PALEOCEANOGRAPHY, VOL. 14, NO. 6, PAGES 744-752, DECEMBER 1999

Evidence for a reduction in the carbonate ion content of the deep sea during the course of the Holocene

Wallace S. Broecker,[1] Elizabeth Clark,[1] Daniel C. McCorkle,[2] Tsung-Hung Peng,[3] Irena Hajdas,[4] and Georges Bonani[4]

Abstract. The paleo carbonate ion proxy proposed by *Broecker et al.* [1999] is applied in a search for trends in the Holocene acidity of waters in the transition zone between North Atlantic Deep Water and Antarctic Bottom Water (AABW). A clear signal emerges that the carbonate ion content of waters in this zone declined during the past 8000 years. In order to determine whether this decline represents a strengthening of the northward penetrating tongue of low $CO_3^=$ content AABW or a global reduction of $CO_3^=$ ion, measurements were made on a core from the Ontong Java Plateau in the western equatorial Pacific. Evidence for a similar decline in $CO_3^=$ ion over the course of the Holocene was obtained lending support of the latter explanation. Such a drop is consistent with the recent finding by *Indermühle et al.* [1999] that the CO_2 content of the atmosphere (as recorded in the Taylor Dome Antarctica ice core) rose by 20-25 ppm during the past 8000 years.

1. Introduction

In a separate paper, *Broecker et al.* [1999] have shown that in today's tropical ocean the fraction of $CaCO_3$ contained in grains >63 μm in size is closely tied to the pressure-normalized carbonate ion content of water bathing the seafloor (see Figure 1). While the size proxy proves to be closely related to the pressure-normalized carbonate ion concentration in today's ocean, before it can be accepted as a valid paleoproxy, two assumptions must be tested. First, is it safe to assume that the initial size distribution of the carbonate remains constant with time? Second, does the breakup of foraminifera shells continue after burial beneath the core-top bioturbation zone? To minimize the impact of both of these possible complications, we confined our first study to Holocene-age sediments. Further, as a test of the first assumption, time series measurements were made on cores from within the sensitive size index range and on cores from above the lysocline.

This study began with measurements on sediments from the western tropical Atlantic in an attempt to determine how the $CO_3^=$ ion of deep-sea waters changed during the course of the Holocene. Since the carbonate ion content of a given deep water parcel in the western tropical Atlantic is closely related to its proportions of North Atlantic Deep Water (NADW) and Antarctic Bottom Water (AABW), such a reconstruction could potentially be used to place constraints on changes in the extent of the penetration of AABW into the tropical Atlantic and hence on the relative strengths of production of deep water in the north and south polar regions.

In today's Atlantic the silica content of deep Atlantic provides an excellent index of the proportions of NADW and AABW. New NADW has a low SiO_2 content (12 μmol kg^{-1}), and AABW enters the South Atlantic with a high SiO_2 content (125 μmol kg^{-1}). That very little silica is added to deep waters in the Atlantic by opal dissolution is demonstrated by the straight line correlation between SiO_2 and PO_4^* (PO_4 + O_2/175-195). Ambient NADW in the tropics contains ~33 μmol kg^{-1} SiO_2, suggesting that it has incorporated ~20% of upwelled AABW. As shown in Figure 2, the deep waters in the western equatorial Atlantic range from 100 μmol kg^{-1} at the bottom to ~33 μmol kg^{-1} in the core of the NADW mass. The carbonate ion content of waters in the transition zone between two water masses has an inverse linear relationship to silica content (see Figure 2). We use the more extensive and accurate silica measurements and the mean trend of the carbonate-silica relationship to estimate the $CO_3^=$ ion content of the water currently bathing the cores used in this study as well as to determine their position within the mixing zone.

In the paragraphs that follow we present evidence that suggests that a major reduction in the carbonate ion content of the waters in the transition zone between AABW and NADW occurred during the course of the Holocene. While this decrease might be interpreted as a strengthening of the northward penetration of AABW, it could equally well be the result of a global drawdown of carbonate ion. Much of this research was completed before the publication of a paper by *Indermühle et al.* [1999] that presented measurements from the Taylor Dome Antarctica ice core that clearly demonstrate that the CO_2 content of the atmosphere rose by 20-25 ppm between 8000 years ago and preindustrial time. If, as *Indermühle et al.* suggest, this rise was the result of a decrease in terrestrial biomass, then it must have been matched by a corresponding decrease in the carbonate ion content of deep ocean waters. In an effort to determine whether or not this was the case we made additional measurements on cores from the Ontong Java Plateau.

---

[1] Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York.

[2] Woods Hole Oceanographic Institution, Woods Hole, Massachusetts.

[3] Ocean Chemistry Division, Atlantic Oceanographic and Meteorological Laboratory, NOAA, Miami, Florida.

[4] Institute for Theoretical Physics, Eidgenossische Technische Hochschule Hoenggerberg, Zürich, Switzerland.

Paper number 1999PA900038.
0883-8305/99/1999PA900038$12.00

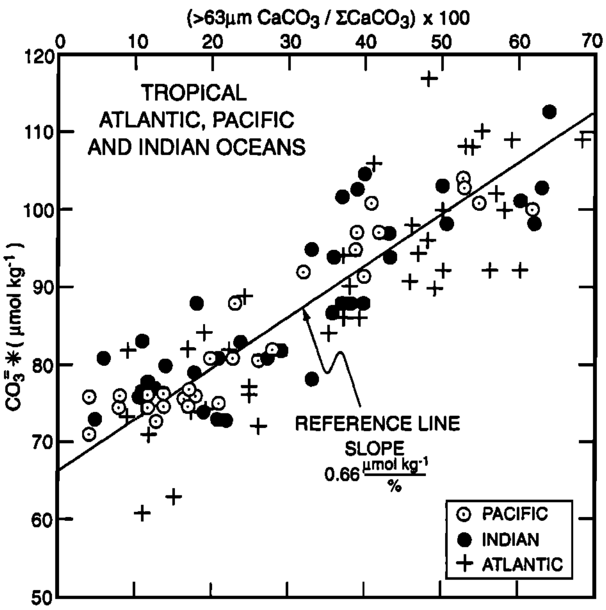

Figure 1. Relationship between the percentage of the $CaCO_3$ in the >63 µm size fraction and the pressure-normalized carbonate ion content of the bottom water at the core site as obtained by *Broecker et al.* [1999]. The latter is calculated as follows: $CO_3^{=*} = CO_3^{=} + 20(4.0\text{-}z)$ µmol kg^{-1} where $CO_3^{=}$ is the in situ carbonate ion content and z is the water depth in kilometers. The pressure-normalized carbonate ion content is equivalent to the $\Delta CO_3^{=}$ (in situ - saturation) and $CO_3^{=}$ (in situ)/ $CO_3^{=}$ (saturation) often used to express the degree of supersaturation or undersaturation. It has the advantage that it dodges the need to select an absolute solubility for calcite.

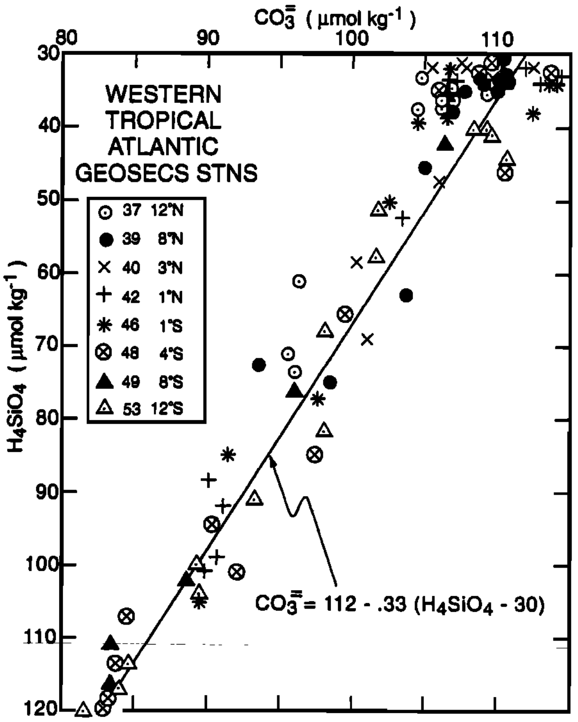

Figure 2. Relationship between silica and carbonate ion contents of deep waters in the western tropical Atlantic as determined during the Geochemical Ocean Sections Study (GEOSECS).

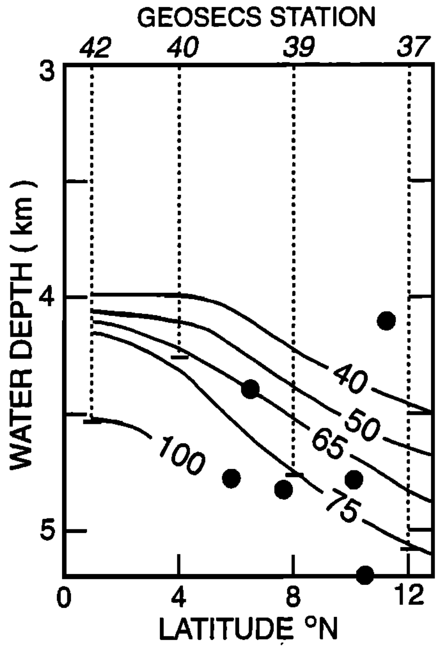

Figure 3. Contours of deep water SiO_2 content (µmol kg^{-1}) along the Geochemical Ocean Sections Study (GEOSECS) track in the western tropical Atlantic. The latitudes and water depths for the GEOSECS stations in the range 0 to 12°N are shown by the dashed lines. The large dots show the latitudes and water depths for the deep-sea cores employed in this study.

2. Measurements

The Atlantic samples employed in this study are piston and trigger weight cores in the Lamont-Doherty collection (see Figure 3). The Pacific samples are from a box core taken by one of us (DM). Radiocarbon data measurements were conducted by the accelerator mass spectrometry (AMS) method at Eidgenossische Technische Hochschule (ETH) in Zurich, Switzerland. A reservoir correction of 400 years was applied. The $CaCO_3$ measurements were made using the Lamont-Doherty Earth Observatory (LDEO) coulometer, and the size fraction results were obtained by weighing the >63 µm sieve fraction and dividing by the weight of the total amount of $CaCO_3$ in the sample. A large number of measurements show that except for highly dissolved samples the $CaCO_3$ content of the >63 µm material averages 94 ± 1%.

The results of the measurements are displayed in Figures 4-9. As can be seen, except for the shallowest, all of the Atlantic cores reveal a broad maximum in the >63 µm $CaCO_3$ percent. This maximum occurs in the early Holocene (between 10,000 and 7000 radiocarbon years). It is matched by a corresponding maximum in the bulk $CaCO_3$ content of the sediment. As summarized in Table 1, the size fraction index decreases by an average of ~17% between the maximum and the core top. On the basis of the slope of 0.66 µmol kg^{-1} per percent change in the index (see Figure 1) this shift corresponds to an 11 µmol kg^{-1} decrease in $CO_3^{=}$ ion concentration. Further, the core-top $CaCO_3$ size fractions for all but one of these cores conform to the trend established for the larger set of tropical cores (see Figure 1). That for core V16-63 at 4.77 km depth is anomalously high. The consistency between the wire out and water depth in the shipboard core records suggests that the depth of this core is correct.

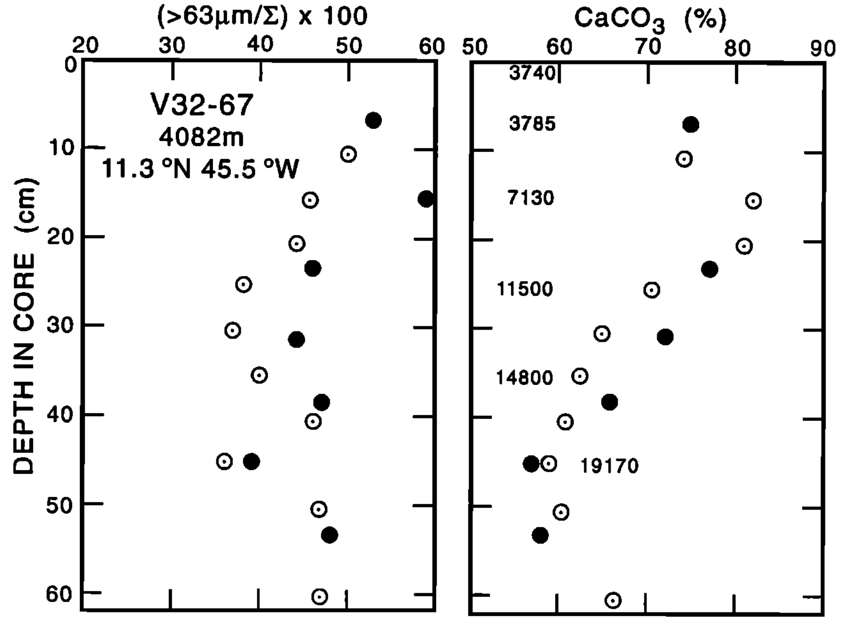

Figure 4. Downcore $CaCO_3$ size fraction and $CaCO_3$ content results for core V32-67 from 4.08 km depth. The open circles represent samples from the piston core, and the solid circles represent samples from the trigger weight core as documented by *Broecker et al.* [1993]. The depths for the latter samples have been multiplied by 1.5 to account for the foreshortening relative to the piston core. Shown also are the reservoir-corrected ^{14}C ages.

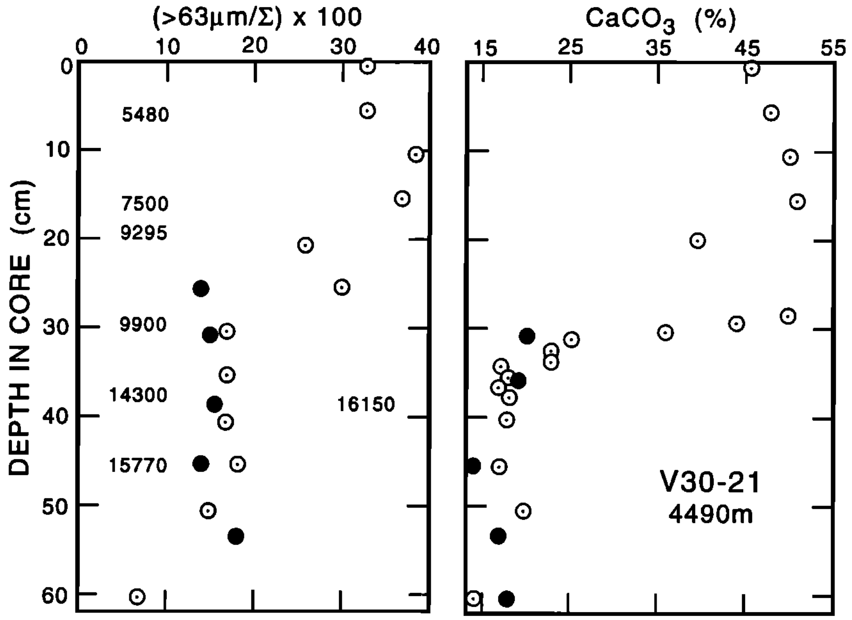

Figure 5. Downcore $CaCO_3$ size fraction and $CaCO_3$ content results for core V30-21 from 4.49 km depth. The open circles represent samples from the piston core, and the solid circles represent samples from the trigger weight core. The depths for the latter samples have been multiplied by 1.5 to account for the foreshortening relative to the piston core as documented by *Broecker et al.* [1993]. Shown also are the reservoir-corrected ^{14}C ages.

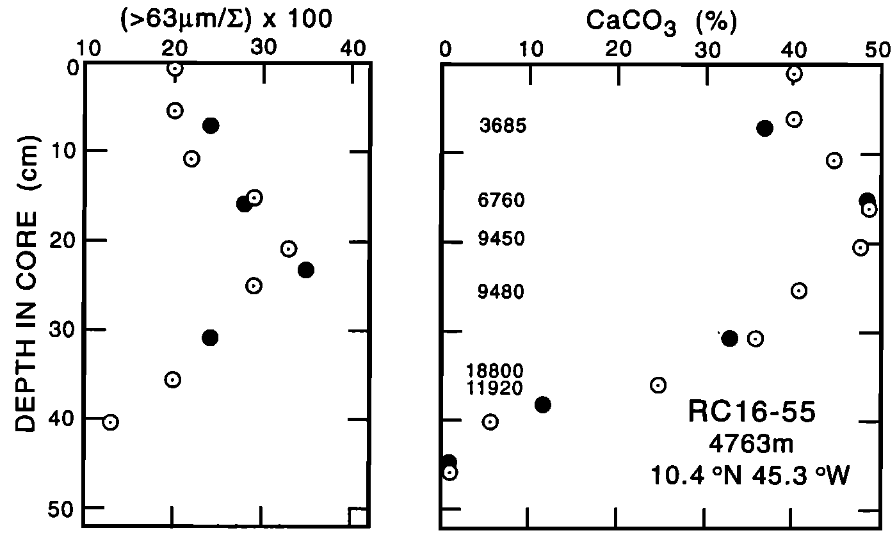

Figure 6. Downcore $CaCO_3$ size fraction and $CaCO_3$ content results for core RC16-55 from 4.76 km depth. The open circles represent samples from the piston core, and the solid circles represent samples from the trigger weight core. The depths for the latter samples have been multiplied by 1.5 to account for the foreshortening relative to the piston core as documented by *Broecker et al.* [1993]. Shown also are the reservoir-corrected ^{14}C ages.

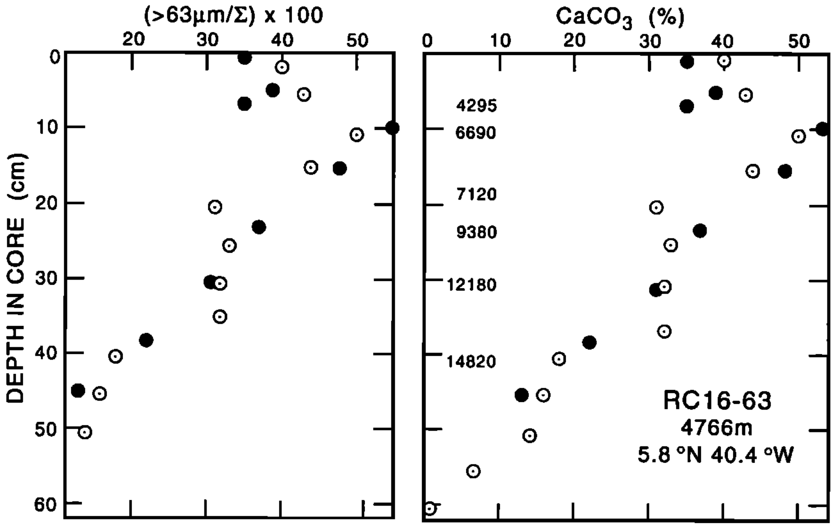

Figure 7. Downcore $CaCO_3$ size fraction and $CaCO_3$ content results for core RC63-16 from 4.77 km depth. The open circles represent samples from the piston core, and the solid circles represent samples from the trigger weight core. The depths for the latter samples have been multiplied by 1.5 to account for the foreshortening relative to the piston core as documented by *Broecker et al.* [1993]. Shown also are the reservoir-corrected ^{14}C ages.

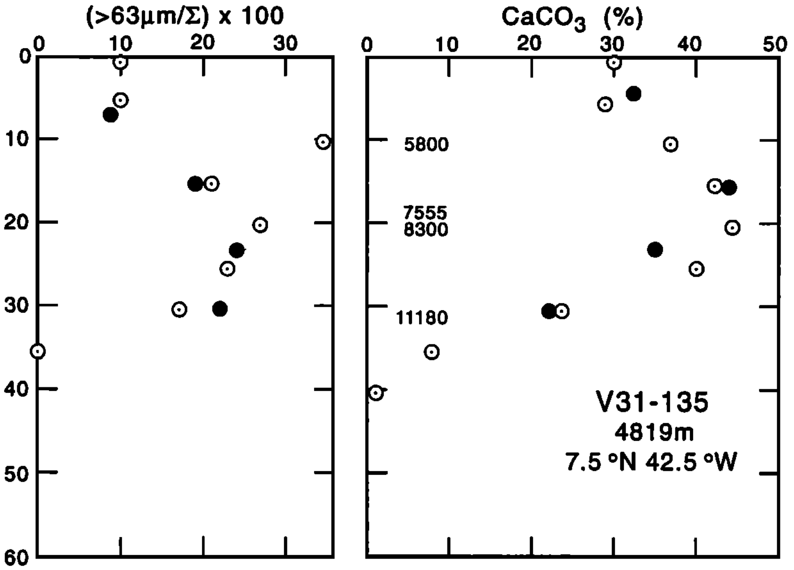

Figure 8. Downcore $CaCO_3$ size fraction and $CaCO_3$ content results for core V31-135 from 4.82 km depth. The open circles represent samples from the piston core, and the solid circles represent samples from the trigger weight core. The depths for the latter samples have been multiplied by 1.5 to account for the foreshortening relative to the piston core as documented by *Broecker et al.* [1993]. Shown also are the reservoir-corrected ^{14}C ages.

3. Discussion

Had this study been confined to the Atlantic Ocean, the most obvious interpretation would be that the extent of penetration of AABW into the northern Atlantic increased during the course of the Holocene. This, of course, would imply a progressive weakening of the conveyor. This conclusion is consistent with the absence of $CaCO_3$ size decrease in the shallowest Atlantic core (V32-67 at 4.08 km) and the smaller magnitude of the decrease in the next shallowest Atlantic core (V30-21 at 4.49 km). However, it must be kept in mind that as the present-day pressure-normalized carbonate ion content of the water bathing the V32-67 lies above the limit of 105 µmol kg^{-1} which marks the onset of the reduction of the size fraction index [see *Broecker et al.*, 1999]. Hence were the carbonate ion concentration even higher than today's during the early Holocene, then no increase in solution would be expected. Thus, while the results for this set of cores suggest that the drop in carbonate ion content was confined to the transition zone separating the two water masses, this need not have been the case.

Indeed, this was our thinking at the time we received a paper by *Indermühle et al.* [1999], which documents a steady increase in the CO_2 content of the atmosphere from ~260 ppm 8000 years ago to ~282 ppm in the year 1800 AD. As the time span over this rise exceeds by an order of magnitude the mixing time of the ocean, if biomass driven, as *Indermühle et al.* [1999] contend, it must have been accompanied by a drop in carbonate ion content of the deep ocean. As there is a roughly inverse relationship between $[CO_3^=]$ and pCO_2, the change in $CO_3^=$ in the deep sea would be as follows:

$$\begin{aligned} \Delta CO_3^= &= [CO_3^=]_{8K} - [CO_3^=]_{0K} \\ &\cong \left(\frac{p^{0K}_{CO_2}}{p^{8K}_{CO_2}} - 1\right)[CO_3^=]_{0K} \\ &\cong \left(\frac{282}{260} - 1\right) 120\ \mu mol\ kg^{-1} \\ &\cong 10\ \mu mol\ kg^{-1}, \end{aligned} \tag{1}$$

where 120 µmol kg^{-1} is the $CO_3^=$ ion content of newly formed deep waters in today's ocean. Actually when the role of borate is

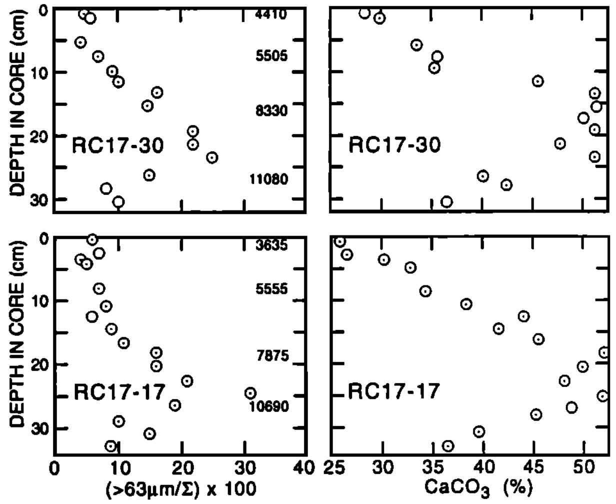

Figure 9. $CaCO_3$ size fraction and $CaCO_3$ content from two piston cores raised from 5.20 km depth at 11°N. Shown also are the reservoir-corrected ^{14}C ages.

Table 1. Locations, Water Depths and Sedimentation Rates for the Eight Cores on Which This Study is Based

Core	Latitude	Longitude	Depth, m	Sedimentation Rate, cm 10^3yr^{-1}	$CaCO_3$ Top, %	$CaCO_3$ Maximum, %	63µ/Σ Top	63µ/Σ Maximum	Δmax top	Today's SiO_2, µmol kg^{-1}	Today's $CO_3^=$, µmol kg^{-1}	Today's $CO_3^=$*, µmol kg^{-1}	Core-Top Proxy $CO_3^=$*, µmol kg^{-1}
						Western Tropical Atlantic							
V32-67	11.3°N	45.5°W	4082	2.5	74	82	53	no max	-	36	110	108	>105
V30-21	6.6°N	42.8°W	4490	3.0	46	50	33	39	6	65	100	90	89
RC16-55	10.4°N	45.3°W	4763	2.7	39	49	20	35	15	70	99	84	80
RC16-63	5.8°N	40.4°W	4766	2.4	37	52	37	52	15	~80	95	80	90
V31-135	7.5°N	42.5°W	4818	2.3	30	44	10	27	17	80	95	79	72
RC17-30	11.0°N	41.0°W	5200	2.5	29	53	5	24	19	~80	~94	~70	70
RC17-17	10.8°N	41.2°W	5204	2.5	26	54	5	27	22	~80	~94	~70	70
						Ontong Java Plateau							
M91-9-BC56	0.0	162°E	4040	1.7	76	84	22	39	17	-	82	81	81

Also given are the $CaCO_3$ contents and the >63 µm percentages for core top and for Holocene maximum sediment. In the next to last three columns are given the silica content, carbonate ion content, and the pressure-normalized-carbonate ion content for today's bottom water at these core sites. The latter is calculated as follows: $CO_3^=* = CO_3^= + (4.0\text{-}z)20$ µmol kg^{-1}. In the last column is given the pressure-normalized $CaCO_3$ content calculated from the core-top $CaCO_3$ size distribution using the relationship obtained by *Broecker et al.* [1999] (summarized in Figure 1).

taken into account, the expected drop in deep ocean carbonate ion turns out to be a bit smaller, i.e., 8.3 μmol kg^{-1}.

We have also carried out the calculation using the 10-box Pandora model [*Broecker and Peng*, 1989]. We did this by prescribing that the trend in atmospheric CO_2 content follow the observations of *Indermühle et al.* [1999]. We exclude interaction with the $CaCO_3$ in bottom sediment. The results are shown in Figure 10. Because of the finite mixing time of the ocean, the drop in $CO_3^=$ concentration is a bit smaller than would be the case were steady state to have been established.

Upon learning about these new CO_2 results, we turned our attention to a box core (B56) from the western equatorial Pacific at a depth of 4.04 km, which places it within the transition zone separating shallower $CaCO_3$-rich sediment from the deep $CaCO_3$-free sediment. As shown in Figure 11, this core has a pronounced

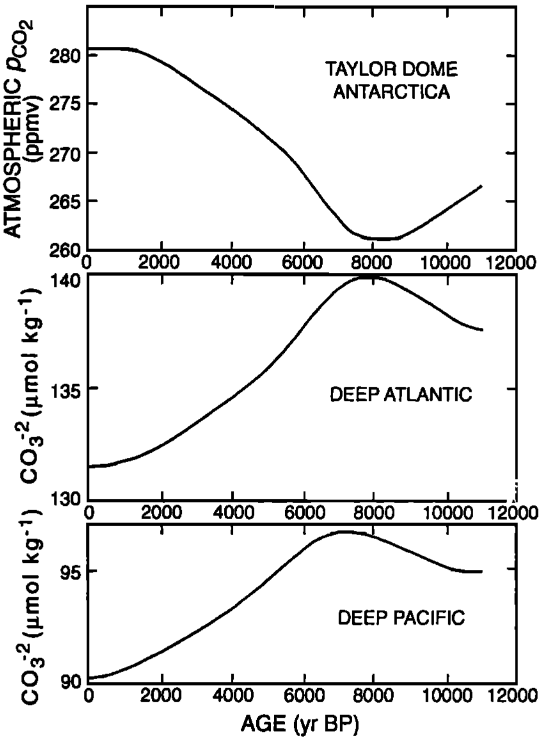

Figure 10. Calculations carried out using the 10-box Pandora model [*Broecker and Peng*, 1989]. The CO_2 record of *Indermühle et al.* [1999] is used to drive the model. As can be seen, $CO_3^=$ concentration in the model's deep Atlantic reservoir drops by a little over 8 μmol kg^{-1}, and the model's deep Pacific reservoir drops by a little under 7 μmol kg^{-1}. The fluxes in the Pandora model have been selected to best fit the present-day distributions of natural radiocarbon, phosphorus, alkalinity, and total dissolved inorganic carbon.

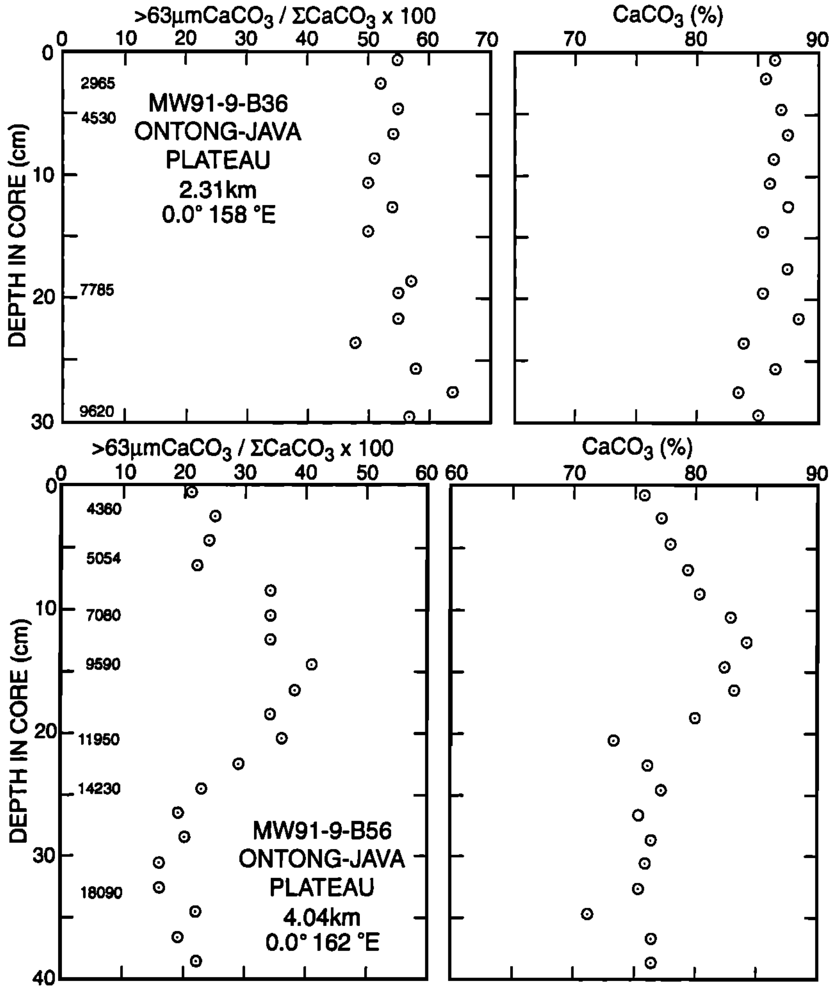

Figure 11. Downcore $CaCO_3$ size fraction and $CaCO_3$ results for two box cores raised from the equator on the Ontong Java Plateau (western Pacific Ocean). One core (B56) is located within the depth zone where breakup of calcite grains is occurring, and the other core (B36) is located well above the depth at which breakup commences.

early Holocene maximum (centered at ~9600 ^{14}C years B.P.) in the $CaCO_3$ size fraction index (and in bulk $CaCO_3$ as well). In order to exclude the possibility that this change is the product of changing ecology of the calcite producers in overlying surface waters we also made measurements on a nearby box core from well above the lysocline (B36 from 2.3 km). As can be seen, there is no significant change in size index during the past 8000 years.

We have also made reconnaisance measurements on several other cores from the equator on the Ontong Java Plateau. As summarized in Table 2, those from water deep enough to be currently bathed in corrosive waters show decreases in CO_3 ion between early Holocene time and the core top. So also do cores from the tropical Indian Ocean studied by *Peterson* [1984] as part of his Ph.D. thesis research.

Indermühle et al. [1999] attribute the increase in atmospheric CO_2 content to a large reduction in terrestrial biomass during the course of the Holocene. They point to results of measurements of the δ^{13}C for CO_2 extracted from Taylor Dome ice as support for this hypothesis. However, as the ^{13}C decline expected from their hypothesis is only ~0.25‰ in light of the magnitude of the measurement errors (±0.08‰) and of the extent scatter of the measurements around the model curve, the ^{13}C constraint is not strong enough to exclude alternate explanations.

One such alternate explanation was suggested by *Broecker et al.* [1993]. As reproduced in Figure 12, *Broecker et al.* called upon an early Holocene increase in terrestrial biomass. The magnitude of this increase (i.e., 500 GtC) has been estimated on the basis of the 0.35‰ decrease during glacial time of the δ^{13}C for

Table 2. Low Resolution Records for Cores From the Ontong Java Plateau and for Cores From the Ninety East Ridge

Core	Latitude	Longitude	Water Depth, km	Depth in Core, cm	^{14}C Age, 10^3 yrs	>63/Σ Index, %	Δ Index 8k - 0k, %
			Ontong Java Plateau				
BC37	0.0	159°E	2.45	2	3.58	53	
				20	7.70	53	0
BC22	0.0	160°E	2.96	2	2.55	59	
				25	7.98	48	+11
BC63	0.0	161°E	3.16	2	3.01	39	
				20	8.33	46	-7
BC51	0.0	161°E	3.43	2	3.04	32	
				20	8.66	43	-11
BC53	0.0	161°E	3.71	2	3.72	23	
				20	11.00	31	-8
BC56	0.0	162°E	4.04	2	4.36	20	
				20	11.95	27	-7
			Ninety Degree East Ridge				
V34-55	6.0°S	89°E	2.99	top	~3	60	
				12	~8	66	-6
V34-54	6.1°S	89°E	3.25	top	~3	54	
				10	~7	57	-3
V34-53	6.1°S	90°E	3.81	top	~3	49	
				5	~6	60	
				10	~10	49	(-6)
V34-52	6.2°S	90°E	3.98	top	~3	29	
				10	5	34	
				20	10	51	(-10)
V34-49	6.4°S	91°E	4.09	top	~3	47	
				10	~10	52	-5
V34-51	6.2°S	90°E	4.38	top	3	23	
				10	~7	34	-6

The Ontong Java Plateau data are from *Broecker et al.*, [1999], and the Ninety East Ridge data are from *Peterson* [1984]. As can be seen, 10 of the 12 cores show a decrease in the size fraction index between early Holocene and the core top. The average decrease for the Pacific cores from deeper than 3 km is 7%, while that for the Indian Ocean cores is 6%. It must be kept in mind that as the core tops represent a mixture of sediment deposited over the past several thousand years, these changes must be considered lower limits. The decrease in carbonate ion content has likely continued during the interval represented by the core-top material. Also, the single early Holocene sample may not correspond to the $CO_3^=$ maximum.

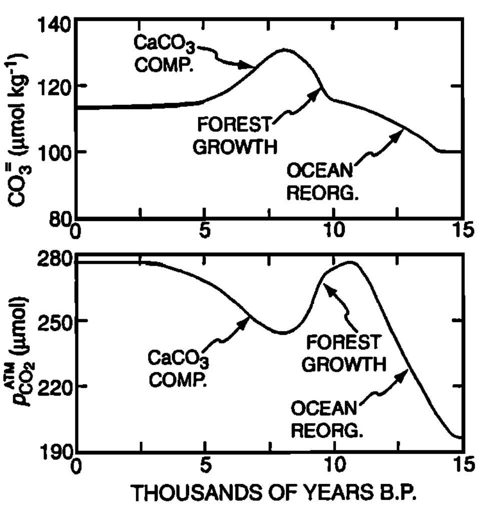

Figure 12. Scenario presented by *Broecker et al.* [1993] to explain the Holocene CO_2 record from Byrd Station, Antarctica, published by *Neftel et al.* [1988] indicating that a 0.35% rise in the $\delta^{13}C$ for ocean ΣCO_2 would lower the CO_2 content of the atmosphere by ~25 ppm. As the regrowth phase came to a close, $CaCO_3$ compensation would reestablish the steady state depth of the lysocline and thereby lower the $CO_3^=$ concentration in the deep sea and raise the CO_2 content of the atmosphere. The time constant for this recovery would be several thousand years.

benthic foraminifera [*Curry et al.*, 1988]. The subsequent rise in atmospheric CO_2 content was attributed to $CaCO_3$ compensation in the deep ocean. The rise in oceanic $CO_3^=$ concentration caused by the early Holocene CO_2 uptake would have deepened the lysocline, causing the accumulation of $CaCO_3$ on the seafloor to exceed the supply to the ocean of the ingredients for $CaCO_3$. Hence the ocean's $CO_3^=$ ion content would have been drawn down, and as a result, the CO_2 content of the atmosphere would have risen. Of course, were this scenario the correct one, then it would induce no early to late Holocene change in the $\delta^{13}C$ for atmospheric CO_2.

A comparison of the size-fraction-index- based changes in carbonate ion content and those expected from the CO_2 record is as follows. As summarized in Table 1, the index change for the Ontong-Java core is about the same as that for the deep western Atlantic cores (i.e., 17 ± 3%). This translates to an 11 ± 2 µmol kg^{-1} reduction $CO_3^=$ ion. The expected decline based on the 260-282 ppm rise in atmospheric CO_2 content is 8 ± 1 µmol kg^{-1}. While the observed reduction is somewhat larger than the predicted one, the difference is too small to merit extended discussion. Two caveats must be stated in this regard. First, were the change in atmospheric CO_2 over the past 8000 years the result of a reduction in the strength of the ocean's biological pump, then, of course, the simple tie between deep ocean $CO_3^=$ concentration and atmospheric CO_2 concentration would not apply. The second is that were the *Archer and Maier-Reimer* [1994] hypothesis correct, as has been suggested by *Sanyal et al.* [1995], then an even larger Holocene $CaCO_3$ compensation event would be expected. As part of the next paper in this series that concerns glacial to Holocene changes in the index, we plan to discuss this aspect.

4. Conclusions

The fraction of the $CaCO_3$ in the >63 µm size fraction has decreased over the past 8000 years in cores from both the western tropical Atlantic and Pacific Oceans. The magnitude of this decline suggests an 11 ± 2 µmol kg^{-1} drop in $CO_3^=$ content of waters in the deep sea. Such a drop is consistent with the finding by *Indermühle et al.* [1999] that the CO_2 content of the atmosphere rose by ~22 ppm over the past 8000 years. As the explanation involving an 8000 year to present decrease in Holocene biomass presented by *Indermühle et al.* [1999] and the explanation involving $CaCO_3$ compensation presented by *Broecker et al.* [1993] require similar deep ocean $CO_3^=$ concentration changes, these results do not allow either of these explanations to be eliminated. This distinction awaits a highly precise reconstruction of the record for the $\delta^{13}C$ for atmospheric CO_2.

Thus what started out as an application of our paleocarbonate ion proxy to assess the magnitude changes in the position of the interface between NADW and AABW in the western Atlantic underwent a midcourse correction. With the publication by *Indermühle et al.* [1999] of a Holocene atmospheric CO_2 record we quickly switched our strategy and used this new finding as a test of our proxy. Could our size fraction index reproduce the $CO_3^=$ concentration decline that likely accompanied the observed CO_2 rise? It did.

Acknowledgments. Financial support was provided by National Science Foundation grant ATM 97-30546. This is LDEO contribution number 5964.

References

Archer, D., and E. Maier-Reimer, Effect of deep-sea sedimentary calcite preservation on atmospheric CO_2 concentration, *Nature, 367*, 260-263, 1994.

Broecker, W. S., and E. Clark, $CaCO_3$ size distribution: A paleocarbonate ion proxy, *Paleoceanography*, in press, 1999.

Broecker, W. S., and T.-H. Peng, The cause of glacial to interglacial atmospheric CO_2 change: A polar alkalinity hypothesis, *Global Biogeochem. Cycles, 3*, 215-239, 1989.

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

Curry, W. B., J. C. Duplessy, L. D. Labeyrie, and N. J. Shackleton, Changes in the distribution of $\delta^{13}C$ of deep water ΣCO_2 between the last glaciation and the Holocene, *Paleoceanography, 3*, 317-342, 1988.

Indermühle, A., et al., Holocene carbon cycle based on a high-resolution CO_2 ice core record from Taylor Dome, Antarctica, *Nature, 398*, 121-126, 1999.

Neftel, A., H. Oeschger, T. Staffelbach, and B. Stauffer, CO_2 record in the Byrd ice core 50,000-5,000 years BP, *Nature, 331*, 609-611, 1988.

Peterson, L. C., Late Quaternary deep-water paleoceanography of the eastern equatorial Indian Ocean: Evidence from benthic foraminifera, carbonate dissolution, and stable isotopes, Ph.D. thesis, 429 pp., Brown Univ., Providence, R. I., 1984.

Sanyal, A., N. G. Hemming, G. N. Hanson, and W. S. Broecker, Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera, *Nature, 373*, 234-236, 1995.

G. Bonani and I. Hajdas, ITP ETH Hoenggerberg, CH-8093 Zürich, Switzerland.

W. Broecker and E. Clark, Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964 (broecker@ldeo.columbia.edu)

D. C. McCorkle, Woods Hole Oceanographic Institution, Woods Hole, MA 02543.

T.-H. Peng, OCD, AOML, NOAA, Miami, FL 33149-1026.

(Received April 6, 1999;
revised June 25, 1999;
accepted July 1, 1999.)