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What caused the atmosphere's CO_2 content to rise during the last 8000 years?

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[1] **Abstract:** We make a case that the 20 ppm rise in atmospheric CO_2 content over the last 8000 years was at least in part a consequence of the 500 Gt C increase in terrestrial biomass early in the present interglacial rather than of a 200 Gt C decrease in terrestrial biomass during the latter part of the Holocene as proposed by *Indermühle et al.* [1999]. In support of this claim, we present new ^{13}C measurements from an Ontong Java Plateau box core, which do not reproduce the trend deduced from measurements on CO_2 from the Taylor Dome ice core. In attempt to distinguish between scenarios put forth to accounting for the late Holocene rise in atmospheric CO_2 content, we also made foraminifera shell weight measurements on three box cores from the Ontong Java Plateau. We were surprised to find that the early Holocene $CaCO_3$ preservation event we sought was strongly depth dependent. The largest magnitude was at 4 km where $CO_3^=$ ion concentrations appear to have been 30 μmol/kg higher than today's and hence nearly as high as those in today's North Atlantic Deep Water.

Keywords: Paleocarbonate ion; Holocene CO_2; glacial ^{13}C; foraminifera shell weights.

Index terms: Geochemical cycles; biogeochemical processes; marine sediments—processes and transport; meteorology and atmospheric dynamics—general or miscellaneous.

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1. Introduction

[2] *Indermühle et al.* [1999] postulate on the basis of CO_2 and ^{13}C data from the Taylor Dome Antarctica ice core that a large decrease in terrestrial biomass (∼200 Gt C) occurred during the last 8000 years. If correct, this finding has important implications for it suggests that our planet's biomass inventory is highly responsive to the rather small changes in climate. If so, then it might be expected to undergo a sizable change in response to the ongoing greenhouse warming. Were this warming to produce a comparable change in biomass, it would significantly impact projections of the increase in the atmosphere's CO_2

content for 200 Gt C is equivalent to 30 years of fossil fuel CO_2 emissions at the current rate.

[3] However, can the biomass reduction scenario be accepted at face value? The case rests on a set of ^{13}C to ^{12}C ratios measured on CO_2 contained in Antarctic ice. M. Wahlen (personal communication, 2001) is frank to admit serious experimental problems had to be overcome in order to avoid contamination introduced by CO_2 absorbed onto surfaces of his apparatus. The small signal (0.2‰) to measurement error (0.06‰) ratio and the scatter of the results (0.08‰) around the model curve offer no assurance that, despite his monumental effort, these difficulties were fully conquered. We maintain that this data set does not exclude the possibility that there has been no measurable trend in ^{13}C of atmospheric CO_2 during the last 8000 years. Thus the conclusion that a large decrease in terrestrial biomass occurred is at risk.

[4] The demonstration that the CO_2 rise was accompanied by a draw down in the carbonate ion concentration in the deep sea restricts the range of alternate scenarios which could be put forward to account for the atmospheric CO_2 rise during the last 8000 years. Size-fraction measurements for cores from both the western tropical Atlantic and the western tropical Pacific suggest that the carbonate ion concentration declined over the last 8000 years by an amount consistent with that expected if the whole ocean remained close to chemical equilibrium with the atmosphere [*Broecker et al.*, 1999]. This finding appears to rule out scenarios involving changes in the strength of the ocean's biological pump. For in this case, the carbonate ion concentration in the deep ocean would not have changed. However, of course, this carbonate ion reconstruction does not exclude the *Indermühle et al.* [1999] biomass hypothesis.

[5] However, the deep-sea carbonate ion concentration record is also consistent with a quite different scenario, indeed the one that we favor (see Figure 1). It is as follows. The 0.35‰ glacial-interglacial change in the $\delta^{13}C$ for benthic foraminifera is widely interpreted as signaling a 500 Gt C reduction in terrestrial biomass during glacial time [*Curry et al.*, 1988]. The restoration of this missing biomass during early postglacial time would have caused a large (up to 17 μmol/kg) increase in the carbonate ion concentration in the deep ocean causing the saturation horizon for calcite to deepen by up to one kilometer [*Broecker and Peng*, 1987]. Such a deepening would have thrown the ocean's $CaCO_3$ budget out of kilter, causing the accumulation of $CaCO_3$ in sediments to exceed the supply to the ocean of the ingredients for $CaCO_3$. This would have led to a draw down in the carbonate ion content of the entire ocean and of course a complementary increase in the partial pressure of CO_2 in ocean waters and hence in the atmosphere. The timing and magnitude of this CO_2 rise depends on the time course of the biomass restoration and on the response time for the subsequent carbonate ion draw down. As the latter has been estimated to be of the order of 5000 years [*Broecker and Takahashi*, 1977; *Sundquist*, 1990a, 1990b] broadly speaking, there is no inconsistency between the CO_2 rise over the last 8000 years and expectation from this compensation scenario. Further, the magnitude of the response (i.e., ~20 μatm) is consistent with expectation.

[6] The biomass restoration hypothesis is not the only one that could be substituted for that proposed by *Indermühle et al.* [1999]. So also could the respiration CO_2 hypothesis [*Archer and Maier-Reimer*, 1994]. In an attempt to explain the glacial-interglacial cycle of atmospheric CO_2 content, this hypothesis calls for a glacial increase in the intensity of dissolution

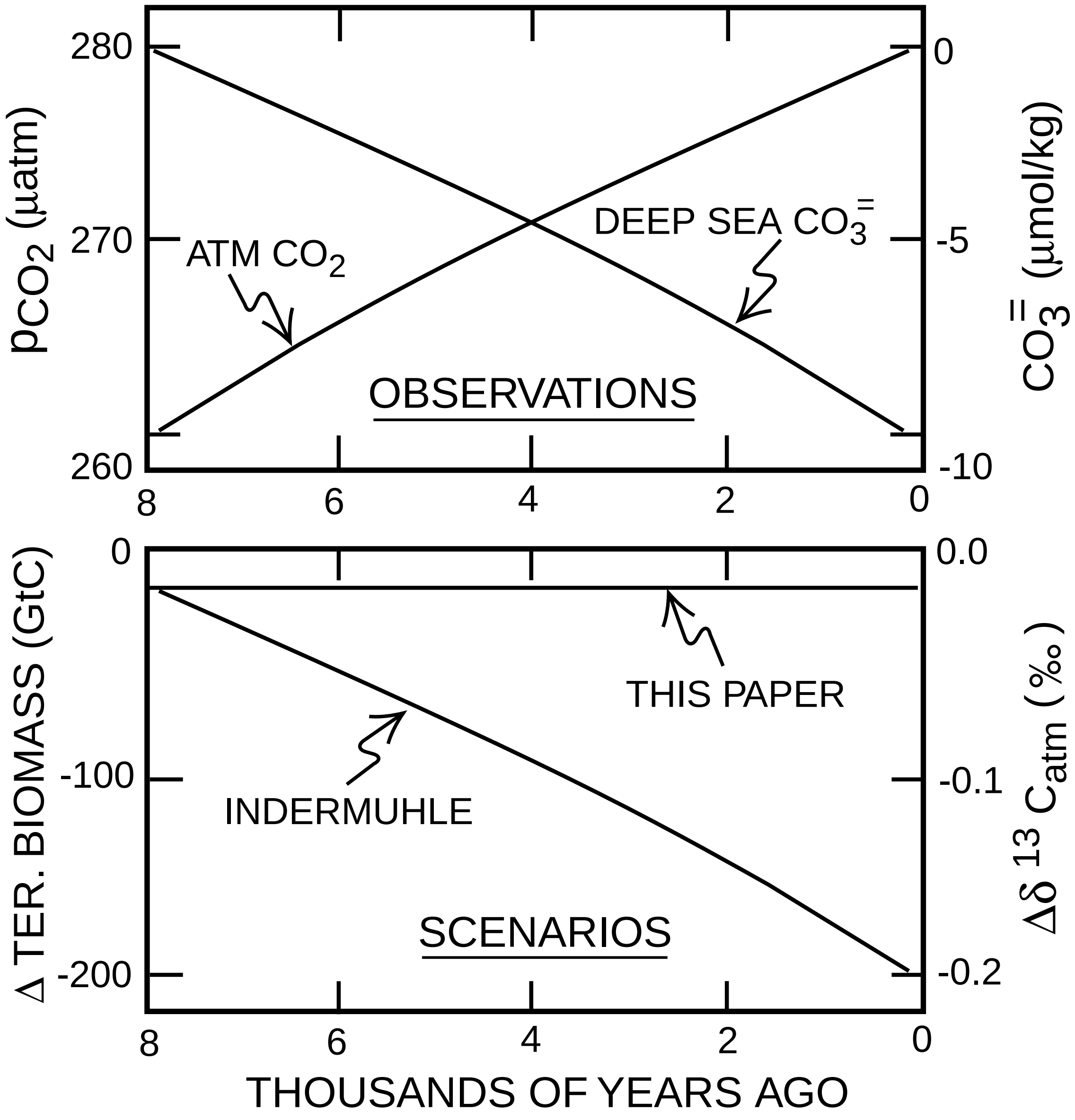

Figure 1. Measurements from the Taylor Dome ice core [*Indermühle et al.*, 1999] document that the CO_2 content of the atmosphere rose from ~260 µatm 8000 years ago to about 280 µatm prior to the Industrial Revolution. Measurements of the size fraction index in deep-sea cores from the Atlantic and Pacific Oceans [*Broecker et al.*, 1999] suggest that a drop in the carbonate ion concentration of deep-seawater complimented this rise. *Indermühle et al.* [1999] attribute the CO_2 rise to a 200 Gt C reduction in terrestrial biomass and present ^{13}C measurements on CO_2 trapped in Taylor Dome ice bubbles in support of their scenario. We challenge this explanation and substitute for it one that involves a readjustment of ocean chemistry in response to a 500 Gt C increase in terrestrial biomass during early postglacial time (i.e., before 8000 years ago).

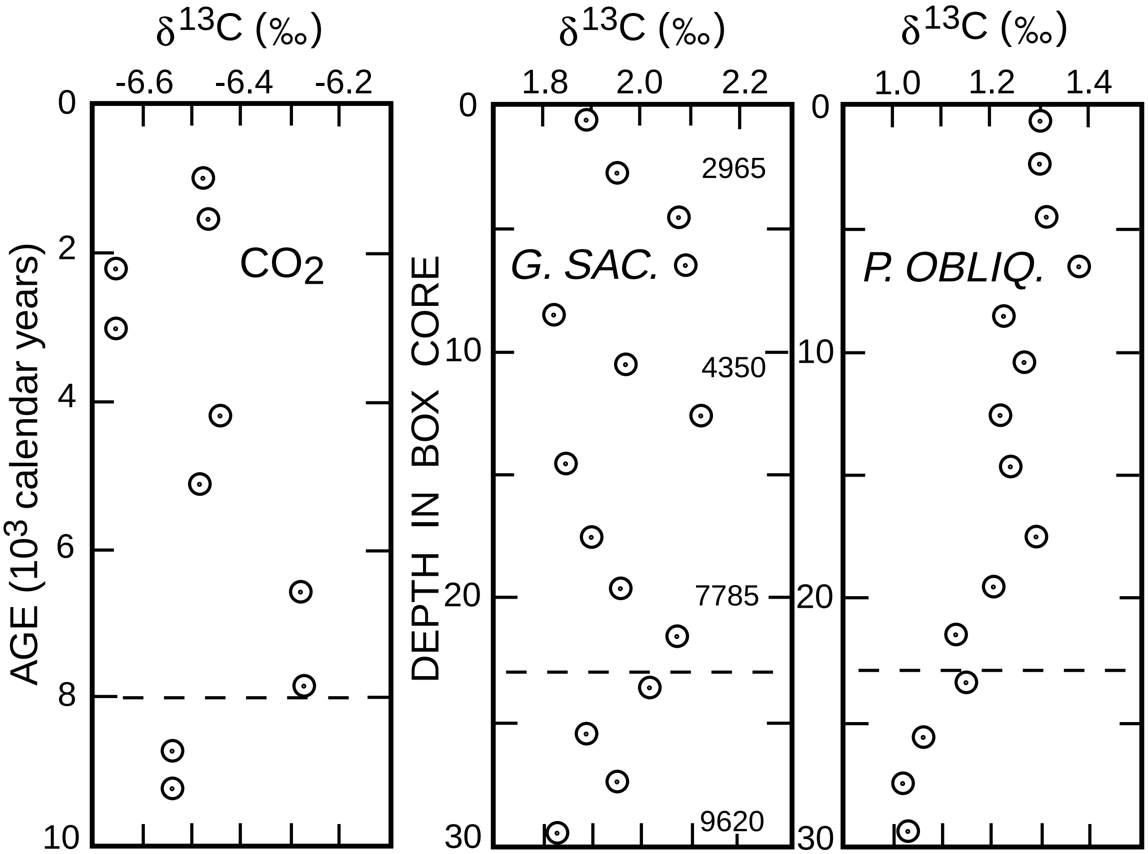

Figure 2. Comparison of the $\delta^{13}C$ records for the last 8000 years as recorded in the Taylor Dome ice core CO_2 [*Indermühle et al.*, 1999] and in planktonic foraminifera for a core raised from a depth of 2.3 km on the equator at 158°E on the Ontong Java Plateau. The radiocarbon ages (obtained at ETH Zurich) are on bulk $CaCO_3$ and have been corrected for a 400-year reservoir effect. Carbon isotope measurements were made using a Micromass Optima equipped with a Multiprep individual acid bath carbonate preparation device. For each depth, 15 *G. sacculifer* and 10 *P. obliquiloculata* were measured. Data were converted to PDB via NBS-19 and an internal lab standard. Replicate analyses of the lab standard had a standard deviation (1 sigma) of 0.02 per mil.

of calcite by respiration CO_2-charged sediment pore waters. In order to balance the impact of this excess pore water CO_2, the carbonate ion concentration in deep waters would have risen. Then at the close of glacial time when the supply of excess CO_2 to the pore waters was cut off, $CaCO_3$ deposition would have exceeded ingredient supply. Hence this scenario also calls for a $CaCO_3$ preservation event during the early Holocene time. As is the case for the compensation for an increase in terrestrial biomass, the time constant for the restoration of balance between supply and burial would be of the order of 5000 years. The difference is that were the respiration scenario to explain the entire glacial to interglacial CO_2 change, then the magnitude of the carbonate ion decline and of the complementary CO_2 rise would be about 5 times that associated with the change in biomass inventory [*Sanyal et al.*, 1995]. Interestingly enough, *Spero et al.* [1997] have pointed out

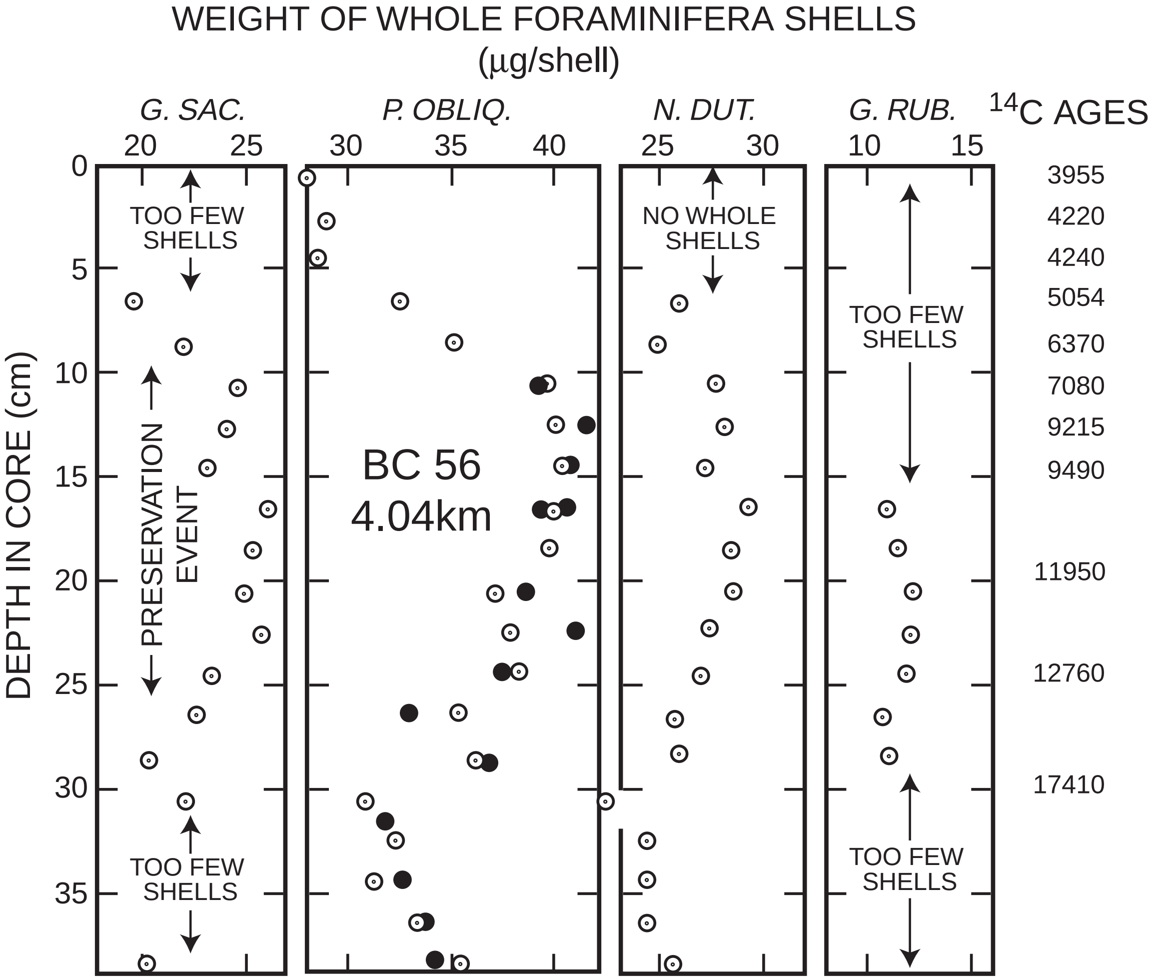

Figure 3. Mean whole shell weights for samples from a box core from a water depth of 4.04 km on the Ontong Java Plateau. Also shown are the reservoir-corrected radiocarbon ages. The intervals marked "too few shells" represent times when dissolution became sufficiently intense to cause shell breakup. The black dots represent measurements made early on in our foram weight program.

that were the respiration CO_2 mechanism to have governed the entire atmospheric CO_2 change, then it could also account for the 0.35‰ glacial to interglacial shift in benthic ^{13}C. The reason is that these authors demonstrated that the carbon isotope fractionation factor between ocean $\sum CO_2$ and foraminifera calcite is dependent on carbonate ion concentration. Hence, at least as far as carbon isotopes go, the impacts due to the glacial to interglacial respiration CO_2 and biomass changes are additive and must total the observed 0.35‰ [*Curry et al.*, 1988].

[7] So how can we decide among these scenarios? We have already stated that the magnitude of the Holocene atmospheric CO_2 rise and deep-ocean $CO_3^{=}$ decline appears to be consistent with the glacial to interglacial biomass change scenario but is perhaps too small to be consistent with the respiration CO_2 hypothesis. However, the boron isotope results

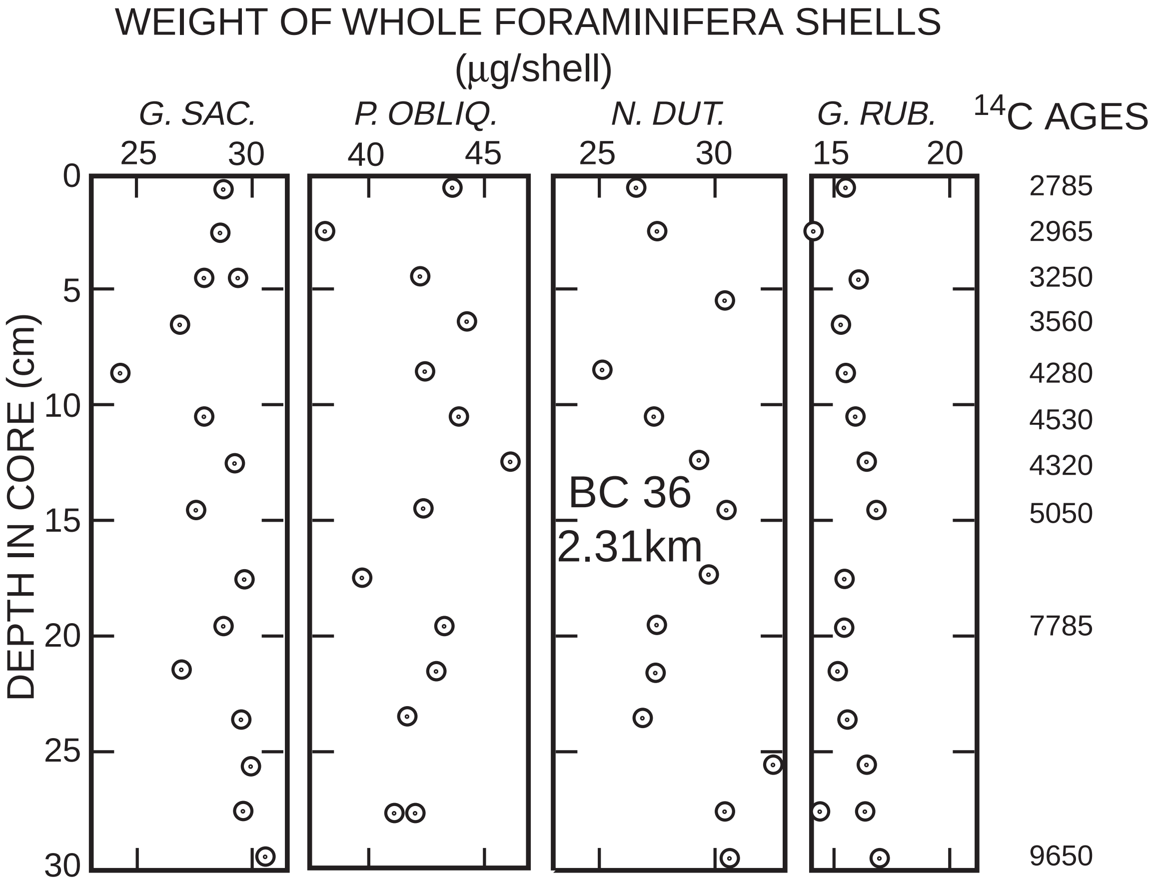

Figure 4. Mean shell weights from a core from 2.31 km depth on the Ontong Java Plateau. Also shown are the reservoir-corrected radiocarbon ages.

for benthic foraminifera [*Sanyal et al.*, 1995] suggest a 0.3 pH unit shift in the deep sea and hence appear to support the respiration CO_2 scenario. However, other observations and model results are at odds with the respiration CO_2 scenario. The total absence (at the 0.1% level) of $CaCO_3$ in the upper few centimeters of deep Pacific red clay sediments appears to be unexplainable if 3 g of $CaCO_3$ per cm^2 of seafloor were deposited across the entire ocean floor during the early phases of interglacials as required by the respiration CO_2 scenario. Further, model results [*Sigman et al.*, 1998] have shown that the several kilometer separation between the saturation horizon and the calcite lysocline required by the respiration scenario cannot be sustained.

2. Support From ^{13}C Results on Planktonic Foraminifera

[8] As shown in Figure 2, we have attempted to place limits on the extent of change in the ^{13}C to ^{12}C ratio in upper ocean carbon during the last 8000 years. We made these measurements on planktonic foraminifera from an Ontong-Java Plateau box core with a Holocene accumulation rate of ~3 cm/10^3 years. As can be seen, there is no discernable trend in the $\delta^{13}C$ for either *G.*

Table 1. Summary of the Mean Weight of Foraminifera Shells for Two Time Intervals: the Late Holocene (i.e., the Core Top Mixed Layer) and Early Holocene (i.e., the Preservation Maximum)[a]

Core No.	Water Depth, km	Weight *G. sac.*, μg	Weight *P. obl.*, μg	Weight *N. dut.*, μg	Weight *G. rub.*, μg
			Core Top Mixed Layer		
36	2.31	29	41 ± 3	27	15
51	3.43	23	36	24	<11
56	4.04	<20	29		<11
			Early Holocene Preservation Max		
36	2.31	29	42	30	16
51	3.43	28	41	30	14
56	4.04	25	40	28	12
			ΔEHPM - CTML		
36	2.31	0	1	3	1
51	3.43	5	5	6	>3
56	4.04	>5	11		>1

[a] Also shown are the weight drops between the preservation maximum and the core top mixed layer. For *G. sacculifer* and *G. ruber*, we have not found shells in their respective size fractions weighing less than 20 and 11 micrograms, respectively. We use these limits for the core top mixed zone where no whole shells were present.

sacculifer or *P. obliquiloculata* during the last 8000 years. However, these results alone cannot eliminate the possibility that the $\delta^{13}C$ for atmospheric CO_2 dropped by 0.2‰ over this time period. First the ^{13}C to ^{12}C ratio in planktonic foraminifera is an imperfect proxy for the $\delta^{13}C$ of upper ocean $\sum CO_2$, and second the $\delta^{13}C$ for upper ocean $\sum CO_2$ at any one locality need not precisely follow that for the atmosphere. Similar records will have to be obtained from a number of oceanic sites before firm conclusions can be drawn.

3. Support From Foraminifera Shell Weight Measurements

[9] In an attempt to better document the existence of a preservation event at the onset of the present interglacial, we made a series of weight measurements on foraminifera shells from Ontong Java Plateau box cores. Following Lohmann, we carefully cleaned the >63 micron size fraction and then separated out the 355–410 micron size fraction and picked and weighed 50 whole shells of three species: *G. sacculifer, P. obliquiloculata, and N. dutertrei*. We also picked and weighed 50 *G. ruber* shells from the 300–355 micron fraction. As can be seen in Figures 3, 4, and 5, shells recovered in the 10–25 cm interval in the deepest core weigh more than those from above or below. Those intervals marked "too few shells" represent times when dissolution had proceeded to a point where shell breakup occurred. On the basis of the radiocarbon ages (corrected for a reservoir effect of 400 years), the preservation event spans the interval from ~13,000 to ~7000 radiocarbon years. As shown by pollen records from many places on the globe, the time of onset corresponds to the appearance of interglacial flora and likely therefore the onset of the increase in terrestrial biomass. It is also a plausible time for the cutoff of the supply of Archer and Maier-Reimer's excess respiration CO_2.

[10] We also performed shell-weight measurements on a core from a much shallower depth (see Figure 4) and found no significant decrease in shell weights over the last 10,000 years. The

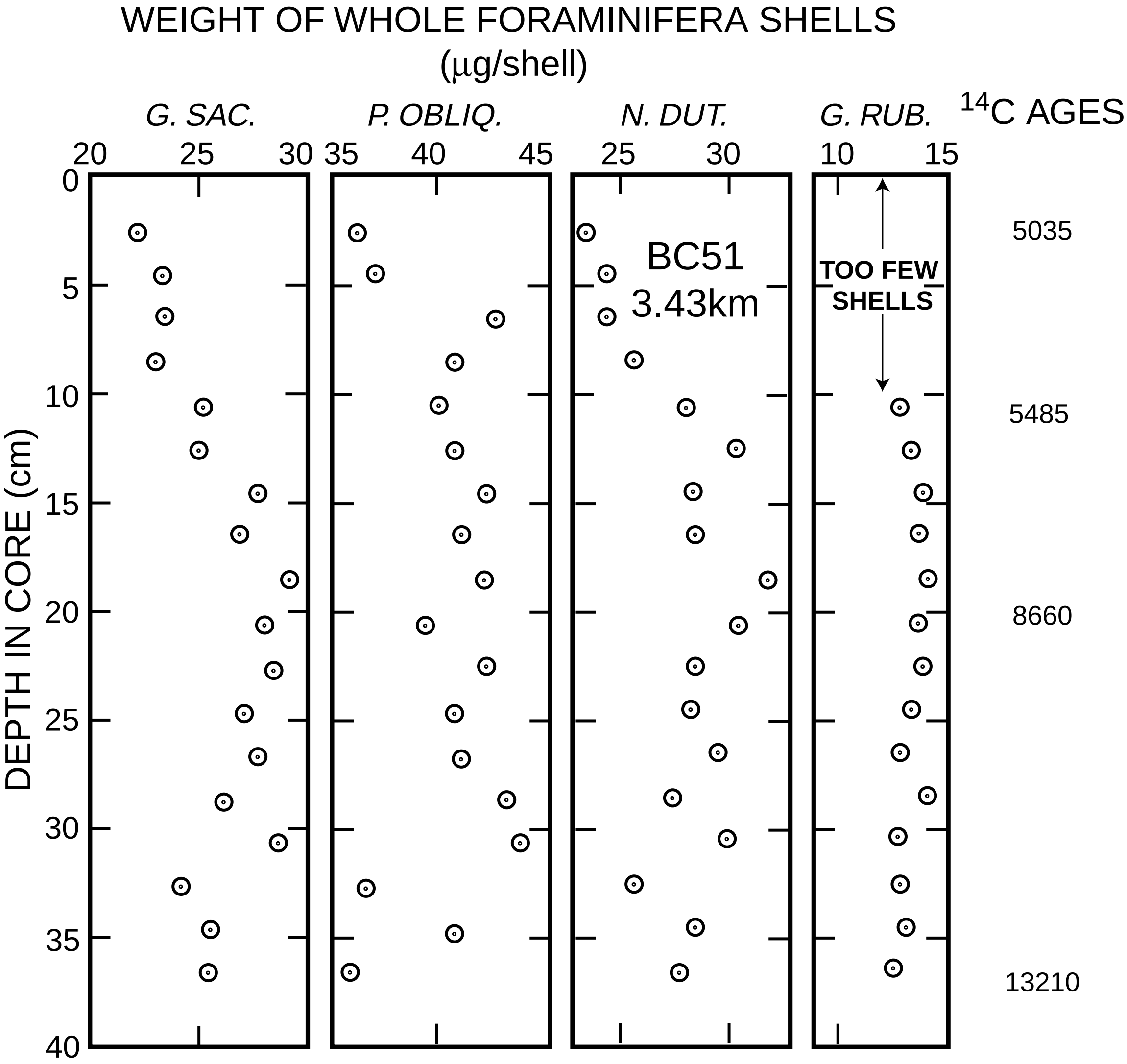

Figure 5. Mean whole shell weights for samples from a box core from a whole depth of 3.43 km on the Ontong Java Plateau. Also shown are reservoir-corrected radiocarbon ages. The interval marked "too few shells" represents a period in the late Holocene when dissolution became sufficiently intent to lead to breakup of the *G. ruber* shells.

results scatter in accord with our estimate of the reproducibility of our weight measurements (i.e. ±6%). The variability is mainly the result of the range in size and in wall thickness of the shells. Also, by comparing the results in Figures 3 and 4, it can be seen that, as expected, the shell weights are for late Holocene examples greater at 2.31 km than at 4.04 km. The difference in pressure-normalized carbonate ion concentration $[CO_3^{=}* = CO_3^{=} + 20(4 - z)]$ between these two depths on the Ontong Java Plateau is currently ~35 µmol/kg. On the basis of the slope of 0.3 µgrams weight per micromole per kg drop in pressure-corrected carbonate ion concentration established by *Broecker and Clark* [2001] for *G. sacculifer, P. obliquilocu-*

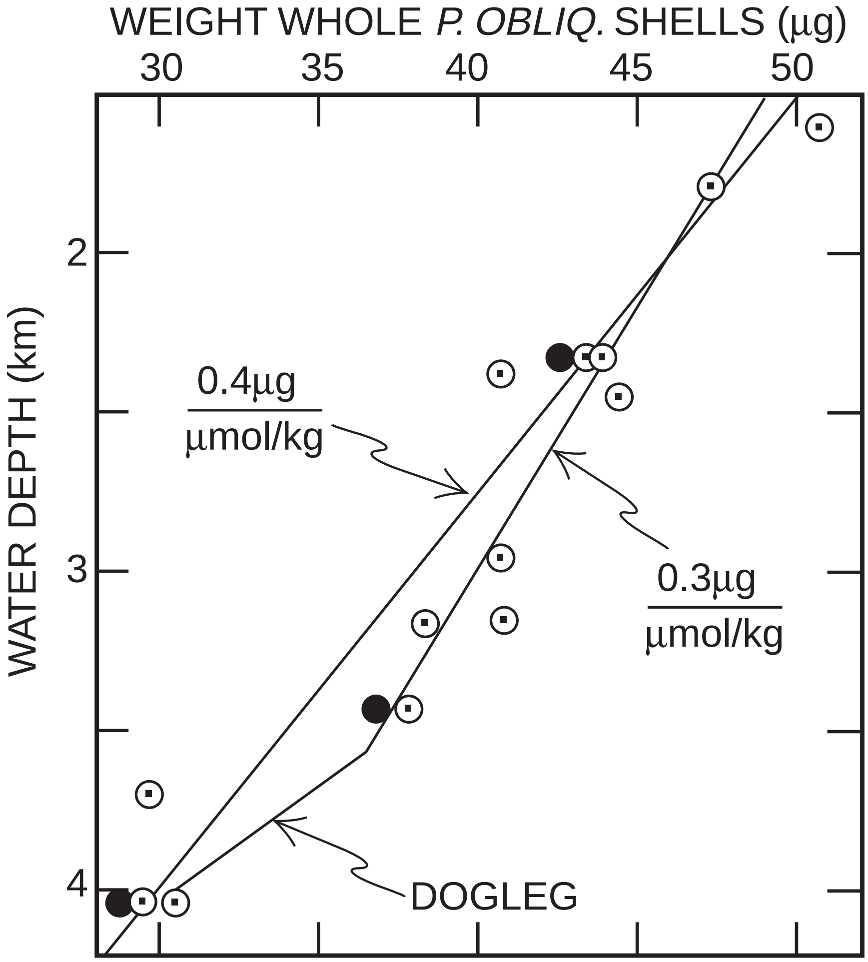

Figure 6. Mean weights for whole *P. obliquiloculata* shells from the core top mixed layers of Ontong Java Plateau sediment as a function of water depth. The open circles are results published separately by *Broecker and Clark* [2001]. The closed circles are measurements made for this paper. As the carbonate ion concentration at this locale is nearly constant over the depth range of interest, the pressure-normalized carbonate ion concentration decreases by 20 µmol/kg per km. The 0.3 µg per µmol/kg slope is that proposed by *Broecker and Clark* [2001]. However, in order to account for the shell weights at 4 km, there would have to be a dogleg in the weight-depth relationship somewhere below 3.5 km. If, instead, a single curve with a slope of 0.4 µg per µmol/kg is adopted, then the five results for cores in the 2.9–3.5 km depth range fall to the right of the calibration line.

lata, and *N. dutertrei*, the weight difference between foraminifera at 2.31 and 4.04 should be ~10 micrograms. Our core top results are consistent with this expected difference. However, at peak of the preservation event, the weight differences between 2.31 and 4.04 kilometers are much smaller (see Table 1).

[11] In order to explain these results, one might be tempted to conclude that even today the shells in the core from 2.31 km do not experience significant weight loss. Hence the drop in $CO_3^{=}$ concentration over the last 8000 years produced no weight change. However, as shown by *Broecker and Clark* [2001] and

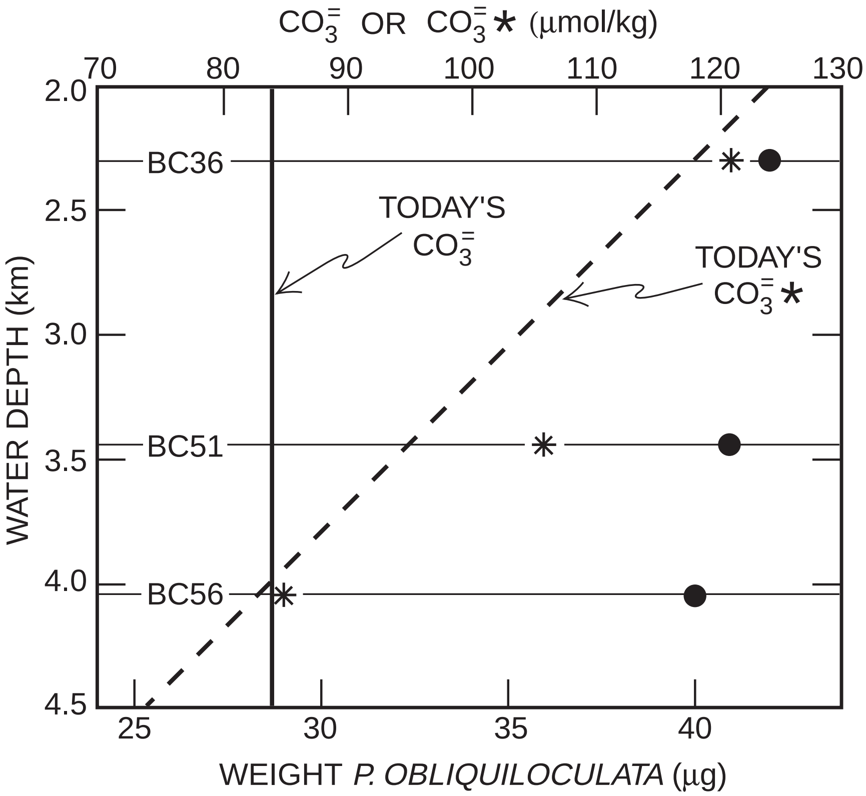

Figure 7. Plots of carbonate ion concentration and pressure-normalized carbonate ion concentration [i.e., $CO_3^=* = CO_3^= + 20\,(4 - z)$] versus water depth ($z$) on the Ontong Java Plateau (a la GEOSECS). Also shown are the weights of *P. obliquiloculata* for core top mixed layer samples (stars) and for preservation maximum samples (circles). The carbonate ion and the weight scales are set to match the 0.3 μg/μmol/kg relationship established by *Broecker and Clark* [2001]. The weights are those given in Table 1.

reproduced in Figure 6, the 0.3 microgram per micromole change in $CO_3^=$* continues up to at least 1.6 km. Hence this cannot be the explanation. As a further check, we made measurements on a third core from 3.43 km water depth (see Figure 5). As summarized in Table 1, during the preservation event, the weights at 3.43 km were only 1 ± 1 micrograms smaller than those for the core from 2.31 km. As the critical carbonate ion concentration at 3.43 km depth is ~22 μmol/kg lower than at 2.31 km depth, this is consistent with little dissolution at either depth during the preservation event. However, for the late Holocene, the weight difference is consistent with a 15 ± 5 μmol lower pressure-normalized carbonate ion concentration at 3.43 km than at 2.31 km. As summarized in Figures 7 and 8, the impression is given that late Holocene rise in carbonate ion concentration was not uniform with depth. Rather, it was quite large at 4.04 km (~35 μmol kg) and quite small at 2.31 km (~3 μmol/kg). Hence the view that the carbonate ion change is simply a whole ocean response cannot be the entire story. Perhaps as hinted at by *Keir* [1984] and *Berelson et al.* [1997], who postulated a late Holocene dissolution event in the deep Pacific, a reorganization of

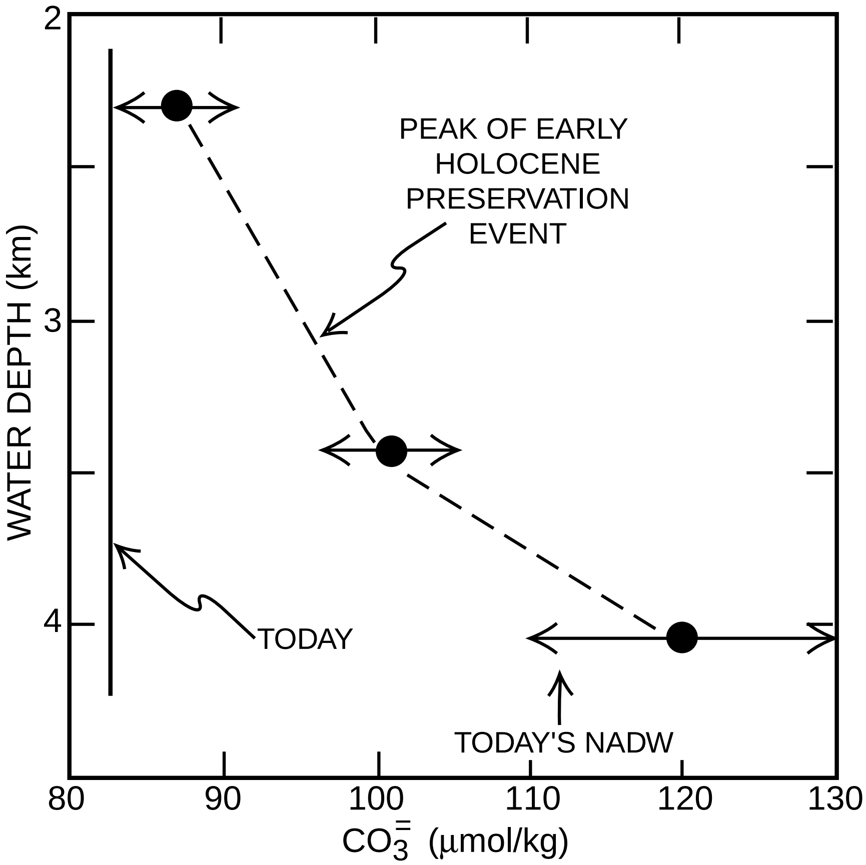

Figure 8. On the basis of the foraminifera shell weights summarized in Table 1 and the assumption that the shells lose 0.3 µg per micromol/kg drop in $CO_3^=$*, a tentative reconstruction of the depth dependence of the carbonate ion concentration during the peak of the early Holocene preservation event has been made. As can be seen, the carbonate ion concentration at 4 km appears to have been in the range of that for today's North Atlantic Deep Water (NADW).

ocean operation is also involved. The shell weights give the impression that during the preservation event the pressure-normalized carbonate ion concentration at 4.04 km was only about 5 µmol/kg lower than that at 2.31 km. As the shell weights suggest that the carbonate ion concentration at 2.31 was close to today's (i.e., ~83 µmol/kg) and as the pressure correction is [(4.04 − 2.31) × 20 or 35 µmol/kg], the shell weights during the preservation event suggest that the carbonate ion concentration at 4.04 km was nearly as high as that in today's North Atlantic Deep Water. We hesitate to elaborate for this preliminary study is part of a long-term effort to understand the limitations of *Lohmann*'s [1995] shell weight method.

4. Conclusions

[12] We challenge the interpretation by *Indermühle et al.* [1999] that the 20 ppm rise in atmospheric CO_2 over the last 8000 years was the result of a 200 Gt drop in terrestrial biomass. Rather, our ^{13}C and foraminifera weight data are consistent with the scenario that the CO_2 rise was the result of a drop in carbonate

ion concentration in the deep sea related to the aftermath of some combination of an early Holocene increase in terrestrial biomass (and hence removal of CO_2 from the oceanic reservoir) and an early Holocene demise of the supply of excess respiration CO_2 to sediment pore waters. However, clearly our observation that the Holocene $CO_3^=$ concentration decline was not uniform with water depth in the equatorial Pacific raises the possibility that the situation is more complicated.

Acknowledgments

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