Impact of the ocean carbonate chemistry on living foraminiferal shell weight: Comment on "Carbonate ion concentration in glacial-age deep waters of the Caribbean Sea" by W. S. Broecker and E. Clark

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1. Introduction

[1] *Broecker and Clark* [2002] use the "size normalized weight" of planktic foraminifera to estimate the carbonate ion concentration ($[CO_3^=]$) of Atlantic glacial upper deep water. This method was introduced by *Lohmann* [1995] and is based on the fact that, within a defined size fraction, dissolution decreases shell weight in proportion to the degree of undersaturation with respect to $CaCO_3$. On the basis of the following assumptions: (1) the thickness of the foraminiferal shell wall does not depend on growth conditions, (2) the saturation $[CO_3^=]$ for calcite, $[CO_3^=]_{sat.}$, increases by 20 μmol kg^{-1} km^{-1} [*Broecker and Clark*, 2001], (3) the weight loss slope is universal and ca. 0.3 μg (μmol kg^{-1})$^{-1}$ [*Broecker and Clark*, 2001], and (4) the offset between the bottom water and pore water $[CO_3^=]$ was the same during glacial time as during the Holocene, *Broecker and Clark* [2002] calculate that

the $[CO_3^=]$ of Atlantic glacial upper deep water was 14 μmol kg^{-1} higher than during the Holocene. Although they recognize that some of their assumptions are not strictly valid, they do not assess the impact of those assumptions on their $[CO_3^=]$ estimate. Here we comment on several of those assumptions and attempt to quantify their impact on *Broecker and Clark*'s [2002] calculations.

2. Assumption 1

[2] *Broecker and Clark* [2002] provide evidence that this assumption is not valid. At the same pressure-normalized $[CO_3^=]$, *P. obliquiloculata* from the Pacific Ocean is consistently 10 μg heavier than those from the Indian Ocean. *Spero and Lea* [1993] have shown that *G. sacculifer* cultured under high light intensities grows bigger and is more massive than under lower light conditions. *Hemleben et al.* [1987] have demonstrated that *G. sacculifer* cultured

at higher temperatures grows larger. Unfortunately they did not measure shell weight. Chamber number/size/weight relationships for the symbiont barren species *G. bulloides* differ from location to location [*Spero and Lea*, 1996]. For instance, comparable ontogenetic stages from the Chatham Rise are bigger and heavier than those from the San Pedro Basin. Apparently, besides potential genetic differences [e.g., *Darling et al.*, 1999, 2000; *Huber et al.*, 1997], growth conditions affect the size normalized weight.
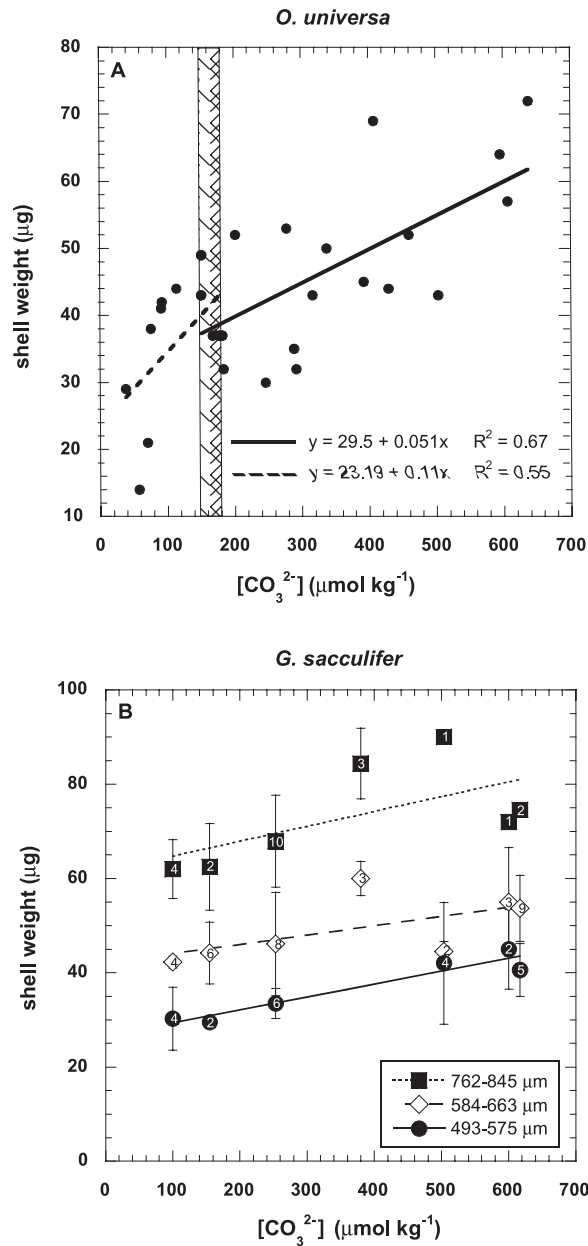
[3] *Broecker and Clark* [2002] point out that temperature and $[CO_3^=]$ are likely candidates. Elderfield (personal communication, 2001) showed that shell wall thickness is closely related to growth temperature. On the other hand, *Bijma et al.* [1999] demonstrated that shell weight of *O. universa* is primarily a function of the $[CO_3^=]$ of the ambient water (Figure 1a). It can be demonstrated that $[CO_3^=]$ primarily affects shell thickness and that shell weight is a derived parameter of that relationship. For reasons of comparability and simplicity we use the $[CO_3^=]$-weight relationship here.

[4] At the same $[CO_3^=]$, *O. universa* shells grow heavier under high light than under low light conditions. Apparently, the $[CO_3^=]$ at the site of calcification (SOC) reflects the ambient $[CO_3^=]$ but is modified by physiological processes (respiration, calcification, and photosynthesis) of the foraminifer and its symbionts [*Wolf-Gladrow et al.*, 1999]. *Broecker and Clark* [2002] point out that in today's ocean a very tight correlation exists between surface water $[CO_3^=]$ and temperature and that core top shell weights can thus not be used to distinguish between a temperature or a carbonate ion dependence (in equilibrium with today's atmosphere, the temperature impact on $[CO_3^=]$ varies roughly between 5 and 6 $\mu mol\ kg^{-1}\ K^{-1}$ for surface alkalinities between 2100 and 2400 $\mu mol\ kg^{-1}$, respectively).

[5] *Barker and Elderfield* [2002] have adopted an approach where they follow the evolution of shell weight through time and compare this to predictions made from carbon system modeling. They demonstrate that shell weight of *G. bulloides* decreases from the last termination toward the

Holocene. This trend suggests that $[CO_3^=]$ controls weight rather than temperature since $[CO_3^=]$ decreases while temperature increases during the deglaciation. This finding is corroborated by laboratory experiments. We have evidence, albeit less well constrained than for *O. universa*, that shell weight of *G. sacculifer* depends on the carbonate chemistry of the ambient water (Figure 1b), and there is a priori no reason to assume that this phenomenon is restricted to these two species or to foraminifera in general. A similar impact of the carbonate chemistry has been demonstrated for corals [*Gattuso and Buddemeier*, 2000; *Gattuso et al.*, 1998; *Kleypas et al.*, 1999] and for coccolithophorids [*Riebesell et al.*, 2000; *Zondervan et al.*, 2001]. The experimental results suggest that shell weight of individual *G. sacculifer* increases by 3 μg for every 100 $\mu mol\ kg^{-1}$ increase in $[CO_3^=]$. It should be noted that only a part of the life cycle has been spent under controlled laboratory conditions and hence that the real slope may be steeper. The point of the matter is that growth differences have to be considered, not only between species and in space but in time as well.

[6] If we accept *Sanyal et al.*'s [1995] glacial surface water pH reconstruction, which is in agreement with the ice core pCO$_2$ measurements, and assume that the sites investigated by *Broecker and Clark* [2002] were in equilibrium with the atmosphere, the glacial $[CO_3^=]$ must have been significantly higher. Depending on which scenario is followed to achieve glacial pCO$_2$ values, CO$_2$ extraction or CaCO$_3$ addition, the tropical glacial surface ocean $[CO_3^=]$ was 50 to 120 $\mu mol\ kg^{-1}$ higher, respectively, compared with the Holocene [*Lea et al.*, 1999]. Hence before *G. sacculifer* settled to the ocean floor, glacial specimens must have been heavier in weight than their Holocene counterparts from the same site. Using our empirical relationship, 1.5 to 3.6 μg of the glacial weight increase in *G. sacculifer* was due to the fact that shells grew heavier. On the basis of a glacial-interglacial temperature difference for tropical surface waters of 3°C, an average slope of $[CO_3^=]$ versus temperature of 5.5 $\mu mol\ kg^{-1}\ K^{-1}$, and an experimental slope of 3 μg weight increase for every 100 $\mu mol\ kg^{-1}$ increase in $[CO_3^=]$, the impact on shell weight of temperature alone is

O. universa

$y = 29.5 + 0.051x$ $R^2 = 0.67$
$y = 23.19 + 0.11x$ $R^2 = 0.55$

G. sacculifer

762–845 μm
584–663 μm
493–575 μm

<0.5 μg. Hence the effective glacial-Holocene weight difference decreases. It is reasonable to assume that the change in the glacial surface $[CO_3^=]$ was brought about by a combination of both scenarios. Assuming that the average weight of glacial *G. sacculifer* was 2.6 μg heavier, the glacial-interglacial weight difference for this species reduces from 4.9 to 2.3 μg. Consequently, using the 0.3 μg $(\mu mol\ kg^{-1})^{-1}$ calibration of *Broecker and Clark* [2002], the glacial $[CO_3^=]$ increase reduces from 14 μmol kg^{-1} to 8 μmol kg^{-1}.

3. Assumption 2

[7] Although the true relationship between pressure and $[CO_3^=]_{sat.}$ is exponential, a linear approximation

Figure 1. (opposite) Planktonic foraminifera were grown in the laboratory in a 12 hour light/dark cycle under a range of $[CO_3^=]$ until gametogenesis (for details see *Bijma et al.*, 1999). Empty shells were dried, measured, and weighed individually. (a) Individual *O. universa* shell weights of the size fraction 500–600 μm plotted as a function of $[CO_3^=]$. The shaded area represents the range of ambient $[CO_3^=]$. The data from several experiments (constant alkalinity, constant ΣCO_2, and constant pH) are combined [*Bijma et al.*, 1999]. Linear regressions were fitted to data below and above ambient $[CO_3^=]$. (b) *Globigerinoides sacculifer* was only grown at constant ΣCO_2. Average shell weights of three different size ranges (closed circles: 493–575 μm; open diamonds: 584–663 μm; closed squares: 762–845 μm). Numbers in the symbols indicate the number of specimens for each data point. Statistical analysis based on the individual data points shows that the slopes are significant at the 90%, 95%, and 95% confidence level, respectively for the size intervals 493–575 μm, 584–663 μm, and 762–845 μm. Regression analysis yields slopes of 2.5, 2.1, and 3.6 μg per 100 μmol kg^{-1}, demonstrating that ontogeny has little effect on the relationship:

$493-575\ \mu m$: $Wgt\,(\mu g) = 27.3 + 0.025 \cdot \left[CO_3^=\right]$ $(r^2 = 0.39)$

$584-663\ \mu m$: $Wgt\,(\mu g) = 41.4 + 0.021 \cdot \left[CO_3^=\right]$ $(r^2 = 0.22)$

$762-845\ \mu m$: $Wgt\,(\mu g) = 59.8 + 0.036 \cdot \left[CO_3^=\right]$ $(r^2 = 0.28)$

The sieve size range used by *Broecker and Clark* [2001, 2002] (350–415 μm) can be converted to a real shell size range of 493–575 μm by using the growth curve for *G. sacculifer* provided by *Hemleben and Bijma* [1994]. In other words, the shell weight of *G. sacculifer* increases ca. 3 μg for every 100 μmol kg^{-1} increase in $[CO_3^=]$.

for the depth range between 3 and 4 km water depth is quite acceptable. However, the coefficient of 20 μmol kg^{-1} km^{-1} [*Ingle*, 1975] used by *Broecker and Clark* [2002] is the largest among a range of values. For instance, on the basis of the relationship $[CO_3^=]_{sat.} = 90 \cdot e^{(0.16 \cdot (z-4))}$ [*Broecker and Takahashi*, 1978] the change in the saturation $[CO_3^=]$ between 3 and 4 km depth equals 13 μmol kg^{-1} km^{-1}. Using the parameterization of *Millero* [1995], the saturation $[CO_3^=]$ increases by 16 μmol kg^{-1} between 3 and 4 km depth. Although *Broecker and Clark* [2002] acknowledge that the true slope may be in the range of 15 ± 2 μmol kg^{-1} km^{-1}, they choose to use 20 μmol kg^{-1} km^{-1}. *Jansen et al.* [2002] fitted the (more convenient) equation of *Broecker and Takahashi* [1978] to the critical $[CO_3^=]$ as calculated by *Millero* [1995]. Using this approximation ($[CO_3^=]_{sat.} = 88.7 \cdot e^{(0.189 \cdot (z-3.82))}$), the slope for the depth range between 3 to 4 km is 16 μmol kg^{-1} km^{-1}. A smaller pressure impact tends to increase the weight loss slope and hence reduces the glacial $[CO_3^=]$ estimate even more.

4. Assumption 3

[8] *Berger* [1968] and *Parker and Berger* [1971] and many others after that demonstrated that planktic foraminifera are differently susceptible to dissolution. Hence one could argue that the critical $[CO_3^=]$ is slightly different for each species and that therefore the weight loss slopes must be species dependent and not universal. The fact that *G. ruber* does not show the glacial-Holocene weight difference as the other species studied by *Broecker and Clark* [2002] bolsters this contention. To verify the assumption that weight loss slopes are species dependent, we have replotted shell weights from Table 1 in *Broecker and Clark* [2001] against the pressure corrected $[CO_3^=]$ (Figure 2). On the basis of the 20 μmol kg^{-1} km^{-1} change in $[CO_3^=]_{sat.}$ used by *Broecker and Clark* [2001] the slopes of the linear regressions are 0.46, 0.57, and 0.68 μg (μmol kg^{-1})$^{-1}$ for *G. sacculifer*, *P. obliquiloculata*, and *N. dutertrei*, respectively. Using the smaller pressure effect on $[CO_3^=]_{sat.}$ of *Jansen et al.* [2002], the slopes amend to 0.45, 0.66, and 0.65 μg (μmol kg^{-1})$^{-1}$, respectively (Figure 2). Note that the inconsistency between the weight loss slopes and
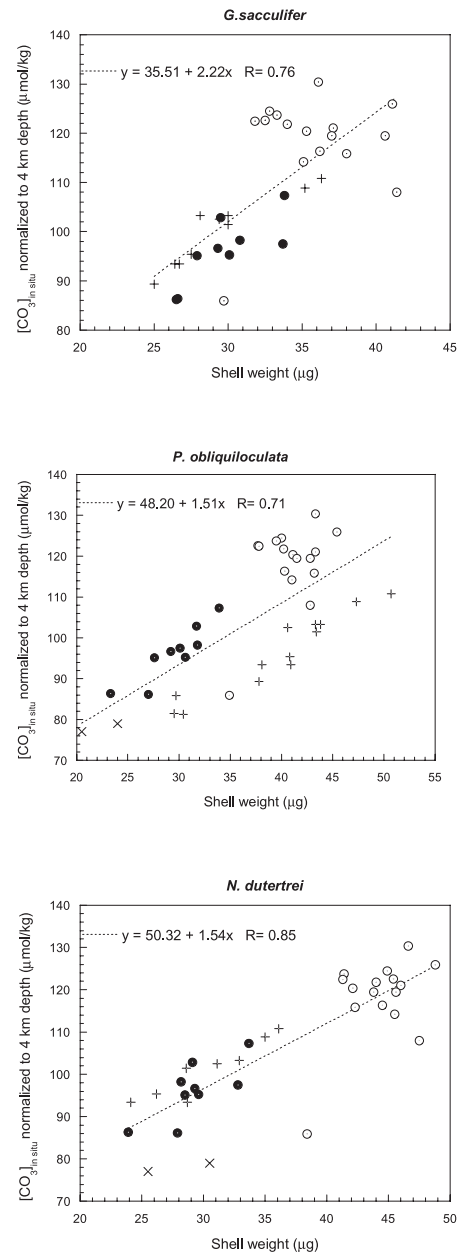

Figure 2. Plots of whole shell weights (size range 355–415 μm) as determined by *Broecker and Clark* [2002] versus the pressure corrected $[CO_3^=]$, $[CO_3^=]^* = [CO_3^=]_{in\ situ} + \Delta[CO_3^=]_{(4-z)}$, where $\Delta[CO_3^=]_{(4-z)}$ is the difference in $[CO_3^=]$ between the water depth at the core site and 4 km and $[CO_3^=]_{at\ 4km\ depth}$ is calculated after *Millero* [1995]. Open circles represent Atlantic data, closed circles are from the Indian Ocean, and crosses (+) and x are from the western and eastern Pacific, respectively.

the ranking to dissolution provided by *Parker and Berger* [1971] is most likely due to the combined effect of susceptibility to dissolution and wall thickness (i.e., the initial shell weight). Assuming an average slope of 0.5 μg (μmol kg^{-1})$^{-1}$, the estimated [CO$_3^=$] increase of glacial Atlantic upper deep water, as calculated by *Broecker and Clark* [2001], decreases by 43% from 14 to 8 μmol kg^{-1}. However, as argued above, the slopes are species specific, and Δ[CO$_3^=$] should therefore be calculated on a per species basis. For the Caribbean cores the glacial-Holocene increase in [CO$_3^=$] is then estimated to be 11 and 5 μmol kg^{-1} on the basis of *G. sacculifer* and *N. dutertrei*, respectively. Apparently, the critical [CO$_3^=$] for *G. sacculifer* is higher than that for *N. dutertrei* (i.e., at the same water depth, the Holocene-glacial weight difference for *G. sacculifer* is larger than for *N. dutertrei*). The average of the two species is, of course, 8 μmol kg^{-1}, but the question arises which of the two species provides the best estimate? Combining the impact of a steeper weight loss slope for *G. sacculifer* with that of higher glacial surface water [CO$_3^=$] on *G. sacculifer* shell weight reduces the glacial [CO$_3^=$] increase estimate to 5 μmol kg^{-1}.

5. Assumption 4

[9] In addition to the assumption that the difference between the bottom and pore water [CO$_3^=$] was the same during glacial time as during the Holocene, *Broecker and Clark* [2001] assume that the offset between bottom and pore water [CO$_3^=$] is constant with depth and between different sites. However, because the rain ratio (carbonate carbon/organic carbon) changes with depth and differs from location to location, these assumptions may not be valid. In fact, *Broecker and Clark* [2001] note that the observed correlation between the weights of *G. sacculifer*, *P. obliquiloculata*, and *N. dutertrei* for the core top samples from the Ceara Rise demonstrates the variability of the [CO$_3^=$] offset between bottom and pore water.

[10] Because of nonlinear dissolution kinetics, the offset between bottom and pore water [CO$_3^=$] changes drastically from above to below the saturation horizon (SH). Above the SH, pore water is less saturated with respect to calcite than bottom water (because of respiration-driven pore water dissolution). Bottom water [CO$_3^=$] reaches the critical value at the SH; "interface" dissolution starts and progresses exponentially toward greater depths. Because the dissolution kinetics are not infinitely fast, an offset is created between the SH and the lysocline. In this depth interval, called the transition zone, the saturation state of the pore water increases from less saturated to more saturated than the bottom water. Note that there is a depth where the [CO$_3^=$] of bottom and pore water converge. This demonstrates that the offset between bottom and pore water is not constant with depth and hence that the slope of the weight loss per unit change in [CO$_3^=$] changes below the SH. Consequently, the size-normalized weight method should probably be restricted to cores that have never seen in situ bottom water [CO$_3^=$] below the critical [CO$_3^=$].

[11] One could argue that the variability in the [CO$_3^=$] offset between bottom and pore water is a fatal blow for Lohmann's method. However, we should keep in mind that we are dealing with a proxy and that such complications are to be expected. They basically set the limit for the accuracy of the method. A better understanding of the [CO$_3^=$] variations between bottom and pore water is needed to improve the robustness of the method.

[12] Above the saturation horizon the range of pH offsets between bottom and pore water, for instance at the Ontong-Java Plateau, is somewhere between 0.02 and 0.04 pH units [*Hales and Emerson*, 1996]. This translates roughly to a [CO$_3^=$] offset between 5 and 10 μmol kg^{-1}. Using the average weight loss slope of 0.5 μg (μmol kg^{-1})$^{-1}$, this implies that weight differences between 2.5 and 5 μg are within the uncertainty for reconstructing bottom water [CO$_3^=$].

[13] The restriction to cores that have never bathed in waters below the critical [CO$_3^=$] has also been noted by *Broecker and Clark* [2002]. In addition, they argue that data from shallow cores bathing in water with a [CO$_3^=$] higher than 120 μmol kg^{-1} should be omitted (because the reduction in [CO$_3^=$]

resulting from the release of respiration CO_2 in the pore water is more than compensated by the excess of bottom water $[CO_3^=]$ over calcite saturation).

[14] Some of the cores used by *Broecker and Clark* [2001] to determine the weight loss slopes are from below the SH (based on *Jansen et al.*, 2002) or from in situ $[CO_3^=]$ higher than 120 μmol kg^{-1}. Limiting their data to $[CO_3^=]_{sat.} < [CO_3^=]_{in\ situ} < 120$, the weight loss slopes for *G. sacculifer* and *N. dutertrei* become 0.62 and 0.93 μg (μmol kg^{-1})$^{-1}$, respectively. The estimated glacial increase in $[CO_3^=]$ for the Caribbean cores now decreases to 8 and 4 μmol kg^{-1} on the basis of *G. sacculifer* and *N. dutertrei*, respectively.

[15] If we combine the new estimate of the weight loss slope for *G. sacculifer* with the impact of higher glacial surface water $[CO_3^=]$ on this species, the $\Delta[CO_3^=]$ estimate based on *G. sacculifer* reduces to 4 μmol kg^{-1}. This brings the predicted average increase in $[CO_3^=]$ of Atlantic glacial upper deep water based on *G. sacculifer* (including the impact of higher glacial surface water $[CO_3^=]$ on initial shell weight) close to the prediction of 4 μmol kg^{-1} based on *N. dutertrei* (without an impact of higher glacial surface water $[CO_3^=]$ on initial shell weight). This could suggest that during growth the shell weight of *N. dutertrei* does not respond strongly to the $[CO_3^=]$, if at all. However, the predicted increase in $[CO_3^=]$ of 4 μmol kg^{-1} for Atlantic glacial upper deep water is within the range of uncertainty related to the variability in the $[CO_3^=]$ offset between bottom and pore water, leaving the question open for further debate.

Acknowledgments

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