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Holocene atmospheric CO_2 increase as viewed from the seafloor

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[1] Three scenarios have been proposed to explain the 20-ppm post-8000 BP rise in atmospheric CO_2 content. *Indermühle et al.* [1999] call on a climate-induced decrease in terrestrial biomass. W. F. Ruddiman (personal communication, 2002) calls on an anthropogenically induced decrease in terrestrial biomass. *Broecker et al.* [2001] suggest instead that this rise in CO_2 was a response to a $CaCO_3$ preservation event induced by an early Holocene increase in terrestrial biomass. The biomass decline hypothesis not only rests on shaky ^{13}C data, but also requires an unreasonably large decrease in biomass (195 ± 40 GtC). While evidence for a decrease in deep sea carbonate ion concentration over the last 8000 years reconstructed from $CaCO_3$ size index and foraminifera shell weight measurements appears to support the idea that the CO_2 rise was caused by a change in the inventory of terrestrial biomass, the decrease appears to be too large to be explained solely in this way. Regardless, the $CO_3^{=}$ decline cannot be used to distinguish between the late Holocene biomass decrease and early Holocene biomass increase scenarios. Only when a convincing ^{13}C record for atmospheric CO_2 has been generated will it be possible to make this distinction. *INDEX TERMS:* 1030 Geochemistry: Geochemical cycles (0330); 4267 Oceanography: General: Paleoceanography; 4806 Oceanography: Biological and Chemical: Carbon cycling; *KEYWORDS:* $CaCO_3$ dissolution, paleocarbonate ion concentration, whole foraminifera shell weights, atmospheric CO_2

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1. Introduction

[2] Based on measurements of gases trapped in Antarctic ice, *Indermühle et al.* [1999] demonstrate that the CO_2 content of the atmosphere rose by 20 ppm between 8000 BP and the onset of the Little Ice Age (see Figure 1). Based on ^{13}C measurements in ice core CO_2 (see Figure 2), these authors conclude that this CO_2 increase was the result of a decline in terrestrial biomass. W. F. Ruddiman (personal communication, 2002) goes a step further, calling on an anthropogenic-driven biomass decline. In our estimation, the situation regarding the cause of the CO_2 rise is far from clear. The ^{13}C measurements upon which the biomass decline hypothesis rests are, to us, far from convincing. As the small decrease over the last 8000 years in $\delta^{13}C$ (−0.2‰) is comparable to the scatter of individual measurements around the best-fit trend, it is possible that, in reality, no ^{13}C trend exists. If so, no decrease in terrestrial biomass need be called upon.

[3] At issue is the sensitivity of terrestrial biomass to environmental change. A controversy exists as to how the ongoing CO_2 buildup in our atmosphere will impact carbon storage in the terrestrial biosphere. A consensus exists that the availability of extra CO_2 (and also of fixed nitrogen) will tend to increase storage and that soil warming will tend to decrease storage. But it is far from clear which of these impacts will be the greater. As the decrease in biomass of 195 ± 40 gigatons of carbon called upon by *Indermühle et al.* [1999] to account for the Holocene CO_2 rise is equivalent to one third the pre-industrial forest biomass, it would be surprising if such a large change in storage could have been induced by the small changes in climate which have occurred during the course of the Holocene or, for that matter, by the activities of the rather small human population. Hence it is of great importance that the cause of this CO_2 rise be established. While at this point such a resolution is not possible, it is worthwhile discussing where we stand.

[4] An alternate scenario of interest to us is that the CO_2 rise is driven by an oceanic response to the increase in terrestrial biomass thought to have accompanied deglaciation [*Shackleton*, 1977; *Broecker et al.*, 2001]. The CO_2 extracted from the ocean-atmosphere reservoir in order to accomplish this regrowth would have led to an increase in the carbonate ion concentration in the entire ocean. As a consequence, the lysocline would have deepened and hence the oceanic $CaCO_3$ budget would have been thrown out of balance. Accumulation of $CaCO_3$ in marine sediments would have outstripped ingredient supply. As a result the carbonate ion concentration would have been gradually drawn down until a balance between burial and ingredient supply had been reestablished. As the isotopic composition of marine carbonates is nearly identical to that of oceanic

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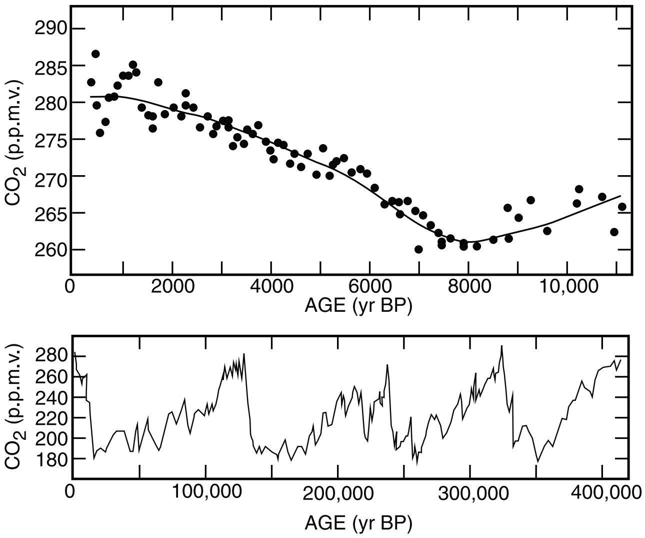

Figure 1. (top) Taylor Dome Antarctica CO_2 record for the last 10,000 years as obtained by *Indermühle et al.* [1999]. (bottom) Vostok Antarctica CO_2 record for the past 420,000 years as obtained by *Petit et al.* [1999].

dissolved inorganic carbon, in this case, there would be no associated ^{13}C change. The time constant for such an adjustment is on the order of 5000 years [*Broecker and Takahashi*, 1977; *Sundquist*, 1990]. As a consequence of this $CO_3^=$ drawdown, the CO_2 concentration in seawater (and hence also content in the atmosphere) would have increased.

[5] At the time we received the reviews to this paper, we also received a preprint [*Brovkin et al.*, 2002]. The result of this modeling exercise is to attribute part of the CO_2 rise to a warming of the surface ocean and thereby reduce the magnitude of the required Holocene biomass decrease to 90 Gt.

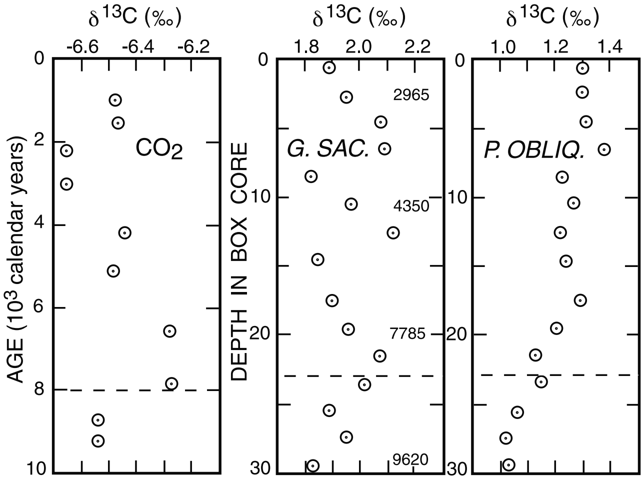

Figure 2. Comparison of the ^{13}C records for the last 8000 years as recorded in the Taylor Dome ice core CO_2 [*Indermühle et al.*, 1999] and in planktonic foraminifera for a core raised from a depth of 2.3 km on the equator at 158°E on the Ontong Java Plateau [*Broecker et al.*, 2001].

Table 1. Calcite Solubility and Slope in Calcite Solubility in Cold Seawater as a Function of Water Depth Based on a 1-atm Solubility of 45 μmol$CO_3^=$/kg and a ΔV of 40 cm^3/mol[a]

Water Depth, km	Calcite Sol., μmol $CO_3^=$/kg	Sol. Slope, μmol/kg/km	$CO_3^=$ Versus Shell Wt., μmol/kg/μg
1.5	58.8	10.3	1.4
2.0	64.2	11.4	1.5
2.5	70.2	12.5	1.6
3.0	76.7	13.6	1.8
3.5	83.8	14.9	2.0
4.0	91.6	16.3	2.1
4.5	100.1	17.9	2.3

[a] Also shown is the slope of the shell weight loss-carbonate ion concentration relationship for various water depths. The 0.7 μmol/kg per km increase in carbonate ion concentration in the Ontong-Java Plateau deep water column is taken into account.

2. CO_2 Record

[6] Reproduced in Figure 1 are the ice core CO_2 results for the present interglacial [*Indermühle et al.*, 1999]. It is difficult to find fault with these numerous and extremely precise measurements. Also shown are the results for the three previous interglacials. A point in favor of W. F. Ruddiman's (personal communication, 2002) proposal that human activity caused the 20-ppm rise during the last 8000 years is that a similar feature is not seen in the records for the previous interglacials (see Figure 1).

3. ^{13}C Record

[7] Reproduced in Figure 2 are the $\delta^{13}C$ results reported by *Indermühle et al.* [1999]. Also reproduced are those for two species of planktonic foraminifera from an Ontong-Java Plateau deep sea core reported by *Broecker et al.* [2001]. While admittedly the foraminifera results need not reliably track the atmospheric trend, they certainly cannot be used to support the trend based on the ice core results. What is needed is more detailed measurements on CO_2 from ice cores with improved accuracy (i.e., ±0.05‰).

4. $CO_3^=$ Record

[8] On a timescale of several tens of years, the CO_2 content of the atmosphere must reflect the carbonate ion concentration in surface ocean water. If the change in $CO_3^=$ is the result of CO_2 uptake by or release from the terrestrial biosphere, then given enough time, it must permeate the entire ocean. If the $CO_3^=$ concentration in the ocean changes, then the content of CO_2 in the atmosphere must change in the opposite direction. The reason is that the CO_2 consumed or released when the terrestrial biomass inventory changes is ultimately derived from or returned to the oceanic reservoir. If, for example, CO_2 is extracted from the oceanic reservoir to create biomass, the $CO_3^=$ ion concentration in the ocean will correspondingly rise. As the ocean mixes about once per millennium, on the timescale of 8000 years this rise will

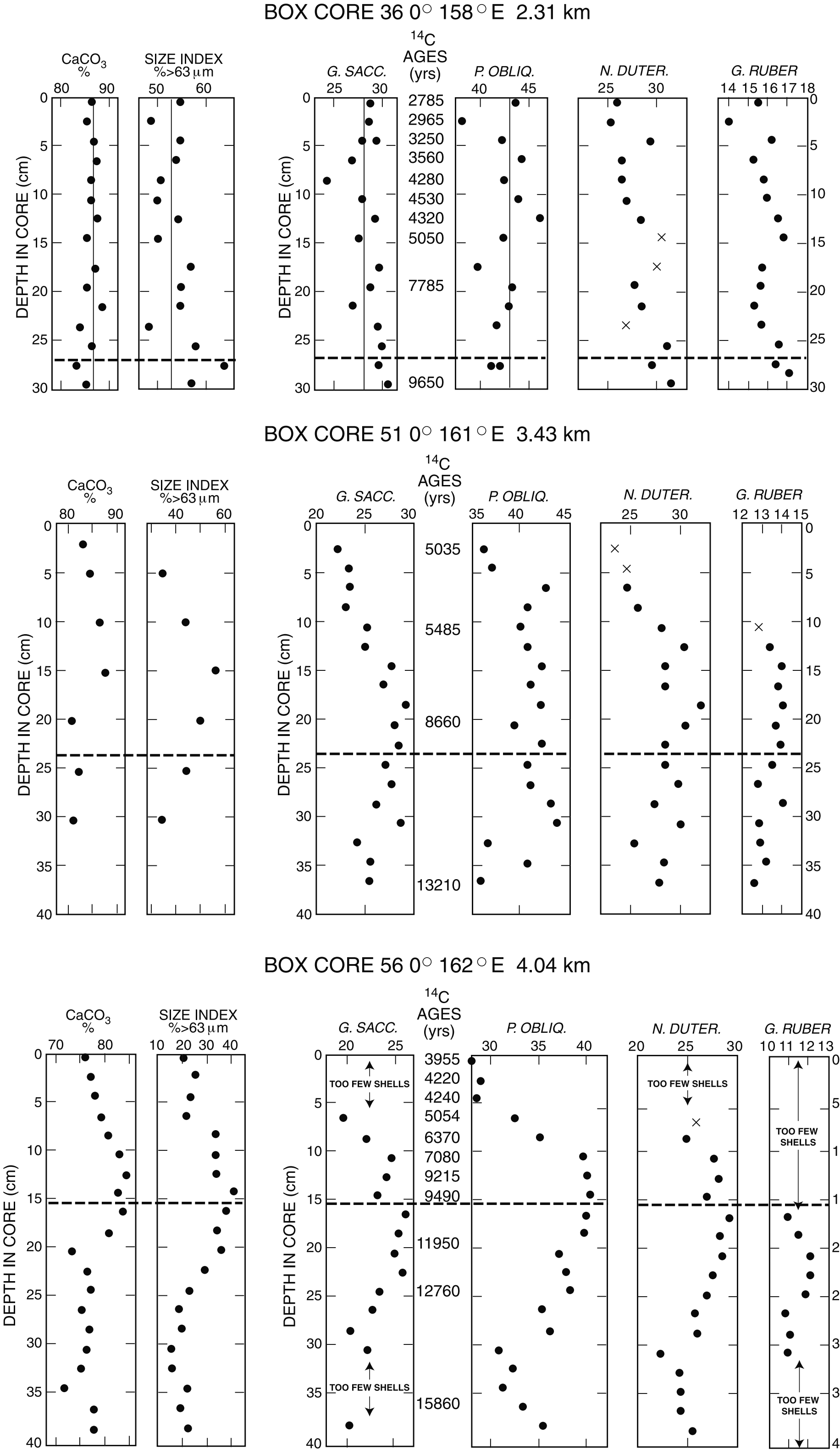

Figure 3. Plots of CaCO$_3$ content, CaCO$_3$ size index and shell weights (in μg) versus depth in three equatorial cores from the Ontong-Java Plateau (western equatorial Pacific). Fifty whole shells of *G. sacculifer*, of *P. obliquiloculata*, and of *N. dutertrei* were picked from the 350 to 420 μm size fraction. Fifty *G. ruber* were picked from the 300 to 350 size fraction. The *x*s indicate those samples in which only 15 to 30 whole shells were found. Also shown are reservoir-corrected (by 400 years) radiocarbon ages. The dashed line denotes that depth where the ^{14}C age is about 9500 years.

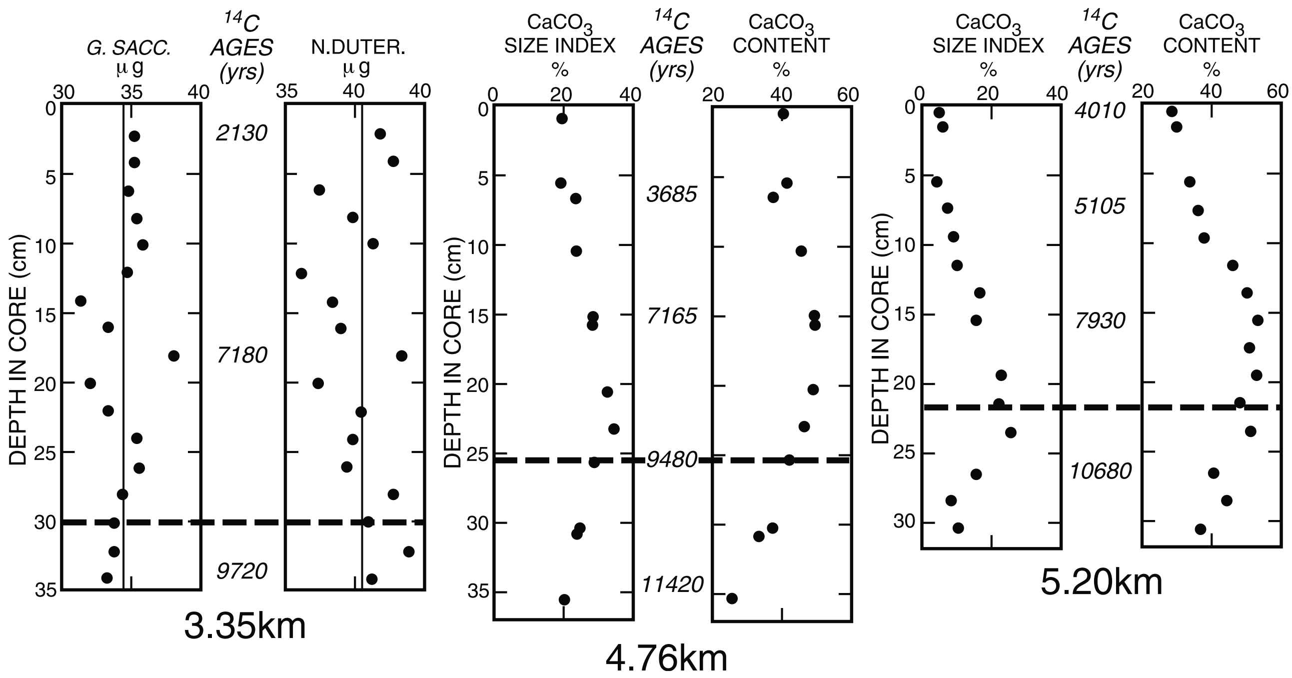

Figure 4. Results from Ceara Rise (western equatorial Atlantic) cores. (left) Shell weights for two planktonic species from core RC15-175 from a depth of 3.35 km. As can be seen, there is no evidence for an early Holocene preservation event. (right) $CaCO_3$ and $CaCO_3$ size index records for two deep cores (RC16-55: 10°N 45°W, 4.76 km and RC17-30: 11°N 41°W, 5.20 km). Both of these cores record an early Holocene preservation event. Foraminifera weights are not shown for these cores because no whole shells survived dissolution-induced breakup. As in Figure 3, the dashed lines denote that level in the core where the ^{14}C age is 9500 years.

be well distributed throughout the entire ocean. Similarly, if CO_2 is released from the terrestrial biosphere to the ocean-atmosphere reservoir, the $CO_3^=$ concentration will be reduced everywhere in the sea. Hence, changes in terrestrial biosphere must be reflected in changes in the carbonate ion concentration in the deep sea.

[9] Three methods can be employed in order to assess changes in the extent of dissolution in the deep sea during the course of the Holocene. The most obvious one involves measurements of the $CaCO_3$ content of the sediment. Increased dissolution will lower the $CaCO_3$ content. However, this approach has a possible drawback; that is, as changes in the extent of dissolution in high $CaCO_3$-content open-ocean sediments convert to only small changes in $CaCO_3$ content, changes in the ratio of $CaCO_3$ to non $CaCO_3$ rain to the seafloor during the course of the Holocene might obscure the dissolution imprint. The second approach involves measurements of the fraction of $CaCO_3$ contained in entities greater than 63 microns in size. As shown by *Broecker and Clark* [1999] in core-top sediments from the tropics, this so-called size index undergoes a decline with decreasing pressure-normalized $CaCO_3$ content. It reflects the progressive breakup of foraminifera shells as they dissolve. While *Broecker and Clark* [2001a] found that during glacial time, the initial value of the size index (i.e., the value for samples which have experienced little or no dissolution) appears to have been somewhat smaller than that characterizing the late Holocene, the assumption that it has remained nearly constant through the course of the Holocene is more likely to be valid. The third approach is that based on the weights of whole foraminifera shells picked from narrow size range [*Lohmann*, 1995]. As shown by *Broecker and Clark* [2001b], once under saturation is achieved in the sediment pore waters, shell weights decline with decreasing pressure-normalized carbonate ion concentration in bottom water.

[10] In our previous papers we overestimated the pressure dependence of calcite solubility [see *Bijma et al.*, 2002]. We used a ΔV for the dissolution of calcite in seawater of 45 cm^3/mol and at a depth of 4 km obtained a slope of 20 $\mu molCO_3^=/kg$ per km. If, as we now suspect, a better choice of the ΔV is 40 cm^3/mol and if we take into account the increase in slope of the solubility with water depth, then this dependence is reduced (see Table 1).

[11] A complication in the application of shell weights as a paleo carbonate proxy has been introduced by *Barker and Elderfield* [2002] who show that the initial thickness of foraminifera shell walls depends on the carbonate ion concentration in the surface waters in which they form. The higher the $CO_3^=$ concentration, the thicker are the shells. Hence a portion of the reduction in shell weight reported here may be attributable to the decrease in surface water carbonate ion which must have accompanied the 8000 BP to present rise in atmospheric CO_2 content. However, as the decrease in the $CO_3^=$ concentration in tropical surface ocean waters induced by a 20-ppm rise in atmospheric CO_2 content

Table 2. Foraminifera Weights, $CaCO_3$ Contents and $CaCO_3$ Size Indices for Cores From Greater Than 4.1 km Depth on the Ceara Rise[a]

		G. sacculifer			*P. obliquiloculata*			*N. dutertrei*			*G. ruber*			$CaCO_3$		$CaCO_3$ Size Index	
Core Number	Water Depth, m	Top, μg	10–15 cm, μg	Δwt., μg	Top, μg	10–15 cm, μg	Δ, μg	Top, μg	10–15 cm, μg	Δ, μg	Top, μg	10–15 cm, μg	Δ, μg	Top, μg	10-15 cm, μg	Top, μg	10-15 cm, μg
V18-22	4145	37.3 (50)	40.0 (50)	−2.7	41.1 (50)	42.8 (50)	−1.7	45.5 (50)	43.3 (50)	+2.3	18.9 (50)	18.5 (50)	+0.4	53.4	54.1	46	52
V25-64	4235	36.0 (50)	36.0 (50)	0.0	41.3 (49)	42.0 (50)	−0.7	42.4 (50)	40.6 (50)	+1.8	17.2 (50)	17.9 (50)	−0.7	50.4	54.1	47	49
RC13-186	4296	32.9 (50)	36.1 (49)	−3.2	37.8 (50)	39.5 (50)	−1.7	40.0 (50)	41.1(50)	−1.1	16.3 (50)	16.8 (50)	−0.5	47.5	47.7	43	44
RC13-185	4299	32.1 (50)	36.4 (50)	−4.3	38.0 (50)	38.6 (50)	−0.6	39.5 (50)	37.7 (50)	+1.8	15.3 (50)	16.7 (50)	−1.4	45.4	48.6	48	38
RC16-58	4305	32.8 (50)	35.1 (50)	−2.3	38.4 (50)	37.2 (50)	−1.2	41.1 (50)	41.7 (50)	−0.6	15.1 (50)	15.7 (50)	−0.6	46.2	28.1	37	43
RC16-60	4391	34.7 (50)	40.8 (50)	−6.1	39.0 (50)	40.4 (50)	−1.4	39.0 (50)	40.4 (50)	−1.4	18.4 (50)	18.8 (50)	−0.4	47.7	46.4	53	47
RC8-6	4555	30.8 (50)	34.4 (49)	−3.6	36.3 (50)	37.1 (50)	−0.8	37.6 (50)	40.4 (50)	−2.8	14.8 (39)	16.4 (50)	−1.6	45.0	45.8	36	40
V30-27	4567	25.7 (50)	30.4 (50)	−4.7	29.0 (50)	28.7 (50)	+0.3	33.5 (49)	35.9 (50)	−2.4	14.1 (17)	14.3 (42)	−0.2	41.9	31.8	36	37
V18-23	4601	30.4 (50)	34.5 (50)	−4.1	32.1 (50)	36.2 (50)	−4.1	36.2 (50)	40.4 (50)	−4.2	14.3 (49)	15.4 (50)	−1.1	55.2	57.4	29	43
V30-24	4697	27.0 (50)	28.4 (27)	−1.4	30.5 (50)	30.8 (39)	−0.3	36.2 (50)	37.4 (30)	−1.2	14.3 (10)	–(4)	–	39.0	25.4	32	25
V25-48	4707	28.7 (10)	25.0 (24)	−3.7	26.8 (26)	28.0 (50)	−1.2	31.3 (24)	34.4 (50)	−3.1	–(2)	–(0)	–	34.4	34.1	15	19
V31-136	4712	24.8 (20)	30.0 (49)	−5.2	30.4 (50)	35.4 (49)	−5.0	33.4 (50)	31.1 (50)	+2.3	14.8 (12)	17.1 (44)	−2.3	37.4	44.1	19	37
RC16-63	4766	–(4)	34.6 (51)	–	29.0 (50)	35.6 (50)	−6.6	32.3 (50)	35.6 (50)	−3.3	–(0)	16.2 (28)	–	39.7	46.4	18	42

[a] Results are presented for both core top samples and for samples from 10 to 15 cm depth in the same core. Given in parentheses are the number of shells picked.

is about 12 μmol/kg, the decrease in shell weight attributable to this decline is only about 2 μg [see *Barker and Elderfield*, 2002]. Further, *Broecker and Clark* [2003] make a case that tropical species foraminifera appear not to follow the Barker and Elderfield trend.

[12] We have applied all three of these methods to cores from a series of water depths in western equatorial Pacific and in the equatorial Atlantic. The results are summarized in Figures 3 and 4. As can be seen, the deepest cores (i.e., that at 4000 m in the western Pacific and that at 5200 m in the western Atlantic) show evidence for a pronounced increase in the intensity of dissolution starting at about 8000 ^{14}C years ago and continuing to the core-top mixed layer. As summarized in Table 2, there is also evidence for an increase in dissolution intensity in a series of cores from deeper than 4.2 km on the Ceara Rise. Foraminifera from core-top samples have, for the most part, smaller weights than those from samples from 10 to 15 cm depth. As we have not gone to the expense of obtaining radiocarbon dates on these cores, it can only be said that the 10 to 15 cm samples likely correspond to sometime in the mid Holocene. Hence these observations are only of qualitative value for it is unlikely that they record the full increase in dissolution intensity. That these decreases in shell weight do not reflect the changes in initial composition is demonstrated by the fact that similar decreases are not seen in cores from shallower water depths (see Table 2).

[13] The magnitude of the late Holocene increase in dissolution intensity becomes smaller with decreasing water depth. No hint of such a trend is seen in the Pacific Ontong-Java Plateau core from 2.31 km depth nor in the record for the Atlantic Ceara Rise core from 3.35 km depth. Were the decrease in carbonate ion concentration over the last 8000 years related to changes in terrestrial biomass, then it must have been nearly uniform throughout the deep sea. The reason is that the time interval over which the atmospheric CO_2 rise took place is many times that required for the ocean to mix. Shown in Figure 5 is a scenario by which this water depth trend might be explained. For this scenario, we adopt a ΔV for the dissolution of calcite in deep seawater of 40 cm^3/mol and it is assumed that the effective CO_3 ion concentration in the pore waters is 10 μmol/kg lower than that in the overlying bottom water. We also assume that the post 8 kyr $CO_3^=$ concentration drop was 8 μmol/kg as would be expected to accompany a 20-ppm rise in atmospheric CO_2 content (see Figure 6). On the basis of these assumptions, in the equatorial Pacific, today's pore waters at a depth of 2.3 km are close to saturation with respect to calcite and all deeper waters are undersaturated. The boundary separating of super from undersaturated waters at the time the preservation maximum was shifted downward from 1.8 km to 3.2 km. In today's tropical Atlantic, the boundary should be at 4.2 km, while during the preservation maximum, it would have been at 4.3 km. While not perfect, the match with observations is encouraging.

[14] A further test of this scenario is provided by the timing of a pteropod preservation event observed in the eastern North Atlantic [*Broecker et al.*, 1993]. The aragonitic shells of pteropods are 1.41 times more soluble than the calcitic shells of foraminifera shells. Further, as aragon-

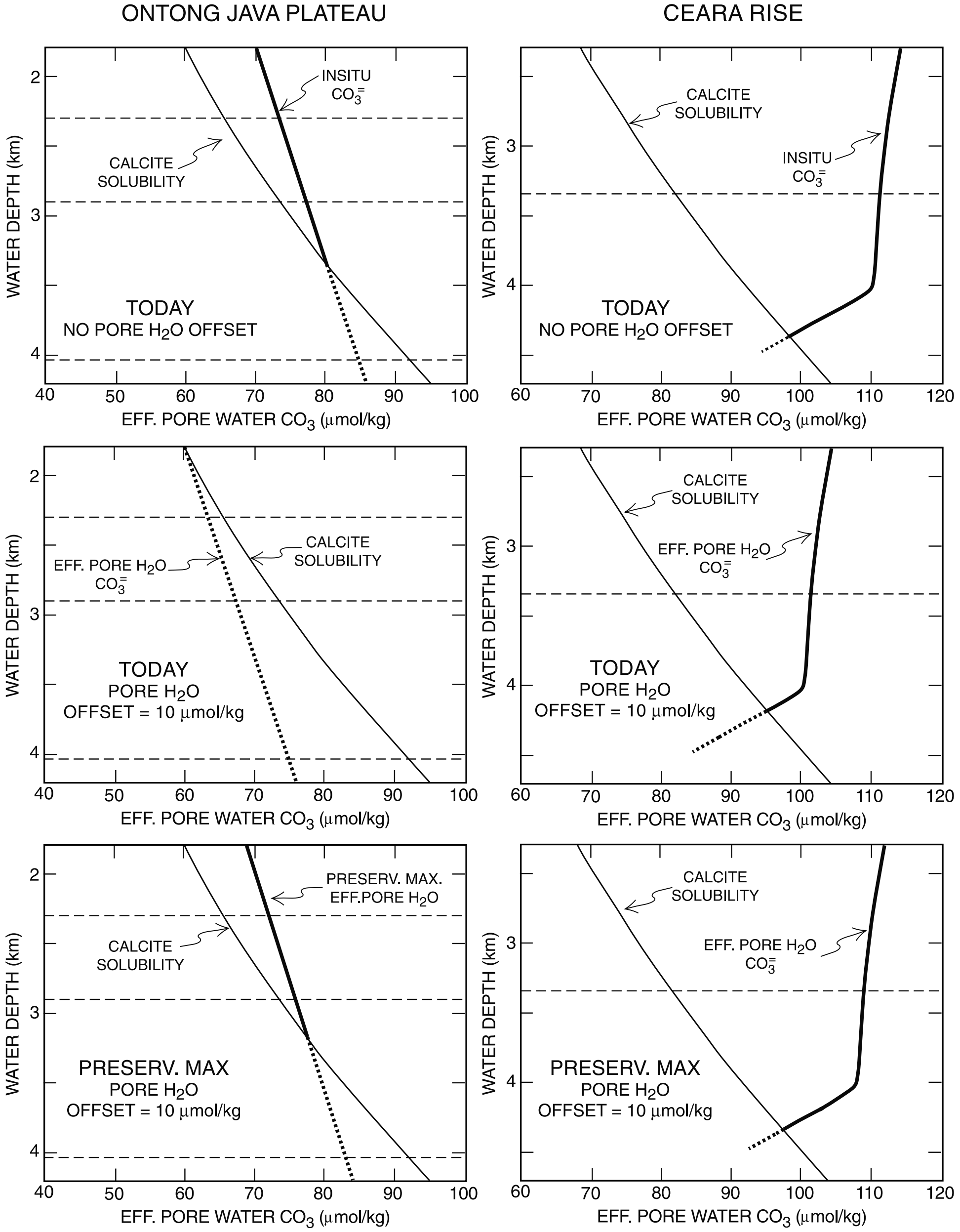

Figure 5. State of calcite saturation in sediment pore waters as a function of depth on the (left) Ontong-Java Plateau and (right) Ceara Rise. The calcite solubility is based on a ΔV of 40 cm^3/mol. Consistent with the atmospheric CO_2 rise over the last 8000 years of 20 ppm, the $CO_3^=$ ion concentration is assumed to have been 8 μmol/kg higher than today's at the peak of the early Holocene preservation event. The dashed horizontal lines represent the depths of the cores in Figures 3 and 4.

ite is more dense than this calcite, its ΔV for dissolution is 37.6 rather than 40 cm^3/mol. As reproduced in Figure 7, this event is centered at about 9000 ^{14}C years BP. Making the same assumptions as above, in today's ocean pteropods should not be preserved at depths greater than 2.8 km. However, during the preservation maximum, this limit would have been displaced downward to 3.2 km. Again, the match is encouraging.

[15] While yielding a plausible fit to the observations, this hypothetical scenario is admittedly "wobbly." First of all, the assumption that the carbonate ion reduction in pore waters is the same at all depths and places is almost certainly not the case. For example, the pH electrode results of *Hales and Emerson* [1996, 1997] suggest that the carbonate ion concentration offset in pore waters is greater for Ceara Rise sediments (0.12 pH units) than for Ontong-Java Plateau sediments (0.02 pH units). Hence our assumption that the $CO_3^=$ concentration offset is 10 μmol/kg (equivalent to 0.06 pH units) may not be correct. It should be mentioned in this regard that numerous studies have

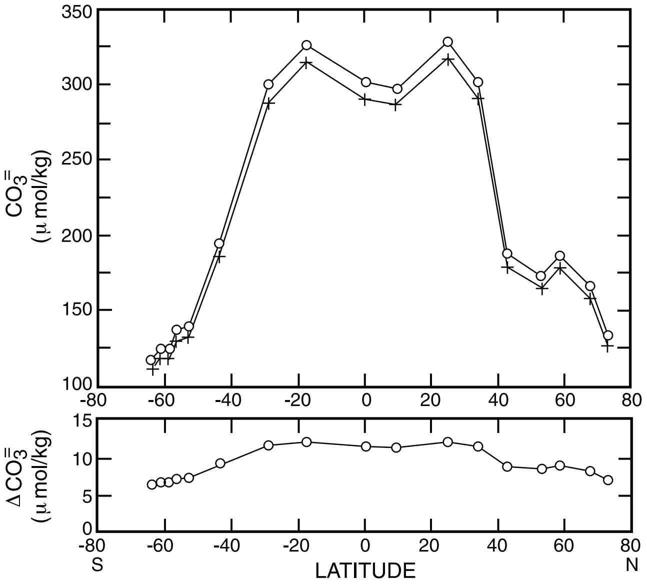

Figure 6. (top) Carbonate ion concentration in surface waters of the Atlantic Ocean as a function of latitude for a pCO$_2$ of 260 μatm (circles) and for a pCO$_2$ 280 μatm (pluses). (bottom) Decrease in carbonate ion concentration corresponding to a rise in atmospheric CO$_2$ concentration form 260 to 280 μatm.

shown that pH electrodes give biased readings in the presence of high concentrations of DOC (as surely exist in sediment pore waters) [*Bradshaw and Brewer*, 1988]. Second, considerable uncertainty remains with regard to the ΔV for the reaction

$$\text{Calcite} \Leftrightarrow \text{Ca}^{++} + \text{CO}_3^=,$$

and hence in the solubility of the mineral calcite at any given water depth.

[16] Another question concerns the depth at which foraminifera shells begin to dissolve. On the basis of the Ontong-Java scenario presented in Figure 6, in today's ocean, dissolution should commence at about 1.8 km in the plateau and 4.2 km on the Ceara Rise. Summarized in Figure 8 are the weights for samples from core-top samples from the Ceara Rise and in Figure 9, weights for core-top samples from the Ontong-Java Plateau. On the Ontong-Java Plateau, a linear down water column decrease in shell weight is observed. The lack of curvature in this trend is surprising in that, as indicated in Table 1, between 1.5 and 4.0 km the slope of the saturation solubility increases by a factor of 1.6. There is, however, no evidence for shell thinning at depths shallower than 4.2 km on the Ceara Rise. The onset of weight loss ($\sim$4.2 km) corresponds to the upper portion of the transition zone between high carbonate ion content North Atlantic Deep Water (NADW) and low carbonate ion concentration Antarctic Bottom Water (AABW) (see Figure 10). As at this locale sizable vertical and north to south gradients in carbonate ion concentration exist, it proves difficult to establish the relationship between weight loss and pressure-normalized carbonate ion concentration. Also, it is clear that small shifts in the interface between NADW and AABW would lead to sizable $CO_3^=$ changes.

[17] On the Ontong-Java Plateau for both *G. sacculifer* and for *P. obliquiloculata*, core-top samples from 1.8 and 1.6 km depth are heavier than those at 2.3 km, suggesting that the pore waters at 2.3 km depth are currently slightly undersaturated with respect to calcite. The weights of *G. sacculifer* in the core-top samples from 1.8 and 1.6 km depth are similar to those from Ceara Rise core tops suggesting that they have not undergone any dissolution. Hence there appears to be a flaw in the above scenario. If during the preservation event, the $CO_3^=$ ion concentration throughout the deep sea was higher than today's, then shells representing this time in the 2.3 km core should have weights similar to those for the core-top samples from the cores at 1.8 and 1.6 km. However, the weights for shells representing the time of the preservation event at 2.3 km are no heavier than those at the core top.

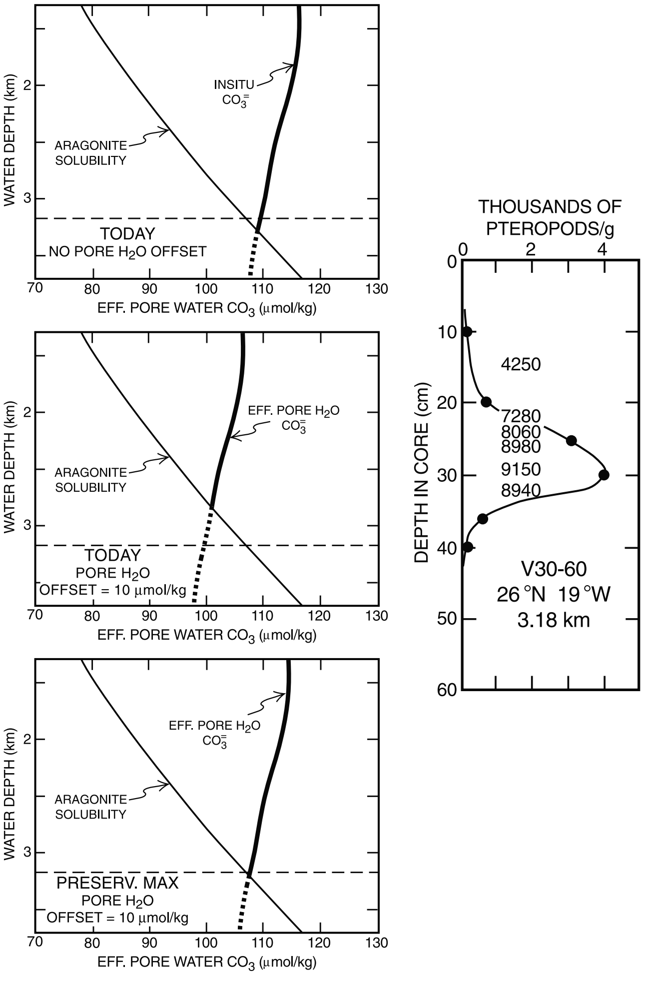

Figure 7. (right) Record of pteropod preservation in core V30-60 from 26°N and 19°W in the northeastern Atlantic [*Broecker et al.*, 1993]. (left) Solubility of aragonite as a function of depth (assuming ΔV for aragonite of 37.4 cm^3/mol and 1 atm solubility of 63 μmol/cm^3).

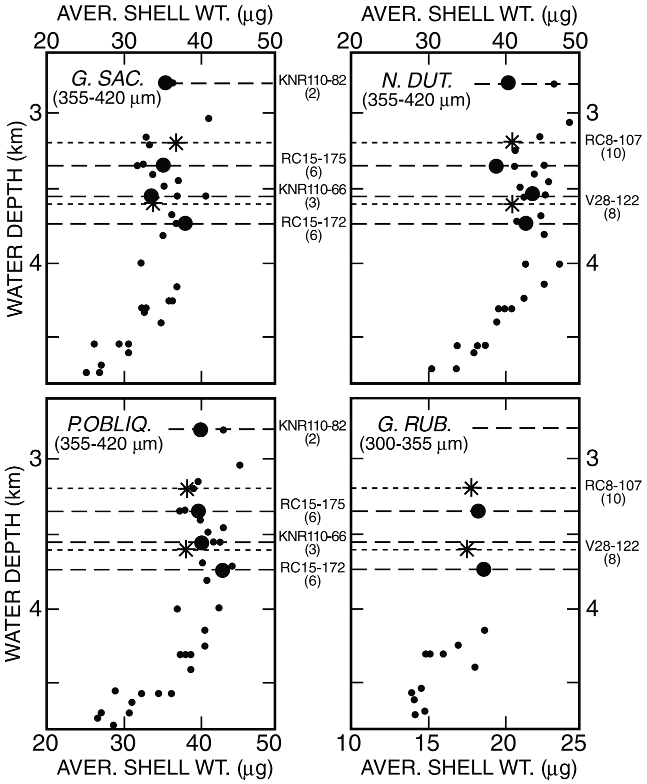

Figure 8. Whole foram average shell weights from core top samples as a function of water depth (small dots). The large circles are the average for Holocene samples from Ceara Rise cores. The stars are averages for cores from the Caribbean Sea. The identity of these cores is shown, and in parentheses the number of sample averages is given.

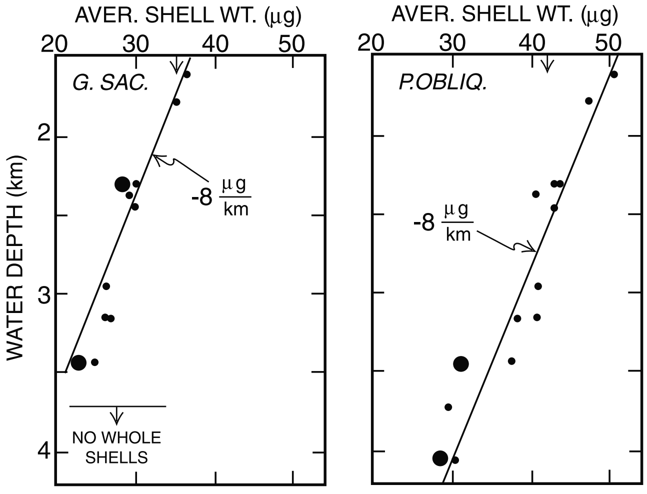

Figure 9. Average whole foraminifera shell weights for core top samples as a function of water depth for late Holocene samples from Ontong-Java Plateau cores (small dots). The large dots are averages for the three cores shown in Figure 3. The arrows represent the average weights for the samples from 2.8 to 4.0 km on the Ceara Rise.

[18] One might ask whether the offset in the depth at which shell thinning commences in the Pacific (i.e., ~1.6 km) is consistent with that at which it commences in the Atlantic (i.e., ~4.2 km). The difference in $CO_3^=$ concentration between waters in these depths in the western equatorial Atlantic and in the western equatorial Pacific is about 38 (108–70) μmol/kg (see Figure 10). As shown diagramatically in Figure 11, if a ΔV for calcite dissolution of 40 cm^3/mol is adopted, then the difference between the depths of the onset of dissolution on the Ontong-Java Plateau and the Ceara Rise can be explained if the pore waters at both sites have an effective carbonate ion concentration 10 μmol/kg less than that in the overlying bottom water.

[19] Admittedly there are problems with the scenario shown in Figure 5. First, at a depth of 3.5 km on the Ontong-Java Plateau at the time of the preservation event, the sediment pore waters may have been supersaturated with respect to calcite. If so, the bottom water carbonate ion change estimates given in Table 3 for this depth are minima. Second, as the radiocarbon ages of the core-top $CaCO_3$ for the Ceara Rise core at 5.2 km and for the Ontong-Java Plateau core at 4.0 km are about 4000 years, the deep sea dissolution record covers only a portion of the time interval over which the CO_2 rise occurred. Because of this, the estimates of the carbonate ion concentration decreases summarized in Table 3 are minima. The problem is that the carbonate ion decrease calculated for the 4 km core is already much greater than the expected 8 μmol/kg. Hence the apparent agreement with expectation of the scenario in Figure 5 cannot be taken as a demonstration that the drop in $CO_3^=$ concentration was close to the expected 8 μmol/kg. While qualitative, the $CaCO_3$ and size index results sum-

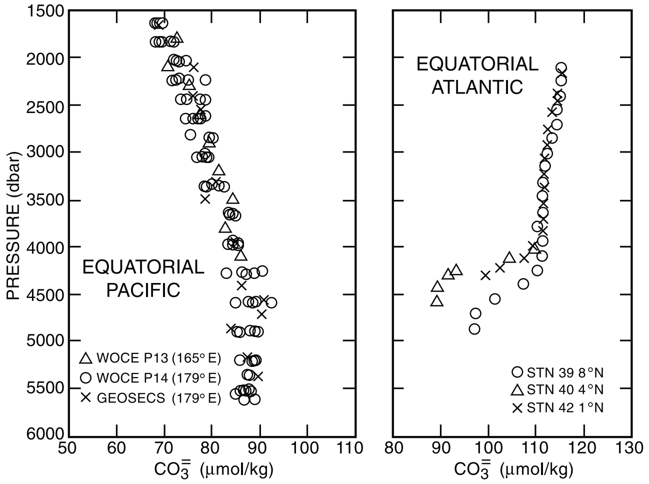

Figure 10. Carbonate ion concentration versus water depth (expressed as pressure in decibars) for the western equatorial Pacific and western equatorial Atlantic. In order to reduce the scatter, the Atlantic data have been calculated from the relationship $CO_3^= = 112 - 0.33(H_4SiO_4 - 30)\frac{\mu mol}{kg}$ [see *Broecker et al.*, 1999]. The Pacific data were supplied by LDEO's Stew Sutherland.

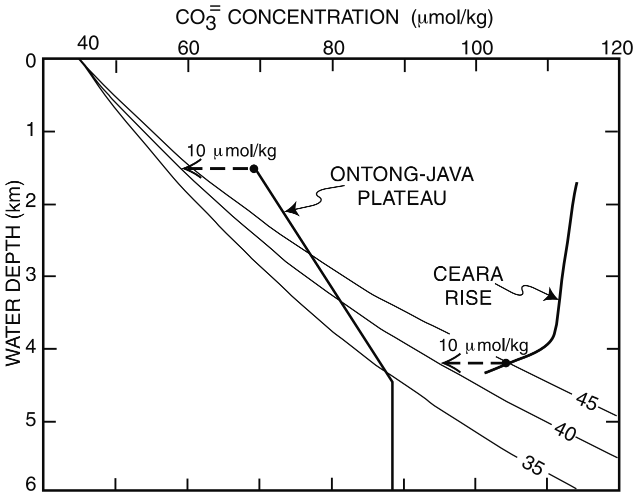

Figure 11. Carbonate ion concentration versus water depth for the Ontong-Java Plateau and Ceara Rise (see Figure 9). Also shown is the solubility of calcite as a function of water depth for three values of ΔV for calcite dissolution in seawater. Finally, the depths at which shell weight loss is initiated at the two locales are shown by the horizontal arrows. If a ΔV of 40 cm^3/mol is adopted, then at both locales a bottom water-pore water carbonate ion concentration offset of about 10 μmol/kg would produce the observed depths of the onset of shell weight loss.

marized in Table 4 suggest a sizable $CO_3^=$ concentration decline during the last 8000 years.

5. An Alternate Scenario

[20] Perhaps the $CO_3^=$ reduction since 8000 years ago was not uniform throughout the deep sea. Rather, it was anomalously large in the deepest waters. For the Atlantic, there is a simple explanation as to why this might have been the case, namely, that the extent of penetration of low $CO_3^=$ concentration Antarctic Bottom Water (AABW) into the abyssal western Atlantic has increased during the last 8000 years thereby reducing the $CO_3^=$ concentration of the deepest waters. However, if this explanation is to be extended to the Ontong-Java Plateau, a far more dramatic change in water mass distribution must be called upon. It is difficult to think of a scenario where this might be accomplished.

Table 4. $CaCO_3$ Content and $CaCO_3$ Size Index for Core Top Mixed Layer And Preservation Maximum Horizon Samples in Two Piston Cores From the Deep Western Tropical Atlantic[a]

Depth in Core	$CaCO_3$, %	$CaCO_3$ Size Index, %>63 μm
	Piston Core 4.76 km	
Core top mixed layer	20 [−56]	40
Preserv. max	36	50
	Piston Core 5.20 km	
Core top mixed layer	5 [−85]	27
Preserv. max.	26	55

[a] The numbers in brackets represent the fraction of the $CaCO_3$ dissolved (referenced to the preservation maximum in the same core).

[21] We have obtained evidence that during marine isotope stages 4 and 5 in the deep Atlantic there were three preservation - dissolution cycles [*Broecker and Clark*, 2003]. They appear to have been paced by the precession-induced cycle in the seasonal distribution of insolation. Hence, by analogy, one might conclude that the deep Atlantic is currently headed for an insolation-pace dissolution maxima. Further, these stage 5 results suggest that the Holocene deep sea carbonate ion concentration decrease is not anthropogenic. Finally, as these marine isotope stage 4 and 5 oscillations in $CO_3^=$ concentration are not present in the atmospheric CO_2 record, there appears to be a disconnect between atmospheric CO_2 content and deep sea carbonate ion concentration.

6. Conclusions

[22] As would be expected, were the rise in the atmosphere's CO_2 content over the last 8000 years to have been

Table 3. $CaCO_3$ Content, $CaCO_3$ Size Index and Whole Shell Weights for Samples From the Core Top Mixed Layer and the Preservation Maximum Horizon in Box Cores From Three Depths on the Ontong-Java Plateau[a]

Depth in Core	$CaCO_3$, %	$CaCO_3$ Size Index, %>63μm	*G. sac.*, μg/Shell	*P. obl.*, μg/Shell	*N. dut.*, μg/Shell	*G. rub.*, μg/Shell
			Box Core 36 2.31 km			
Core top mixed layer	87	53	28	43	26	15.5
Preserv. max.	87	54	30	42	28	16.0
			Box Core 51 3.43 km			
Core top mixed layer	84 [−7]	38	22 (−12)	36 (−12)	25 (−10)	– –
Preserv. max.	87	55	28	42	30	13.7
			Box Core 56 4.04 km			
Core top mixed layer	77 [−27]	23	<18 (>13)	29 (24)	– –	– –
Preserv. max.	83	38	24	40	28	11.5

[a] The numbers in brackets represent the fraction of the $CaCO_3$ dissolved (referenced to the preservation maximum in the same core). The numbers in parentheses represent the apparent carbonate ion concentration reduction (referenced to the preservation maximum in the same core and based on the dependence listed in Table 1).

the result of a change in terrestrial biomass, the carbonate ion concentration of the deep sea has decreased. However, the magnitude of this decrease appears to have been substantially larger than expected. By analogy with the preservation-dissolution cycles in marine isotope stages 4 and 5, this decline appears to have been, at least in part, paced by the 23,000-year precession cycle. But as there is no obvious 23,000-year periodicity in the atmospheric CO_2 record for stage 5, the deep sea $CO_3^=$ concentration and the atmospheric CO_2 content do not appear to be tightly locked. Unfortunately, even if the change in deep sea carbonate ion concentration were consistent with the 20-ppm atmospheric CO_2 rise, the record of carbonate ion concentration in the deep sea could not be used to distinguish between the two terrestrial biosphere scenarios which have been put forth to explain the rise in atmospheric CO_2 content over the last 8000 years. Critical to this distinction is the record of ^{13}C in atmospheric CO_2. More detailed and more accurate measurements on CO_2 from ice cores are needed if the cause of this large Holocene rise in atmospheric CO_2 content is to be pinned down.

[23] **Acknowledgments.** Dan McCorkle of Woods Hole Oceanographic Institution kindly provided sediment samples from his Ontong-Java Plateau box cores. Rusti Lotti provided samples from the LDEO core collection. Stew Sutherland made available water column $CO_3^=$ concentration data for the western equatorial Pacific Ocean. Discussions with Taro Takahashi regarding the best choice of the ΔV for calcite dissolution proved helpful. Financial support was provided by National Science Foundation grant OCE-00-81809. Lamont-Doherty Earth Observatory contribution 6398.

References

Barker, S., and H. Elderfield, Foraminiferal calcification response to glacial-interglacial changes in atmospheric CO_2, *Science*, *297*, 833–836, 2002.

Bijma, J., B. Honisch, and R. E. Zeebe, The impact of the ocean carbonate chemistry on living foraminiferal shell weight: A comment to Broecker and Clark's "Carbonate ion concentration in glacial-age deep waters on the Caribbean Sea", *Geochem. Geophys. Geosyst.*, *3*, November 8, 2002.

Bradshaw, A. L., and P. G. Brewer, High precision measurements of alkalinity and total carbon dioxide in seawater by potentiometric titration: 1. Presence of unknown protolyte(s)?, *Mar. Chem.*, *23*, 69–86, 1988.

Broecker, W. S., and E. Clark, $CaCO_3$ size distribution: A paleo carbonate ion proxy, *Paleoceanography*, *14*, 596–604, 1999.

Broecker, W. S., and E. Clark, Reevaluation of the $CaCO_3$ size-index paleocarbonate ion proxy, *Paleoceanography*, *16*, 669–671, 2001a.

Broecker, W. S., and E. Clark, An evaluation of Lohmann's foraminifera-weight index, *Paleoceanography*, *16*, 531–534, 2001b.

Broecker, W. S., and E. Clark, Pseudo dissolution of marine calcite, *Earth Planet. Sci. Lett.*, in press, 2003.

Broecker, W. S., and T. Takahashi, Neutralization of fossil fuel CO_2 by marine calcium carbonate, in *The Fate of Fossil Fuel CO_2 in the Oceans*, edited by N. R. Andersen and A. Malahoff, pp. 213–248, Plenum, New York, 1977.

Broecker, W. S., Y. Lao, M. Klas, E. Clark, G. Bonani, S. Ivy, and C. Chen, A search for an early Holocene $CaCO_3$ preservation event, *Paleoceanography*, *8*, 333–339, 1993.

Broecker, W. S., E. Clark, D. C. McCorkle, T.-H. Peng, I. Hajdas, and G. Bonani, Evidence for a reduction in the carbonate ion content of the deep sea during the course of the Holocene, *Paleoceanography*, *14*, 744–752, 1999.

Broecker, W. S., J. Lynch-Stieglitz, and E. Clark, What caused the atmosphere's CO_2 content to rise during the last 8000 years?, *Geochem. Geophys. Geosyst.*, *2*, Paper number 2001GC000177, 2001. (Available at http://gcubed.magnet.fsu.edu/main.html)

Brovkin, V., J. Bendtsen, M. Claussen, A. Ganopolski, C. Kubatzki, V. Petoukhov, and A. Andreev, Carbon cycle, vegetation and climate dynamics in the Holocene: Experiments with the CLIMBER-2 model, *Global Biogeochem. Cycles*, *16*, 1139, doi:10.1029/2001GB001662, 2002.

Hales, B., and S. Emerson, Calcite dissolution in sediments of the Ontong-Java Plateau: In situ measurements of porewater O_2 and pH, *Global Biogeochem. Cycles*, *5*, 529–543, 1996.

Hales, B., and S. Emerson, Calcite dissolution in sediments of the Ceara Rise: In situ measurements of porewater O_2, pH and $CO_{2(aq)}$, *Geochim. Cosmochim. Acta*, *61*, 501–514, 1997.

Indermühle, A., et al., Holocene carbon-cycle dynamics based on CO_2 trapped in ice at Taylor Dome, Antarctica, *Nature*, *398*, 121–126, 1999.

Lohmann, G. P., A model for variation in the chemistry of planktonic foraminifera due to secondary calcification and selective dissolution, *Paleoceanography*, *10*, 445–457, 1995.

Petit, J. R., et al., The climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature*, *399*, 429–436, 1999.

Shackleton, N. J., Tropical rainforest history and the equatorial Pacific carbonate dissolution cycles, in *The Fate of Fossil Fuel CO_2 in the Oceans*, edited by N. R. Andersen and A. Malahoff, pp. 401–428, Plenum, New York, 1977.

Sundquist, E. T., Long-term aspects of future atmospheric CO_2 and sea-level changes, in *Sea-Level Change*, edited by R. Revelle, pp. 193–207, Natl. Res. Counc. Stud. in Geophys., Natl. Acad., Washington, D.C., 1990.

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