Is the magnitude of the carbonate ion decrease in the abyssal ocean over the last 8 kyr consistent with the 20 ppm rise in atmospheric CO$_2$ content?

Wallace Broecker$^1$ and Elizabeth Clark$^1$

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[1] Changes in the extent of shell fragmentation, the wall thicknesses of foraminifera shells, and the bulk CaCO$_3$ content of deep Pacific sediments demonstrate that the extent of dissolution has steadily increased during the past 8 kyr. On the basis of measurements on sediment core top material from a range of water depths on the Ontong-Java Plateau, these dissolution proxies have been calibrated, allowing the extent of the decrease in carbonate ion concentration to be quantified. The results suggest that the decrease was larger than that of 6 μmol/km expected to accompany the 20 μatm rise in atmospheric CO$_2$ content that occurred during this time interval. However, the inconsistency between the magnitude of the change based on the decrease in shell weight on one hand and that based on the increase in fragmentation on the other hand is problematic. If indeed the drop in carbonate ion concentration has been larger than expected, then 8 kyr ago either a change in the pattern of thermohaline circulation or in the strength of the biological pump must have kicked in and become ever stronger as the millennia passed. If thermohaline circulation is the villain, then a possible explanation is that the strength of deepwater formation in the northern Atlantic has weakened relative to that in the Southern Ocean.

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1. Introduction

[2] On the basis of a comparison of the rain rate of CaCO$_3$ (as measured in sediment traps) with the CaCO$_3$ dissolution flux (as measured in flux chambers), Berelson et al. [1997] concluded that little, if any, of the CaCO$_3$ currently raining to the equatorial Pacific seafloor between 5°N and 5°S at 140°W is accumulating. Furthermore, as the accumulation rate of CaCO$_3$ was much higher early in the Holocene, these authors concluded that a decrease in carbonate ion concentration had occurred. They estimated the magnitude of this decrease to be 10 to 15 μmol/kg. A similar conclusion had been reached earlier by Keir and Berger [1985] based on radiocarbon measurements. Our measurements of the extent of dissolution of the CaCO$_3$ in deep-sea sediments confirm that a Holocene decline in the carbonate ion concentration in abyssal waters has occurred [Broecker et al., 1999, 2001]. In sediment cores from both the equatorial Atlantic and the equatorial Pacific, observations of the extent of dissolution show that this decline began about 8000 years ago and has continued right up to the present. While the timing of this decline suggests that it is tied to the 20 μatm rise in atmospheric CO$_2$ content which occurred during the same time interval, there is a suggestion that the magnitude of the carbonate ion decline was larger than the 6 μmol/kg expected to match the 20 ppm atmospheric CO$_2$ rise (see Figure 1). In this paper we attempt to evaluate whether the drop in carbonate ion concentration in the abyssal ocean has indeed been larger than expected and, if so, what might account for it.

2. Dissolution Indices

[3] We employ three measures of the extent to which CaCO$_3$ dissolution has increased over the last 8 kyr, the CaCO$_3$ content of the sediment, the fraction of CaCO$_3$ in entities with sizes greater than 63 microns [Broecker and Clark, 1999] and the mean weight of whole foraminifera shells of a given species in a fixed size range [Lohmann, 1995; Broecker and Clark, 2001]. As outlined below, all three of these methods have been calibrated based on measurements on core top material from a range of water depths on the Ontong-Java Plateau.

[4] Two complications prevent the precise establishment of the absolute degree of calcite saturation at any given water depth. The first has to do with the offset between the carbonate ion concentration in sediment pore waters and that in bottom water [Archer et al., 1989]. This offset is maintained by the release of respiration CO$_2$ to the upper sediment. While the existence of this offset is well documented, too few measurements have been made to allow its systematics to be understood. Further, for sediments rich in CaCO$_3$, a serious disagreement exists between the results based on in situ electrode measurements and those based on flux chamber measurements [Jahnke and Jahnke, 2004]. One explanation which has been put forward is that “pseudo dissolution” is biasing the electrode results [Broecker and Clark, 2003; Jahnke and Jahnke, 2004].
The other complication has to do with the uncertainty in the pressure dependence of the solubility of calcite in seawater. To date the solubility has been convincingly determined only at one atmosphere pressure [Mucci, 1983]. Only two laboratory-based estimates of \( \Delta V \) (the volume difference between \( \text{Ca}^{++} \) and \( \text{CO}_3^- \) bound in calcite and the volume these ions occupy when dissolved in seawater) have been made. Culberson and Pytkowicz [1968] obtained 36.4 cm\(^3\)/mol and Ingle [1975], 43.6 cm\(^3\)/mol (both at 2\(^\circ\)C). As shown in Figure 2, because of the uncertainty in the magnitude of \( \Delta V \), both the absolute value of the calcite saturation carbonate ion concentration in the deep sea and its slope with water depth have sizable uncertainties.

Peterson [1966] reported the results of the weight loss experienced by calcite spheres suspended for several months from a mooring deployed 1100 km south of Hawaii. Although little loss occurred for the spheres deployed in waters shallower than 3.4 km, below this depth a steadily increasing weight loss was observed. As can be seen in Figure 3, the scatter in the in situ carbonate ion concentrations as measured by Geochemical Ocean Sections Study (GEOSECS) and by World Ocean Circulation Experiment (WOCE) in the area where Peterson [1966] conducted a dissolution experiment involving calcite spheres deployed on a deep-sea mooring (18.8\(^\circ\)N, 168.5\(^\circ\)W). Peterson found that whereas above 3.4 km little weight loss occurred, below 3.4 km the extent of weight lost increased with depth. Superimposed on this diagram are calcite saturation curves calculated assuming \( \Delta V \) values of 35, 40, and 45 cm\(^3\)/mol.

In the absence of a definitive determination of the magnitude of this volume difference, we adopt a provisional value of 40 cc per mol for \( \Delta V \). However, we admit that
the actual value could be as low as 35 or as high as 45 cc per mol.

3. Calibration of Dissolution Indices

8 For cores from the Ontong-Java Plateau, CaCO$_3$ contents, size indices, and shell weights have been determined on core top samples ranging in water depth from 2.3 to 4.5 km. By size index we mean the ratio of the weight of CaCO$_3$ in entities larger than 63 microns to the total weight of CaCO$_3$ in the sediment sample [Broecker and Clark, 1999]. As shown in Figure 4, the value of this index in core top samples decreases linearly with water depth. The explanation for this decrease is that, as the extent of dissolution increases, foraminifera shells break up into fragments small enough to pass through a 63-micron sieve. The observed rate of decrease in size index is 20% per kilometer water depth (see Figure 4). In sediments which have experienced little or no dissolution, 55 ± 5% of the CaCO$_3$ is in foraminifera shells greater than 63 microns in size. The remainder resides in either coccoliths or juvenile foraminifera shells. While coccoliths likely dominate the fine CaCO$_3$, the only quantitative estimate we know of is that by Ramaswamy and Gaye [2006]. On the basis of sediment trap material from six Indian Ocean sites, they found that the ratio of coccolith CaCO$_3$ to foraminifera CaCO$_3$ ranged from 1.25 to 0.45. Our ratio of 0.82 (i.e., 0.45/0.55) for fine to coarse CaCO$_3$ falls within this range.

9 Assuming a calcite solubility slope of 17.2 μmol/kg per kilometer water depth (i.e., at 4 km for ΔV of 40 cm$^3$/mol) and an increase of 5 μmol/kg in carbonate ion concentration per kilometer water depth (see Figure 5), we obtain slope of 12.2 μmol/kg per kilometer water depth for the difference between the in situ and the calcite solubility CO$_3^−$ ion concentrations. This converts to a 0.61 μmol/kg increase in CO$_3^−$ undersaturation per percent decrease in the size index.

10 Shell weights are obtained by averaging the weights of 50 whole shells of a single planktic species hand-picked from a narrow-size range [Lohmann, 1995; Broecker and Clark, 2001]. For core top samples from the Ontong-Java Plateau, we find that the average weights of both G. sacculifer and P. obliquiloculata shells in the 355 to 420 μm size range decrease by 8 μg per kilometer water depth (see Figure 6). Using a 12.2 μmol/kg per kilometer water depth increase in the difference between the calcite solubility carbonate ion

Figure 4. Size index versus water depth for core top samples from the Ontong-Java Plateau [Broecker and Clark, 1999].

Figure 5. Carbonate ion concentration as a function of water depth in the deep western equatorial Pacific (4°N to 4°S, 150° to 170°E) as determined as part of the WOCE survey. This plot was provided by S. Sutherland of Lamont-Doherty Earth Observatory (LDEO).

Figure 6. Shell weights for two planktic species, G. sacculifer and P. obliquiloculata as a function of water depth for core top samples from the Ontong-Java Plateau [Broecker and Clark, 2001].
concentration and the in situ carbonate ion concentration, this converts to a 1.53 \text{\mu mol/kg} increase in the extent of calcite undersaturation per \mu g weight loss.

[11] Following the same approach used for the size index and shell weight indices, the CaCO$_3$ content dependence on the saturation state of calcite can be calibrated. A plot of percent CaCO$_3$ versus water depth is shown in Figure 7 top. As can be seen, this relationship is not only noisy but also has a strong curvature. An improved way to look at these data is to instead plot the rate of CaCO$_3$ loss against water depth because of dissolution. In order to do this, we assume that the rain rates onto the Ontong-Java Plateau of both CaCO$_3$ and “clay” are uniform along the equator. We reference the CaCO$_3$ loss to the core at a depth of 2.31 km. The CaCO$_3$ losses, \( L \), are calculated from the relationship

\[
L_{\text{CaCO}_3} = 2.58 - \frac{f_{\text{CaCO}_3}}{K_{\text{CaCO}_3}} \times 0.42 \text{ g/cm}^2 \text{ kyr}
\]

Where 2.58 and 0.42 are respectively the rain rates of CaCO$_3$ and “clay” and \( f_{\text{CaCO}_3} \) is the fraction of CaCO$_3$ in the core top sediment. In this case, deeper than 3.4 km there is a linear increase in the rate at which CaCO$_3$ is lost to dissolution. The slope is 1.4 \text{ g/cm}^2 \text{ kyr} per km. Using a 12.2 \text{ \mu mol/kg} per kilometer water depth increase in the difference between calcite solubility concentration and in situ carbonate concentration, this converts to an 8.7 \text{ \mu mol/kg} drop in carbonate ion concentration per g/cm$^2$ kyr loss of CaCO$_3$ due to dissolution.

[12] These calibrations are subject to sizable uncertainties. The uncertainty of \( \Delta V \) gives rise to a ±3 \text{ \mu mol/kg/km} uncertainty in the slope of the solubility at 4 km water depth (see Table 1). Further, if a depth of 3 km rather than 4 km were chosen, the slope of the \( \Delta V = 40 \text{ cm}^3/\text{mol} \text{ solubility curve} \) drops from 17.2 to 13.6 \text{ \mu mol/kg per km}. After subtraction of the 5 \text{ \mu mol/kg per km} increase in CO$_3$ with water depth, the effective slope drops from 12.2 to 8.6 \text{ \mu mol CO}_3^2 per kilometer (see Table 1). The reason for this ambiguity is that, whereas the calibration curves would be expected to

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**Table 1.** Dependence of Index Calibrations on the Choice of \( \Delta V \) and on Whether the Solubility Slope at 3 km or at 4 km Is Used$^a$

<table>
<thead>
<tr>
<th>( \Delta V )</th>
<th>35</th>
<th>40</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>At 3 km</td>
<td>At 4 km</td>
<td>At 3 km</td>
<td>At 4 km</td>
</tr>
<tr>
<td>Calcite solubility slope</td>
<td>10.8</td>
<td>13.2</td>
<td>13.6</td>
</tr>
<tr>
<td>Saturation slope$^b$</td>
<td>5.8</td>
<td>8.2</td>
<td>8.6</td>
</tr>
<tr>
<td>Size index calibration</td>
<td>0.29</td>
<td>0.41</td>
<td>0.44</td>
</tr>
<tr>
<td>( \Delta ) Size index</td>
<td>13.0</td>
<td>13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>Size fraction ( \Delta \text{CO}_3^2 )</td>
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<td>13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>Shell weight coefficient</td>
<td>0.73</td>
<td>1.02</td>
<td>1.10</td>
</tr>
<tr>
<td>( \Delta ) Shell weight</td>
<td>13.0</td>
<td>13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>Shell weight ( \Delta \text{CO}_3^2 )</td>
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<td>13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>CaCO$_3$ loss calibration</td>
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<td>5.9</td>
<td>6.3</td>
</tr>
<tr>
<td>( \Delta \text{CaCO}_3 ) loss</td>
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<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>CaCO$_3$ ( \Delta \text{CO}_3^2 )</td>
<td>0.73</td>
<td>1.02</td>
<td>1.10</td>
</tr>
</tbody>
</table>

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$^a$\( \Delta V \) is given in \text{cm}^3 \text{ mol}^{-1}.

$^b$The 5 \text{ \mu mol kg}^{-1} \text{ km}^{-1} increase in in situ carbonate ion concentration in the Ontong-Java water column is taken into account.

$^c$Change in carbonate ion concentration between 8 kyr preservation maximum and core top based on the 13% drop in the >63 micron fraction recorded in the core from 4.04 km water depth.

$^d$Change in carbonate ion concentration between the 8 kyr preservation maximum and the core top based on the 13 \mu g drop in the weight of *P. obliquiloculata* whole shells in the 4.04 km depth core.

$^e$Change in carbonate ion concentration between the 8 kyr preservation maximum and the core top based on the 10 g cm$^{-2}$ kyr$^{-1}$ increase in CaCO$_3$ dissolution rate at the 4.04 km depth core.
steepen with water depth in concert with the steepening of the slope of the calcite solubility (see Figure 2), as can be seen in Figures 4 and 6, neither the size index nor shell weight versus water depth plot shows a significant curvature.

4. Down-Core Measurements: Ontong-Java Plateau

In Figure 8 the down-core size index, shell weight and CaCO$_3$ content results for four cores spanning the water depth range 2.31 to 4.04 km on the Ontong-Java Plateau are summarized. As can be seen, the core at 4.04 km shows a large decrease in all three indices over the last 8 or so $^{14}$C kyr. By contrast, for the core at 2.31 km depth, none of these three properties undergoes a significant change during this time period. The obvious explanation is that, at the depth of the shallow core, both bottom water and pore water have remained supersaturated with respect to calcite for the last 8 kyr. Further, the constancy suggests that the initial values of these indices remained unchanged during the last 8 kyr. By contrast, the core at 4.04 km appears to have been bathed in waters undersaturated with respect to calcite during this entire 8 kyr time interval. The post preservation maximum drop in size index at 4.04 km is 13 ± 3% (i.e., from 36 ± 2 to 23 ± 2). The drop in the weight of $P.\text{ obliquiloculata}$ whole shells is 13 ± 2 (i.e., from 40 ± 1 to 27 ± 1) $\mu$g. Because too few whole $G.\text{ sacculifer}$ shells are present in the core top sample, only a minimum weight loss (5 ± 1 $\mu$g) can be given. Over the last 8000 years, the CaCO$_3$ content of the core from a depth of 4.04 kilometers drops from 85 to 76% (i.e., by 9%).

Figure 8. Compilation of size index, shell weight, and CaCO$_3$ content results for the Holocene interval in four box cores taken on the equator at four water depths ranging from 2.3 to 4.04 km on the Ontong-Java Plateau in the western Pacific Ocean. The samples were provided by D. McCorkle of Woods Hole Oceanographic Institution.
Taro Takahashi determined for us what would be the change in the deep ocean in situ carbonate ion concentration were cold surface waters to have increased their CO$_2$ partial pressure from 260 to 280 atm. He obtained an increase in total dissolved inorganic carbon in cold surface water of 11.4 µmol/kg. He then added this amount of extra CO$_2$ to deep Pacific water and found that the in situ carbonate ion concentration decreased by 5.7 µmol/kg. This is a bit smaller than the drop of 6.5 µmol/kg obtained by Broecker and Peng [1989].

As can be seen from Table 1, the $\Delta$CO$_3^-$ estimates based a $\Delta$V of 35 to 40 cm$^3$ per mole for the size fraction decrease and for the CaCO$_3$ dissolution loss broadly match this prediction. Those based on shell weight loss are far larger.

We find it difficult to explain the large difference between the results based on the shell weight method on one hand and those by the size fraction method on the other. Stephen Barker, while a post doctoral fellow at Lamont-Doherty, made radiocarbon measurements on whole shells and shell fragments from the top of Ontong-Java core BC74 from a water depth of 4.4 km [Barker et al., 2007]. The age of whole *P. obliquiloculata* shells was 4180 years while fragments of this species dated at 5295 years. The age of whole *G. tumida* shells was 3375 years and the fragments of this species dated at 5750 years. The fragment-whole shell age differences were in the expected sense for the fragment CaCO$_3$ must reside in the bioturbated zone longer than the unbroken shell CaCO$_3$. As discussed below, the fact that the radiocarbon ages of CaCO$_3$ entities in the bioturbated zone are measured in thousands of years, it means that the full reduction in carbonate ion content of the waters bathing the sediment is not recorded. Further, the dissolution lag caused in this way is larger for fragments than for whole foraminifera. Thus we have a clue as to why the estimates based on shell weight are larger than those based on size index.

5. Down-Core Measurements: Abyssal Atlantic

Depicted in Figure 9 are the results of measurement made of two cores from 5200 m depth on the floor of a fracture zone cut through the Mid Atlantic Ridge at 11$^\circ$N. In each, there is a CaCO$_3$ preservation maximum centered at about 8 14C kyr. Following this maximum, the CaCO$_3$ content in both cores drops from about 52% to about 27% [Broecker et al., 1999]. A corresponding drop of the size fraction index from about 25 to about 5% occurs in both cores. This decrease is about half as large as that found for the core from 4.04 km on the Ontong Java Plateau. As shown by Broecker and Clark [1999], the slope of the size fraction versus $\Delta$CO$_3^-$ relationship appears to be the same throughout the tropical ocean. Adopting the 0.6 µmol/kg decrease in CO$_3^-$ per percent decrease in size fraction established in the western equatorial Pacific (see Table 1), the 20% decrease in the >63 µ-size fraction converts to a 12 µmol/kg drop in carbonate ion concentration. As we have no calibration for sediment in this CaCO$_3$ content range, we cannot convert the CaCO$_3$ decrease to a carbonate ion content drop. As no whole shells were present, the weight index could not be determined.

6. Down-Core Measurements: Cape Basin

Hodell et al. [2001] obtained a record of CaCO$_3$ content and foraminifera fragmentation extent for a core...
from 4.6 km depth in the Cape Basin (47°S, 10°E). As reproduced in Figure 10, these results clearly herald a major increase in the extent of dissolution during the Holocene. The percent of foraminifera fragments increases from 20 to 90% and the CaCO$_3$ content drops from 60 to 20%. Although no calibration exists, the fact that the CaCO$_3$ content drop is similar to that for the abyssal Atlantic cores suggests a similar CO$_3^-$ concentration decrease (i.e., $\sim$12 $\mu$mol/kg). However, there appears to be a significant difference in the time of the onset of this decline, i.e., $\sim$12 kyr instead of $\sim$8 kyr. Also, as the sedimentation rate in this core is much higher than for those from the equatorial zone, the lag due to the finite residence time in the bioturbated zone should be much smaller.

7. Pteropod Preservation in the NE Atlantic

[19] Important to answering the question raised in the title of this paper is whether the carbonate ion decrease recorded in abyssal sediments is also seen at shallower water depths. However, because most of these waters are supersaturated with respect to calcite our methods don’t apply. Fortunately, information can be obtained based on the preservation of aragonitic pteropods. As aragonite is 1.4 times more soluble than calcite, a much greater fraction of the deep sea is undersaturated with respect to aragonite. Core V30–60 from 3.2 km depth off the bulge of Africa (26°N, 18°W) shows a prominent peak of pteropod preservation (see Figure 11). Radiocarbon dates on the pteropods show that this peak lasted about two millennia (from 9.2 to 7.0 kyr). Before and after this time interval, the sediment is devoid of pteropods. Taken at face value, in order to achieve aragonite supersaturation 7 to 9 kyr ago and undersatura-

![Figure 10](image-url)  
**Figure 10.** CaCO$_3$ content and fragmentation extent for Cape Basin core 1089 from a water depth of 4.6 km at 47°S and 10°E [Hodell et al., 2001].

![Figure 11](image-url)  
**Figure 11.** (top) Abundance and radiocarbon age (including a 400-year reservoir correction) of pteropods in a northeastern Atlantic sediment core from 26°N, 18°W and 3.2 km water depth [Broecker et al., 1993]. (bottom) Superimposition of today’s in situ carbonate ion concentration on aragonite solubility curves calculated from the relationship $\text{CO}_3^{\text{in situ}} = 65 \exp^{\Delta V/225} \mu$mol/kg, where $\Delta V$ is the water depth in kilometers and $\Delta V$ is the difference in volume between ions and aragonite and ions dissolved in seawater in cm$^3$/mol.
tion for times more recent than 7 kyr, \( \Delta V \) would have to be close to the Culberson and Pytkowicz [1968] value of 36.4 cm\(^2\) per mole.

8. Sediment-Based Constraints on \( \Delta V \)

[20] The results presented here potentially offer constraints to be placed on the magnitude of \( \Delta V \). However, in order to do this, the assumption must be made that dissolution occurs mainly on the seafloor obviating the need to account for the pore H\(_2\)O-bottom H\(_2\)O-carbonate ion offset. As can be seen, in order for the bottom waters at 4.04 km depth on the Ontong-Java Plateau to have been in undersaturated water 8 kyr ago, \( \Delta V \) must have been less than 40 cm\(^3\) per mole. The same is true for the pteropod results. However, to the extent that the dissolution occurred in carbonate-ion-depleted pore waters, these limits would have to be correspondingly increased. Hence the sediments offer no useful constraint on \( \Delta V \).

9. Bioturbation-Dissolution Couple

[21] As already mentioned, there is an ambiguity which has to do with the finite radiocarbon age of the core top CaCO\(_3\). Because of this, the CaCO\(_3\) has not experienced the full impact of the ongoing decline in carbonate ion concentration. As shown in Figure 8, for the Ontong-Java Plateau core from 2.31 km depth, this age is about 2.8 kyr and for the core at 4.04 km, it is about 4.0 kyr. These old ages have been shown to be the result of bioturbation. If, for the moment, dissolution effects are put aside and if, it is assumed that the effective bioturbation depth is the same in both of these cores, then, because the core at 4.04 km has half the accumulation rate as the core at 2.31 km, its core top age would be expected to be twice that for the shallow core. For example, if the bioturbation produced a well-mixed layer 9 cm thick, the ventilation age for the shallow core with its \(~3\) cm per kyr accumulation rate would be about 3 kyr and that for the deeper core with its \(~1.5\) cm per kyr accumulation rate would be 6 kyr. Clearly, the core top radiocarbon age difference between the two cores is smaller than expected.

[22] CaCO\(_3\) dissolution complicates the situation for its impact on the core top radiocarbon age is significant and also quite different depending on whether the CaCO\(_3\) dissolution occurs on the seafloor (i.e., before the CaCO\(_3\) becomes incorporated into the sediment) or after burial of the CaCO\(_3\) in the bioturbated zone. Seafloor dissolution makes the core top \(^{14}\)C age older because it reduces the rate of ventilation of the bioturbated zone with CaCO\(_3\). By contrast, dissolution within the bioturbated zone reduces the core top \(^{14}\)C age. The reason is that it cuts down the mean residence time of CaCO\(_3\) entities in this zone. If the rain rate of material to the seafloor is assumed to be the same at the two water depths and if dissolution is assumed to be negligible in the shallow core, then the unexpectedly low \(^{14}\)C age in the top of the deep core can be explained as shown in Figure 12. As can be seen, to achieve the measured \(^{14}\)C age, about three quarters of the dissolution must have occurred before burial.

[23] Clearly, bioturbation creates a lag in response to the dissolution impetus. Instead of recording the present-day abyssal carbonate ion concentration, the core at 4.04 km on the Ontong-Java Plateau is more nearly recording the concentration 4000 years ago. If so, the \( \Delta \)CO\(_3\) estimates must be increased by a factor of about two. Were this correction to be made to the estimates in Table 1, all the \( \Delta \)CO\(_3\) values would be too large. Further, as the fragments have a greater radiocarbon age than the whole shells, the correction for fragments would be larger than a factor of two.

10. Discussion

[24] Broecker et al. [1999] proposed that the rise in the atmosphere’s CO\(_2\) content during the last 8 kyr was driven by the compensation for the 500 gigatons of carbon withdrawn from the ocean-atmosphere system to regenerate the forest and soil humus destroyed during the last glacial period. The idea is that this CO\(_2\) removal would have raised the carbonate ion concentration throughout the sea unbalancing the ocean’s inorganic carbon budget. More carbon would have been buried as CaCO\(_3\) than was being added by planetary CO\(_2\) degassing and continental limestone weathering. This excess burial would have drawn down the CO\(_3\)
concentration and thereby raised the ocean’s CO$_2$ content. While certainly qualitatively correct, because of complexities associated with events which occurred during the deglacial interval, this argument proves difficult to quantify.

[25] It must be mentioned that other explanations for this CO$_2$ rise have been proposed. Ridgwell et al. [2003] call on the growth of coral reefs. Ruddiman [2005] calls on deforestation conducted by humans. While the former is certainly a competitive proposal, the latter is a nonstarter [see Broecker and Stocker, 2006].

[26] Although ambiguous, the results presented here suggest that the drop in abyssal ocean carbonate ion concentration over the past 8 kyr may have been larger than that required to match the 20 $\mu$atm increase in atmospheric CO$_2$ content. If so, it would require that the carbonate ion decrease in the abyssal ocean was larger than that in the surface ocean. To generate such a difference would require either a change in the pattern of large-scale thermohaline circulation or a change in the power of the biologic pump, or both. As we normally consider the Holocene ocean to have achieved a steady state, had either of these changes occurred, it would be of considerable interest.

[27] One thermohaline scenario comes to mind. The waters in today’s deep Pacific Ocean consist of a roughly 50-50 mixture of deep water produced in the northern Atlantic on one hand and deep water produced in the Southern Ocean on the other [Peacock et al., 2000]. On the basis of the measurements made as part of the GEOSECS program, Broecker and Sutherland [2000] showed that the formere have preformed carbonate ion concentration close to 120 $\mu$mol/kg and the latter a concentration close to 95 $\mu$mol/kg (see Figure 13). So, one way to account for a drop in carbonate ion concentration in excess of the 6 $\mu$mol/kg expected to accompany the 20 $\mu$atm rise in atmospheric CO$_2$ partial pressure would be to call on a progressive weakening of deepwater production in the northern Atlantic relative to that in the Southern Ocean. For the deep Pacific Ocean, this would mean that 8 kyr ago, the contribution of northern source waters to the mix was greater than today’s. Not only could this explain the drop in carbonate ion concentration in the deep Pacific, but also that in the abyssal Atlantic where such a weakening would allow the tongue of Antarctic Bottom Water to penetrate farther north into the Atlantic’s western basin.

[28] Today’s carbonate ion concentration at the site of the core with a pteropod preservation layer (26°N, 3.2 km) is 107 $\mu$mol/kg, a value about 13 $\mu$mol/kg below the preformed concentration in today’s northern end-member. So, in order to account for the preservation of pteropod preservation peak 7 to 9 kyr ago, one would have to postulate that the carbonate ion concentration was closer to the preformed value of 120 $\mu$mol/kg for northern source water.

[29] We have searched to see if evidence for this decline is to be found in high-resolution Holocene $^{13}$C records. Two such benthic records from the northern Atlantic, one at 55°N and 2.2 km depth by Oppo et al., 2003 and the other at 61° and 1.6 km depth by Hall et al. [2004], show small millennial oscillations but no 8 kyr to present trend. Because of their high latitude and shallow depth, these records are ambiguous. What is needed are detailed records from more southerly and deeper cores.

11. Conclusions

[30] The bottom line is that we cannot answer the question posed in the title of this paper. While estimates of the magnitude of the carbonate ion drop during the last 8 kyr based on shell weights and CaCO$_3$ contents suggest that the decrease was larger than the 6 $\mu$mol/kg required to match the 20 $\mu$atm rise in atmospheric CO$_2$ content, the estimate based on the size index decline comes closer. Key to improving these estimates is a proper evaluation of the dissolution lag created by the finite residence time of CaCO$_3$ entities in the bioturbated zone. Further, there is definitely a need to intercompare all existing dissolution indices. To this end, Cardiff’s Stephen Barker is organizing a calibration exercise in which the participants will focus on the Holocene record contained in Dan McCorkle’s set of Ontong-Java Plateau box cores. Until the problems identified here are rectified, attempts to reconstruct glacial age carbonate ion concentrations will remain in limbo. 

[31] Finally, we have put our finger on the possibility that a shift in either circulation pattern or biological pumping has been taking place over the last 8 kyr. One possible explanation is that the production of deep water in the northern Atlantic has weakened relative to that in the Southern Ocean.
Acknowledgments. Discussions with Stephen Barker, Taro Takahashi, Stew Sutherland, Robert Anderson, and Baerbel Hoenisch have proven to be extremely helpful. The sediment samples from the Ontong-Java Plateau were generously provided by WHOI’s Daniel McCorkle. Calculations on in situ calcite concentration changes based on microelectrode results, PA1202

References


