited during the course of the carbonate ion drawdown,
almost nothing remains. Finally, based on model simulations, Sigman et al. (1998) have shown that it is not possible to maintain for tens of thousands of years a several-kilometer separation between the saturation horizon and the transition zone. This “waterloo” was unfortunate for the author considers the boron method to be basically sound and potentially extremely powerful. The answer to the benthic enigma may lie in species-to-species differences in the boron isotope “vital” effect for benthic foraminifera. The measurement method use by Sanyal et al. (1996) required a large number of benthic shells in order to get enough boron to analyze. This created a problem because, as benthics are rare among foraminifera shells, mixed benthics rather than a single species were analyzed. If the boron isotope pH proxy is to become an aid to deep-ocean studies, then techniques requiring smaller amounts of boron will have to be created. There also appears to be a problem associated with variable isotopic fractionation of boron during thermal ionization. As this fractionation depends on the ribbon temperature and perhaps other factors, it may introduce biases in the results for any particular sample. Hopefully, a more reproducible means of ionizing boron will be found.

6.19.10 Zn/Cd RATIOS

The other bottom-water $\text{CO}_3^{2-}$ ion concentration proxy is based on the Zn/Cd ratio in benthic foraminifera shells. As shown by Marchitto et al. (2000), the distribution coefficient of zinc between shell and seawater depends on $\text{CO}_3^{2-}$ ion

Figure 13 Shown on the left is the sequence of events envisioned by Archer and Maier-Reimer (1994) for the transition from interglacial (I) to glacial (G) conditions. An increase in respiration CO$_2$ release to the sediment pore waters enhances calcite dissolution, thereby unbalancing the CaCO$_3$ budget. This imbalance leads to a buildup in CO$_3^{2-}$ ion concentration in the deep sea until it compensates for the extra respiration CO$_2$. On the right is the sequence of events envisioned for the transition from G to I conditions. The input of excess respiration CO$_2$ to the sediments ceases, thereby reducing the rate of calcite dissolution. This leads to an excess accumulation of CaCO$_3$ on the seafloor and hence to a reduction in carbonate ion concentration which continues until steady state is reestablished.
concentration, such that the lower the carbonate ion concentration, the larger the Zn/Cd ratio in the foraminifera shell. Assuming that the Zn/Cd ratio in seawater was the same during the past as it is today, the ratio of these two trace elements should serve as a paleo carbonate ion proxy. However, there are problems to be overcome. For example, in today’s ocean, zinc correlates with silica and cadmium with phosphorus. As silica is 10-fold enriched in deep Pacific water relative to deep Atlantic water while phosphorus is only twofold enriched, differential redistribution of silica and phosphorus in the glacial ocean poses a potential bias. However, as at high carbonate supersaturation the distribution coefficient for zinc flattens out, it may be possible to use measurements on benthic foraminifera from sediments bathed in highly supersaturated waters to sort this out. But, as is the case for the boron isotope proxy, much research will be required before reconstructions based on Zn/Cd ratios can be taken at face value.

6.19.11 DISSOLUTION AND PRESERVATION EVENTS

There are several mechanisms that might lead to carbonate ion concentration transients at the beginning and end of glacial periods. One such instigator is changes in terrestrial biomass. Shackleton (1997) was the first to suggest that the mass of carbon stored as terrestrial biomass was smaller during glacial than during interglacial periods. He reached this conclusion based on the fact that measurements on glacial-age benthic foraminifera yielded lower $\delta^{13}C$ values than those for their interglacial counterparts. Subsequent studies confirmed that this was indeed the case and when benthic foraminifera $^{13}C$ results were averaged over the entire deep sea, it was found that the ocean’s dissolved inorganic carbon had a $^{13}C/^{12}C$ ratio 0.35 ± 0.10 per mil lower during glacial time than during the Holocene (Curry et al., 1988). If this decrease is attributed to a lower inventory of wood and humus, then the magnitude of the glacial biomass decrease would have been 500±150 Gt of carbon. The destruction of this amount of organic material at the onset of a glacial period would create a 20 $\mu$mol kg$^{-1}$ drop in the ocean’s CO$_3^{2-}$ concentration and hence produce a calcite dissolution event. Correspondingly, the removal of this amount of CO$_2$ from the ocean–atmosphere reservoir at the onset of an interglacial period would raise the carbonate ion concentration by 20 $\mu$mol kg$^{-1}$ and hence produce a calcite preservation event. This assumes that the time over which the biomass increase occurred was short compared to the CO$_3^{2-}$ response (i.e., ~5,000 yr). If this is not the case, then the magnitude of the carbonate ion changes would be correspondingly smaller.

Another possible instigator of such transients was proposed by Archer and Maier-Reimer (1994). Their goal was to create a scenario by which the lower CO$_2$ content of the glacial atmosphere might be explained. As already mentioned, it involved a higher ratio of organic carbon to CaCO$_3$ carbon in the material raining to the deep-sea floor during glacial times than during interglacial times, and hence an intensification of pore-water dissolution. As in the case for the terrestrial biomass change, such an increase would have thrown the ocean’s carbon budget temporarily out of kilter. The imbalance would have been remedied by a buildup of carbonate ion concentration at the onset of glacials and a drawdown of carbonate ion concentration at the onset of interglacials (see Figure 14). Hence, it would also lead to a dissolution event at the onset of glacial episodes and a preservation event at the onset of interglacial episodes. Were the changes in organic to CaCO$_3$ rain proposed by Archer and Maier-Reimer to have explained the entire glacial to interglacial CO$_2$ change, then the magnitude of the transients would have been ~4 times larger than that resulting from 500 Gt C changes in terrestrial biomass.

Regardless of their origin, these dissolution events and preservation events would be short-lived. As they would disrupt the balance between

![Figure 14](idealized_scenario_for_carbonate_ion_concentration_changes_associated_with_dissolution_and_preservation_events)
burial and supply, they would be compensated by either decreased or increased burial of CaCO3 and the balance would be restored with a constant time of ~5,000 yr (see Figure 14).

Clear evidence for the compensation for an early Holocene preservation event is seen in shell weight results from a core from 4.04 km depth on the Ontong–Java Plateau in the western equatorial Pacific (see Figure 15). A drop in the weight of _P. obliquiloculata_ shells of 11 mg between about 7,500 yr ago and the core-top bioturbated zone (average age 4,000 yr) requires a decrease in carbonate ion concentration between 7,500 yr ago and today (see Table 1). This Late Holocene CO$_3^{2-}$ ion concentration drop is characterized by an up-water column decrease in magnitude becoming imperceptible at 2.31 km. It is interesting to note that during the peak of the preservation event, the shell weights showed only a small decrease with water depth (see Figure 15), suggesting either that the pressure effect on calcite solubility was largely compensated by an increase with depth in the _in situ_ carbonate ion concentration or that the entire water column was supersaturated with respect to calcite.

In the equatorial Atlantic only in the deepest core (i.e., that from 5.20 km) is the Late Holocene intensification of dissolution strongly imprinted.

![Figure 15](image-url)
As in this core no whole shells are preserved, the evidence for an Early Holocene preservation event is based on CaCO₃ size-index and CaCO₃ content measurements. As can be seen in Figure 15, both show a dramatic decrease starting about 7,500 yr ago. As for the Pacific, the magnitude of the imprint decreases up-water column, becoming imperceptible at 3.35 km.

If either the biomass or the respiration CO₂ mechanisms are called upon, the magnitude of the Early Holocene CO₂ maximum must have been uniform throughout the deep ocean. The most straightforward explanation for the up-water column reduction in the magnitude of the preservation event is that at mid-depths; the sediment pore waters are presently close to saturation with respect to calcite. Hence, the Early Holocene maximum in deep-sea CO₂ ion concentration pushed them into the realm of supersaturation. If so, there is no need to call on a depth dependence for the magnitude of the preservation event.

The post-8,000-year-ago decrease in CO₂ ion concentration of 23 μmol kg⁻¹ required to explain the Late Holocene 11 μg decrease in P. obliquiloculata shell weights observed in the deepest Ontong–Java Plateau core is twice too large to be consistent with the 20 ppm increase in atmospheric CO₂ content over this time interval (İndermühle et al., 1999). The significance of this remains unknown.

In the equatorial Atlantic CaCO₃ content, CaCO₃ size-index and shell-weight measurements reveal three major dissolution events, one during marine isotope stage 5d, one during 5b and one during stage 4 (see Figures 16(a) and (b)). As these events are only weakly imprinted on Pacific sediments, it appears that a major fraction of the carbonate ion reduction was the result of enhanced penetration into the deep Atlantic of low carbonate ion concentration Southern Ocean water. If this conclusion proves to be correct, then it suggests that the balance between the density of deep waters formed in the northern Atlantic and those formed in the Southern Ocean is modulated by the strength of northern hemisphere summer insolation (i.e., by Milankovitch cycles).

### 6.19.12 GLACIAL TO INTERGLACIAL CARBONATE ION CHANGE

In addition to the preservation and dissolution event transients, there were likely carbonate ion concentration changes that persisted during the entire glacial period. These changes could be placed in two categories. One involves a change in the average CO₂ concentration of the entire deep sea necessary to compensate for a change in the ratio of calcite production by marine organisms to ingredient supply. The other involves a redistribution of carbonate ion within the deep sea due to a redistribution of phosphate (and hence also of respiration CO₂) and/or to a change in the magnitude of the flux of CO₂ through the atmosphere from the Southern Ocean to the northern Atlantic.

Based on shell-weight measurements, Broecker and Clark (2001c) attempted to reconstruct the depth distribution of carbonate ion concentration during late glacial time for the deep equatorial Atlantic Ocean and Pacific Ocean. At the time their paper was published, these authors were unaware of the dependence of initial shell weight on carbonate ion concentration in surface water established by Barker and Elderfield (2002) for temperate species. Since during the peak glacial time the atmosphere’s pCO₂ was ~80 ppm lower than during the Late Holocene, the carbonate ion concentration in tropical surface waters must have been 40–50 μmol kg⁻¹ higher at that time. Based on the Barker and Elderfield (2002) trend of ~1 μg increase in shell weight per 9 μmol kg⁻¹ increase in carbonate ion concentration, this translates to an 8 μg heavier initial shell weights during glacial time. Figure 17 shows, while this correction does not change the depth dependence or interocean concentration difference, it does greatly alter the magnitude of the change. In fact, were the correction made, it would require that the carbonate ion concentration in virtually the entire glacial deep ocean was lower during glacial time than during interglacial time. For the deep Pacific Ocean and the Indian Ocean, this flies in the face of all previous studies which conclude that dissolution was less intense during periods of glaciation than during periods of interglaciation. However, as the Broecker and Clark study concentrates on the Late Holocene while earlier studies concentrate on previous periods of interglaciation, it is possible that the full extent of the interglacial decrease in carbonate ion during the present interglacial has not yet been achieved. Of course, it is also possible that significant thickening of foraminifera shells during glacial time did not occur. Until this matter can be cleared up, reconstruction of glacial-age deep-sea carbonate ion concentrations must remain on hold.

### 6.19.13 NEUTRALIZATION OF FOSSIL FUEL CO₂

The ultimate fate of much of the CO₂ released to the atmosphere through the burning of coal, oil, and natural gas will be to react with the CaCO₃ stored in marine sediments (Broecker and Takahashi, 1977; Sundquist, 1990; Archer et al., 1997). The amount of CaCO₃ available for dissolution at any given place on the seafloor depends on the calcite content in the sediment.
Figure 16  (A) CaCO₃, size index and shell weight results for a portion of jumbo pistoncore EW92-9-2 (a) and EW92-9-3 (b) from the northern flank of the Ceara Rise. The results in (a) document dissolution events A (stage 4) and B (stage 5b). (B) The results in (b) document dissolution events B (stage 5b) and C (stage 5d). The δ¹⁸O and δ¹³C records for benthic foraminifera are from Curry (1996). The x's represent samples in which only 15–30 whole shells were found.
and the depth to which sediments are stirred by organisms. The former is now well mapped and the latter has been documented in many places by radiocarbon measurements. The amount of CaCO₃ available for dissolution at any given site is given by

$$\sum \text{CaCO}_3 = \frac{h \rho f_c}{1 - f_c}$$

where $h$ is the depth of bioturbation, $\rho$ is the water-free sediment density, and $f_c$ is the weight-fraction calcite. The high-CaCO₃ sediments that drape the oceans’ ridges and plateaus typically have, 90% CaCO₃ and a water-free density of 1 g cm⁻³. The bioturbation depth in these sediments averages 8 cm. Hence, the upper limit on the amount of CaCO₃ available for dissolution in such a sediment is 72 g cm⁻². As roughly one quarter of the seafloor is covered with calcite-rich sediments, this corresponds to $\sim 6.3 \times 10^{19}$ g CaCO₃ (i.e., 7.560 Gt C). This amount could neutralize $6.3 \times 10^{17}$ mol of fossil fuel CO₂. This amount exceeds the combined oceanic inventory of dissolved CO₂$^-$ (1.6 $\times$ 10$^{17}$ mol) and of dissolved HBO₂⁻ (0.8 $\times$ 10$^{17}$ mol). It is comparable to the amount of recoverable fossil fuel carbon.

I say ‘upper limit’ because once this amount of CaCO₃ has been dissolved, the upper 8 cm of the sediment would consist entirely of a noncarbonate residue. As molecular diffusion through such a thick residue would be extremely slow, the rate of dissolution of CaCO₃ stored beneath this CaCO₃-free cap would be minuscule, and further neutralization would be confined to the fall to the seafloor of newly formed CaCO₃.

The rate of this dissolution of the CaCO₃ stored in the uppermost sediment will depend not only on the magnitude of the reduction of the deep ocean’s CO₂$^-$ content, but also on the rate at which the insoluble residue is stirred into the sediment. This bioturbation not only homogenizes the mixed layer, but is also exhumes CaCO₃ from beneath the mixed layer.

REFERENCES


