Implications of a Carbonate Ion Effect on Shell Carbon and Oxygen Isotopes for Glacial Ocean Conditions

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Abstract: Experimental work demonstrates that the carbon and oxygen isotopic composition of planktic foraminifera shells is directly influenced by the carbonate equilibrium state of seawater (Spero et al. 1997). Because the pCO_2 of the sea surface and the atmosphere must be in approximate equilibrium, the glacial drop in atmospheric carbon dioxide recorded in ice cores must have been accompanied by an increase in surface water carbonate ion concentration. Calculations indicate that increased carbonate ion during glacial episodes can account for much or all of the observed negative $\delta^{13}C$ shift in planktic shells. This discovery provides a novel explanation for the large, negative swings in planktic $\delta^{13}C$ observed in the glacial sections of Southern Ocean cores. It also presents an alternative hypothesis to the terrestrial biosphere-to-ocean transfer of carbon that is generally accepted as an explanation for lower glacial shell $\delta^{13}C$ values (Shackleton 1977). Our analysis suggests that shell isotopic composition can provide a constraint on the extent of oceanic carbonate ion changes, potentially narrowing explanations for the glacial pCO_2 drawdown. Correcting for the influence of the carbonate ion effect on shell $\delta^{18}O$ lowers glacial tropical sea surface temperature (SST) estimates by up to 1°C, which brings oxygen isotope paleotemperatures closer to those marine SST proxies (e.g. coral Sr/Ca) and those terrestrial indicators (e.g. snow-line and ice core $\delta^{18}O$) that suggest more intense tropical cooling at the last glacial maximum (Guilderson et al. 1994; Thompson et al. 1995).

Introduction

Shackleton first pointed out that benthic shells from glacial sections of deep-sea cores are characterized by lower $^{13}C/^{12}C$ values (Shackleton 1977). He interpreted this change as a consequence of the transfer during glacial episodes of organic carbon depleted in ^{13}C from the terrestrial biosphere to the oceanic dissolved inorganic carbon (DIC) pool. Subsequent studies revealed that downcore changes in benthic $\delta^{13}C$ can also be ascribed to changes in other factors, including shifts in the abyssal circulation (Boyle and Keigwin 1982; Curry and Lohmann 1982; Shackleton et al. 1983b), air-sea exchange (Charles et al. 1993) and physiological and/or environmental artifacts (McCorkle et al. 1990; Mackensen et al. 1993). Although the combined influence of these factors complicates the interpretation of benthic $\delta^{13}C$ records, comparison of records from different basins makes it possible to extract the mean ocean shift in $\delta^{13}C$ (Boyle and Keigwin 1985, 1986).

Recent compilations suggest that mean ocean $\delta^{13}C$ was 0.32‰ more negative during the Last Glacial Maximum (LGM), 20 ka (Curry et al. 1988; Duplessy et al. 1988; Boyle 1992). If this shift is entirely attributed to a transfer of carbon from the

From FISCHER G, WEFER G (eds), 1999, *Use of Proxies in Paleoceanography: Examples from the South Atlantic.* Springer-Verlag Berlin Heidelberg, pp 513-522

terrestrial biosphere to the oceans, it is consistent with an addition to the glacial oceans of 450 Gt terrestrial carbon with a $\delta^{13}C$ of -25‰, or about 21% of the present biospheric carbon reservoir (including dead soil organic matter) (1 Gt = 10^{15} g C). Pollen databases from the LGM appear to be consistent with a substantially larger reduction of the terrestrial biosphere (750 - 1350 Gt), although there is considerable uncertainty associated with estimating terrestrial carbon mass and in predicting how efficiently carbon is transferred to the ocean during glaciations (Crowley 1995). An additional complication is that some of the glacial carbon addition might have come from the erosion of continental shelves exposed by lower sea level (Broecker 1982b).

Planktic foraminiferal $\delta^{13}C$ records are complicated by isotopic offsets between species, variations in $\delta^{13}C$ with shell size, and disequilibrium effects attributable to the presence of symbiotic algae (Berger et al. 1978; Spero and Williams 1988; Oppo and Fairbanks 1989; Spero and Lea 1996). Records of *Globigerinoides sacculifer,* the principal species used for tropical reconstructions, reveal that shells deposited in LGM sections average only about 0.2‰ more negative in $\delta^{13}C$ than their Holocene counterparts (Curry and Crowley 1987; Oppo and Fairbanks 1989). In addition, low latitude planktic $\delta^{13}C$ records are characterized by the most negative $\delta^{13}C$ values occurring on the glacial terminations rather than during the LGM. Despite the complexity of these records, an increase in planktic-benthic $\delta^{13}C$ differences in the glacial sections of tropical cores has been cited as evidence of a stronger biological pump during glacial periods (Shackleton et al. 1983a; Shackleton and Pisias 1985; Curry and Crowley 1987; Shackleton et al. 1992). The largest shift in planktic $\delta^{13}C$ is observed in cores from the Southern Ocean, where shells taken from the glacial sections are typically 1‰ more negative than interglacials (Labeyrie and Duplessy 1985; Charles and Fairbanks 1990; Charles et al. 1996). Neither the magnitude nor direction of the Southern Ocean $\delta^{13}C$ shifts have been adequately explained because the large nutrient changes implied by the shifts are not supported by coincident changes in other proxies (Boyle 1988; Lea 1995), are opposite to those expected from a strengthened biological pump (Broecker 1982a), and are greater than could be reasonably inferred from changes in gas exchange (Charles et al. 1993).

Influence of Seawater Carbonate Ion Concentration on Foraminiferal Isotopes

Culturing experiments demonstrate that the $\delta^{13}C$ and $\delta^{18}O$ composition of planktic foraminifera shells responds to changes in seawater carbonate ion concentration (Spero et al. 1997) (Bijma et al. this volume). The average response of shell $\delta^{13}C$ in the growth experiments is -0.006‰ for *Orbulina universa* and -0.012‰ for *Globigerina bulloides* per µmol/kg increase in seawater carbonate ion. The response for shell $\delta^{18}O$ is -0.002 and -0.004‰ per µmol/kg carbonate ion for *O. universa* and *G. bulloides*, respectively. Carbonate ion concentration is utilized as the independent variable because, unlike pH, under different experimental conditions isotopic deviations are a linear function of carbonate ion. However, because pH and carbonate ion vary together in seawater, we do not have proof that carbonate ion concentration is the controlling variable. The isotopic response of the shells to changes in carbonate ion concentration presumably reflects a kinetic response during calcite precipitation (Spero et al. 1997). Newer results reveal a similar affect for two tropical, surface-dwelling species, *Globigerinoides ruber* and *Gs. sacculifer* (Bijma et al. 1998).

Ice core records indicate that atmospheric pCO_2 levels dropped to about 200 ppmV during the LGM, although the cause of the reduction remains unexplained (Barnola et al. 1987; Jouzel et al. 1993). Glacial reconstructions demonstrate that temperature and salinity changes alone cannot account for more than a small fraction of this pCO_2 reduction (Broecker 1982a; Broecker and Peng 1993). Because the surface ocean must on average have the same pCO_2 as the atmosphere and because sea surface temperatures did not drop sufficiently to cause the observed pCO_2 reduction (Broecker and Peng 1993), lower glacial pCO_2 levels must reflect an increase in average sea surface carbonate ion, or more specifically an increase in the ratio of alkalinity (excess base) to CO_2. Based on the results of culturing experiments, this increase in sea surface carbonate ion is expected to influence the isotopic composition of planktic foraminifera.

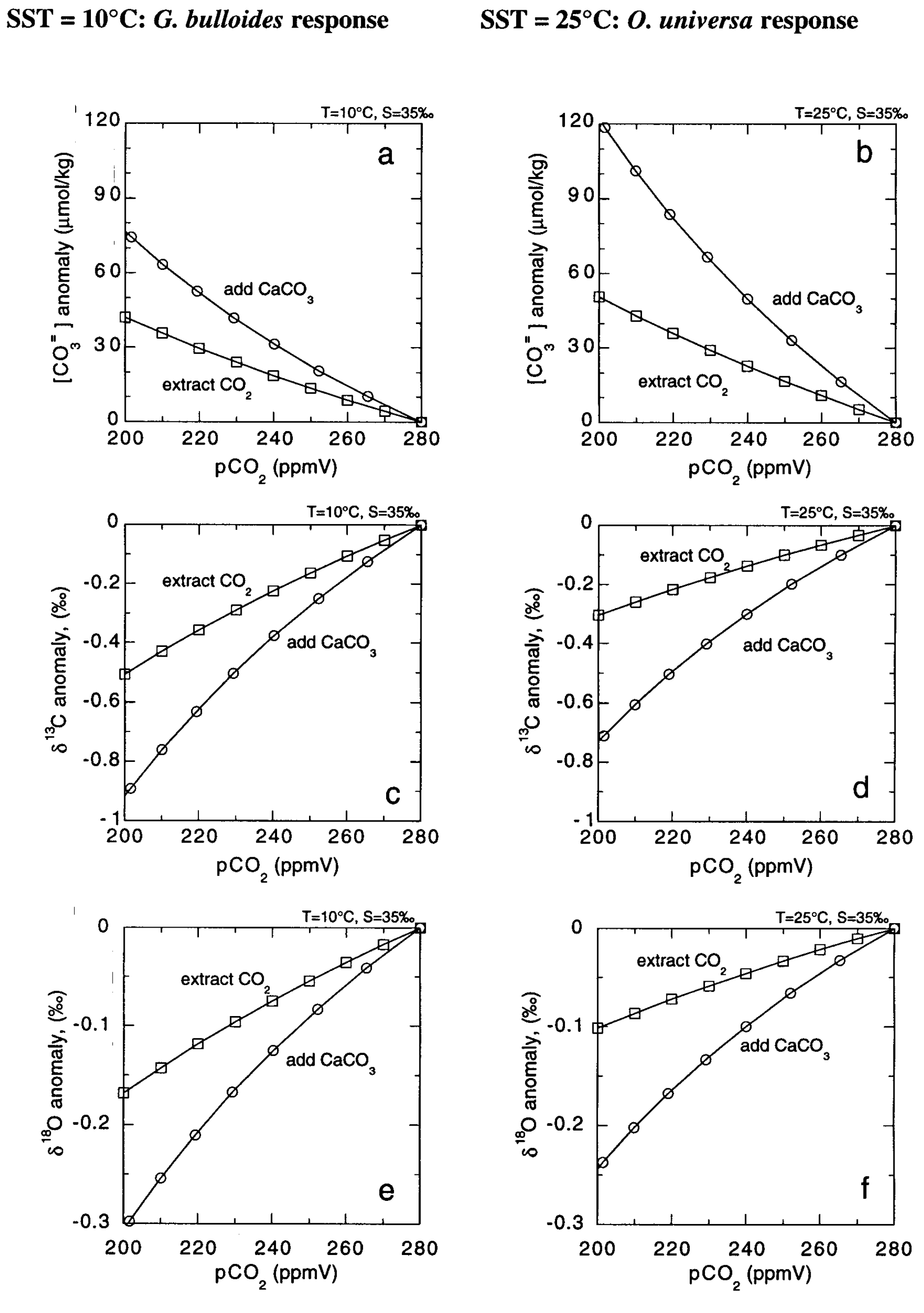
We have calculated surface water carbonate ion anomalies at temperatures of 10°C and 25°C for two hypotheses put forth to explain the glacial decrease in pCO_2: a stronger biological pump, and a rise in whole ocean pH driven by changes in $CaCO_3$ cycling (Berger 1982; Broecker 1982b; Archer and Maier-Reimer 1994; Sanyal et al. 1995). The change in surface ocean carbonate ion is very different in these two scenarios because the ratio of carbonate ion increase to pCO_2 decrease depends on the surface ocean alkalinity: CO_2 change (Fig. 1). A smaller change is associated with the drawdown of dissolved carbon dioxide under conditions of unchanging alkalinity, as would be the case if the biological pump were strengthened solely through an increase in the Redfield ratio of phytoplankton, without any calcite compensation (Broecker 1982b; Broecker and Henderson 1998). In this case, a 40 (at 10°C) to 50 (at 25°C) µmol/kg surface water carbonate ion increase equates to a pCO_2 of 200 ppmV. However, if the same pCO_2 level is achieved by the addition of calcium carbonate to seawater, as in the coral reef hypothesis, carbonate ion increases by 80 (at 10°C) to 110 (at 25°C) µmol/kg (Fig. 1a, b). The change in carbonate ion required to achieve a specific pCO_2 level is smaller in cold waters because they contain less carbonate ion and therefore require smaller fractional changes to match the glacial pCO_2 reduction.

The calculated changes in surface water carbonate ion for the two scenarios are converted to $\delta^{13}C$ anomalies using the experimental response for *G. bulloides,* a sub-polar species, for the 10°C calculation and the response for *O. universa,* a sub-tropical species, for the 25°C calculation (Fig. 1c, d). Predicted anomalies in shell $\delta^{13}C$ due to increased glacial carbonate ion range between -0.3 and -0.9‰, with the largest anomalies predicted for *G. bulloides* under the conditions of $CaCO_3$ addition. In general, the predicted anomalies in shell $\delta^{13}C$ for the $CaCO_3$ addition scenario are twice that of the anomalies predicted for the CO_2 extraction scenario. It should be noted that the contrast in seawater pH increase for the two scenarios is smaller: 0.11 pH units for the CO_2 drawdown scenario versus 0.15 for the $CaCO_3$ addition scenario. Therefore, if pH controls the isotopic deviations in the foraminifer shells, we would predict a less dramatic $\delta^{13}C$ anomaly difference for the two scenarios.

We have also generated general circulation model simulations of surface water carbonate ion concentrations for the interglacial ocean (Fig. 2a) and two glacial simulations with lowered atmospheric pCO_2 (Fig. 2b, c) (Archer et al. in review). The first glacial simulation increases oceanic NO_3^- by 50% (Fig. 2b) and assumes that plankton productivity increases in proportion to the nitrate increase (Broecker and Henderson 1998). There is no $CaCO_3$ compensation in this simulation, which is analogous to the CO_2 extraction scenario discussed above.The second glacial simulation invokes a doubling of ocean H_4SiO_4 (Fig. 2c), which perturbs calcite burial in such a way that oceanic alkalinity increases through $CaCO_3$ compensation (Archer and Maier-Reimer 1994). This simulation is analogous to the $CaCO_3$ addition scenario discussed above. As predicted from the calculations above, the change in surface water carbonate ion generated by the doubling of oceanic H_4SiO_4 ($CaCO_3$ addition) is much larger than for a 50% nitrate increase (CO_2 extraction). In line with these simulations, the predicted negative anomalies in foraminifer shell $\delta^{13}C$ due to the carbonate ion effect would be consequently greater for pCO_2 reduction achieved via ocean alkalinity increase as opposed to a stronger biological pump.

Predicted $\delta^{13}C$ Anomalies Compared to Downcore Records

High resolution isotopic data from core RC11-83 in the sub-polar South Atlantic provides a useful basis of comparison with the $\delta^{13}C$ anomalies predicted for *G. bulloides* (Charles et al. 1996). Carbon isotope anomalies due to the influence of changing surface water carbonate ion concentration are computed for the last 200 kyrs based on the Vostok pCO_2 record and the assumption that surface waters were in equilibrium with the atmosphere (Fig. 3). Our calculations demonstrate that $\delta^{13}C$ anomalies, when computed for the condition of $CaCO_3$ addition (i.e. maximum carbonate anomaly), give



SST = 10°C: *G. bulloides* response **SST = 25°C: *O. universa* response**

Fig. 1. Change in surface water carbonate ion at 10° and 25°C for equilibrium with specific pCO_2 levels relative to a baseline pCO_2 level of 280 ppmV. The change in carbonate ion required to achieve a specific pCO_2 level is smaller in cold waters because polar waters contain the lowest carbonate ion levels and therefore require smaller fractional changes to match the glacial pCO_2 reduction. **(a), (b)** Carbonate ion levels are calculated for two pCO_2 reduction scenarios: addition of $CaCO_3$ (i.e. "Coral Reef" hypothesis), and extraction of CO_2 (i.e. "Biological Pump" hypothesis). The change in surface ocean carbonate ion is larger for $CaCO_3$ addition because 1 mol of CO_2 is added for every 2 equivalents of alkalinity. **(c), (d)** Carbon isotope anomalies calculated from the carbonate ion anomalies and the experimental response for *G. bulloides,* a sub-polar species, and *O. universa,* a sub-tropical species. **(e), (f)** Oxygen isotope anomalies calculated from the carbonate ion anomalies and the experimental responses. A -0.21‰ anomaly in $\delta^{18}O$ is approximately equivalent to a -1°C anomaly in sea surface temperature.

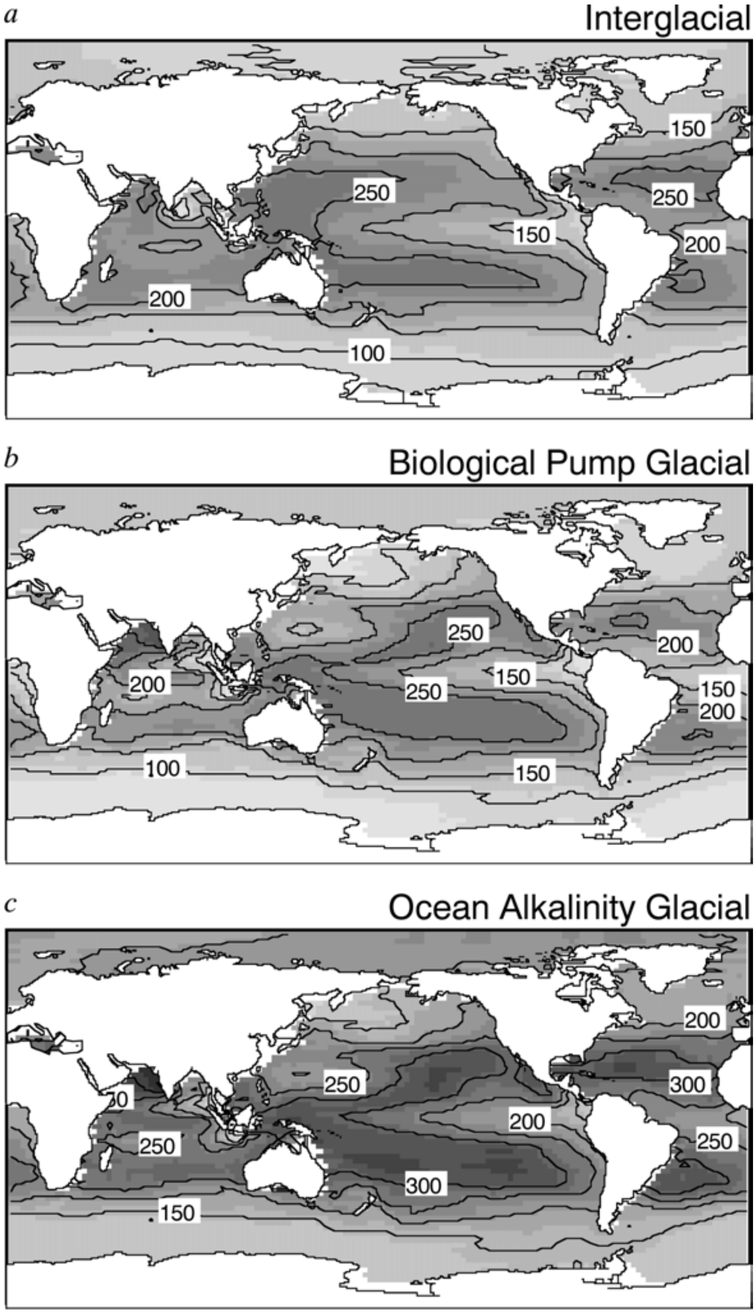


Fig. 2. General Circulation Model (GCM) simulations of surface water carbonate ion concentrations for the interglacial ocean **(a)** and two glacial simulations with lowered atmospheric pCO_2 **(b** and **c)**. The GCM simulations are based on a model described in Archer et al. (in review) and include estimates of glacial flow fields, the effects of terrestrial carbon addition, temperature changes, glacial atmospheric iron deposition and iron limitation on productivity. The first glacial simulation increases oceanic NO_3^- by 50% (Fig. 2b) and assumes that plankton productivity increases in proportion to the nitrate increase (Broecker and Henderson 1998). There is no $CaCO_3$ compensation in this simulation. The second glacial simulation invokes a doubling of ocean H_4SiO_4 (Fig. 2c), which perturbs calcite burial in such a way that oceanic alkalinity increases through $CaCO_3$ compensation (Archer and Maier-Reimer 1994). This simulation is analogous to the $CaCO_3$ addition scenario discussed above. The change in surface water carbonate ion generated by the doubling of oceanic H_4SiO_4 ($CaCO_3$ addition) is much larger than for a 50% nitrate increase (CO_2 extraction). In line with these simulations, the predicted negative anomalies in foraminifer shell $\delta^{13}C$ due to the carbonate ion effect would be consequently greater for pCO_2 reduction achieved via ocean alkalinity increase as opposed to a stronger biological pump.

rise to a reasonably close match with the observed *G. bulloides* $\delta^{13}C$ record (Fig. 3a). The temporal match with the *N. pachyderma* record is also good, but the magnitude of the observed $\delta^{13}C$ shifts is about 0.5‰ greater than the $\delta^{13}C$ anomalies calculated using the *G. bulloides* response (Fig. 3b). The similarity of the $\delta^{13}C$ records of *G. bulloides* and *N. pachyderma* coupled with the difference in the absolute magnitudes of the glacial-interglacial shifts could be explained if *N. pachyderma* shells have a larger response to changes in carbonate ion. Regardless, the carbonate ion effect provides a novel explanation for the large, negative swings in planktic $\delta^{13}C$ observed in the glacial sections of Southern Ocean cores.

Comparison of warm water $\delta^{13}C$ anomalies with tropical planktic $\delta^{13}C$ records is hampered by the availability of very limited paleoceanographic

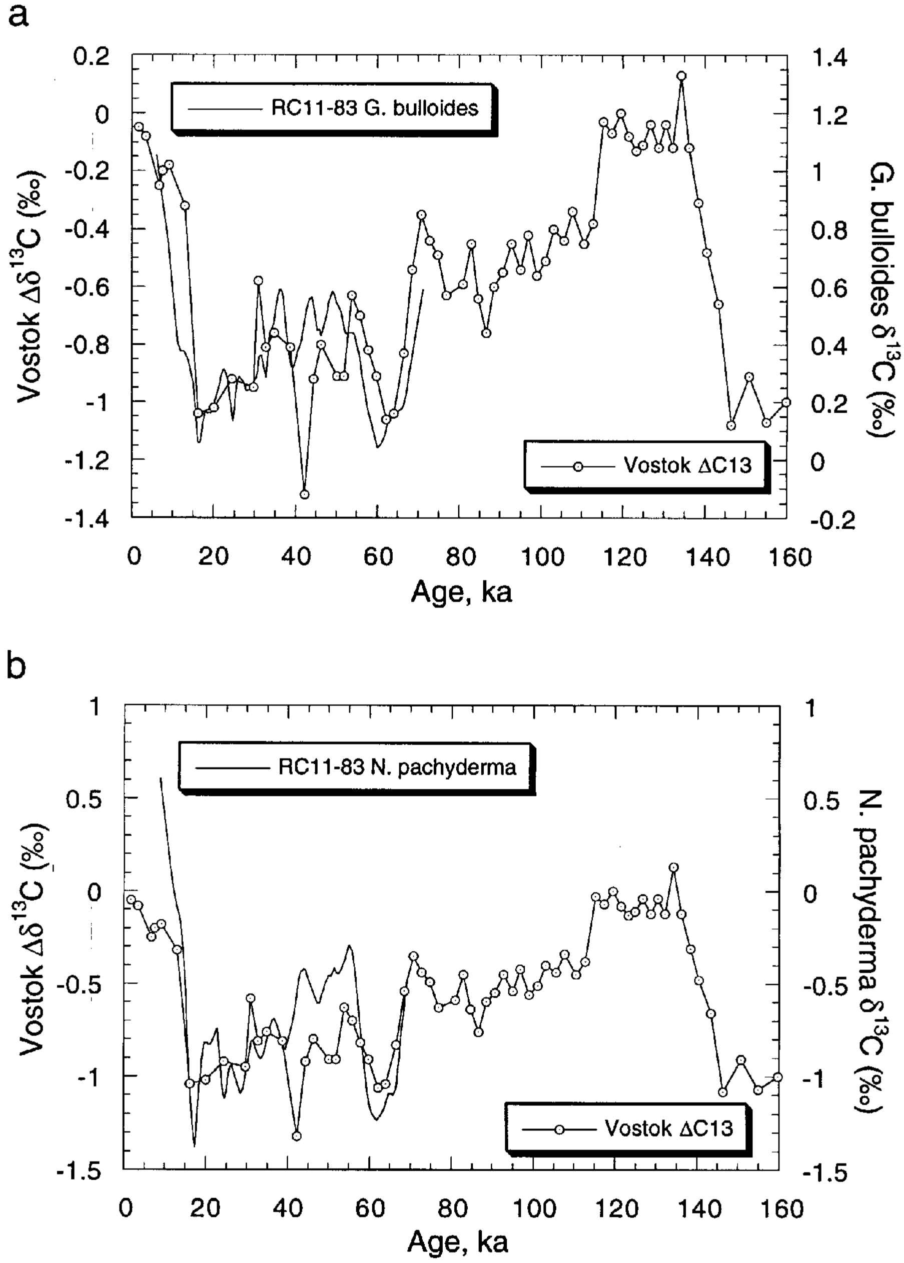


Fig. 3. Comparison of $\delta^{13}C$ anomalies computed from the Vostok pCO_2 record with planktic $\delta^{13}C$ records from South Atlantic core RC11-83 (42°S; 10°E; 4718m) (Charles et al. 1996). Carbonate ion anomalies are computed from the Vostok pCO_2 record relative to a baseline pCO_2 level of 280 ppmV, assuming pCO_2 reductions were attained by $CaCO_3$ addition. The calculations assume surface water-atmosphere equilibrium and a sea surface temperature of 10°C. Vostok $\Delta\delta^{13}C$ values are computed from the carbonate anomalies using the experimental response for *G. bulloides*. Note that the minimum at 42 kyr derives from a pCO_2 minimum in the original Vostok record that is less pronounced in later records (Jouzel et al. 1993). The isotope data from RC11-83 has been smoothed by a locally weighted least squared error method to facilitate comparison. For both plots the Vostok and RC11-83 $\delta^{13}C$ scales are matched in magnitude. **(a)** The negative shift in *G. bulloides* $\delta^{13}C$ matches the magnitude of the calculated $\delta^{13}C$ values computed from the Vostok record. **(b)** The negative shift in *N. pachyderma* $\delta^{13}C$ exceeds the magnitude of the Vostock $\Delta\delta^{13}C$ values calculated using the response for *G. bulloides*.

data for *O. universa.* Planktic $\delta^{13}C$ records from two tropical surface-dwelling species indicate typical interglacial to glacial differences of only -0.2 to -0.3‰ for *Globigerinoides sacculifer,* whereas *Globigerinoides ruber* records indicate shifts of -0.3‰ up to as large as -0.8‰ (Shackleton 1977; Curry and Crowley 1987; Oppo and Fairbanks 1989; Mix 1992; Shackleton et al. 1992; Struck et al. 1993; Linsley and Dunbar 1994; Stott and Tang 1996). The calculated magnitude of the carbonate ion effect in warm waters, -0.3 to -0.7‰ (Fig. 2d), falls within the range of observed $\delta^{13}C$ differences. But in most of the planktic records from warm waters the minimum in $\delta^{13}C$ occurs on the glacial termination, when atmospheric pCO_2 and, by extension, surface water carbonate ion levels were already well on their return to Holocene values (Sowers and Bender 1995). Another important factor that requires explanation is that the most positive shell $\delta^{13}C$ values are often found in the early Holocene rather than at the core-top. The difference in timing between the tropical/sub-tropical $\delta^{13}C$ records and the predicted change in surface ocean carbonate ion appears to preclude carbonate ion concentrations as the principal control on shell $\delta^{13}C$. However, if carbonate ion is an important influence, the paradox of two surface-dwelling tropical species recording such different $\delta^{13}C$ shifts could be explained by a greater carbonate ion response for *G. ruber.* This hypothesis has recently been confirmed by culturing experiments (Bijma et al. 1998).

Carbonate in the Deep Ocean

Because the deep ocean is not in direct contact with the atmosphere, there is no single constraint that can be imposed on the carbonate chemistry of glacial bottom waters. In addition, it is not known if carbonate ion concentrations influence the stable isotopic composition of benthic shells. Proposed scenarios for the glacial abyss range from nearly unchanged carbonate ion, which would match observations of only small glacial-interglacial changes in the lysocline (oceanic depth below which sedimentary calcite dissolves), to a near doubling of deep water carbonate ion concentrations, implied by proxy pH data (Sanyal et al. 1995). Of the two hypotheses for reduced glacial pCO_2 considered here, a strengthened biological pump would lead to negligible changes in abyssal carbonate ion, whereas any of the $CaCO_3$ cycling changes would result in a large increase in abyssal carbonate ion (Archer and Maier-Reimer 1994).

If there is no carbonate ion influence on benthic foraminifera, or if deep water carbonate ion remained constant, correcting solely for the effect of higher glacial carbonate ion on planktic shells would make planktic $\delta^{13}C$ values more positive and therefore increase the true glacial planktic-benthic $\delta^{13}C$ difference ($\Delta\delta^{13}C$). A greater surface-deep $\delta^{13}C$ difference equates to a stronger glacial biological pump. A 0.1‰ increase in $\Delta\delta^{13}C$ translates to an approximate 10 ppmV drop in pCO_2, so a 0.4‰ correction on planktic $\delta^{13}C$ due to higher carbonate ion combined with the observed 0.4‰ average glacial increase in $\Delta\delta^{13}C$ would be sufficient to explain the entire 80 ppmV glacial-interglacial pCO_2 difference (Shackleton et al. 1983a; Shackleton and Pisias 1985; Curry and Crowley 1987; Shackleton et al. 1992).

The alternative scenario is that carbonate ion concentration does influence benthic shell $\delta^{13}C$. In that case, the negative shift in benthic $\delta^{13}C$ during glacial episodes would be consistent with a whole-ocean increase in carbonate ion and pH, as expected for a pCO_2 drawdown due to changes in $CaCO_3$ cycling (Archer and Maier-Reimer 1994; Sanyal et al. 1995). If the benthic response is similar to planktics (i.e. ~-0.01‰ per μmol/kg), the -0.4‰ observed change in glacial benthic $\delta^{13}C$ (Curry et al. 1988) would be equivalent to a 40 μmol/kg increase in abyssal carbonate ion.

Influence of Carbonate Ion on Glacial Oxygen Isotope Ratios

Oxygen isotopic ratios in planktic foraminifera are an important constraint on surface ocean cooling during the LGM. Isotopic paleotemperatures appear to be consistent with CLIMAP reconstructions, which suggest that tropical surface temperatures did not cool by more than 2°C during the LGM (Broecker 1986; Stott and Tang 1996). However, the extent of agreement depends on the actual glacial to interglacial change in seawater $\delta^{18}O$, which might have been smaller than previously thought (Schrag et al. 1996). Other marine SST proxies (e.g. coral Sr/Ca) as well as terrestrial indicators (e.g. snow-line and ice core $\delta^{18}O$) suggest tropical cooling of 4-6°C at the LGM (Guilderson et al. 1994; Thompson et al. 1995). Experimental data demonstrates that shell $\delta^{18}O$ drops -0.002 and -0.004‰ per µmol/kg carbonate ion increase for *O. universa* and *G. bulloides,* respectively (Spero et al. 1997).

Anomalies in $\delta^{18}O$ computed for an 80 ppmV pCO_2 reduction range from -0.1 to -0.3‰, equivalent to an SST anomaly of approximately -0.5 to -1.5°C (Fig. 2e, f). These anomalies in shell $\delta^{18}O$ are negative deviations from apparent equilibrium which translate into overestimates of paleotemperature during periods of low pCO_2. For example, for an observed glacial-interglacial planktic $\delta^{18}O$ difference of 1.5‰ in tropical cores (Broecker 1986; Shackleton et al. 1992; Linsley and Dunbar 1994; Thunell et al. 1994), correcting for the influence of higher carbonate ion on glacial shells could increase the $\delta^{18}O$ difference to 1.7‰. Assuming the more recent 1‰ estimate of the glacial - interglacial ice volume effect (Fairbanks 1989; Schrag et al. 1996), the residual 0.7‰ is compatible with tropical cooling of up to 3.5°C. The influence of carbonate ion on shell $\delta^{18}O$ also influences paleo-salinity estimates based on *G. bulloides* $\delta^{18}O$ (Duplessy et al. 1991). A 0.3‰ correction on $\delta^{18}O$ would reduce calculated LGM salinity anomalies by about 0.6 psu.

Conclusions

Our analysis of the influence of increased carbonate ion on glacial isotopic distributions suggests potential solutions to some intractable paleoceanographic problems, but raises fundamental questions as well. The carbonate ion effect can explain why the amplitude of Southern Ocean *G. bulloides* $\delta^{13}C$ records is larger than observed in other planktic records. However, our analysis does not resolve the extent to which planktic $\delta^{13}C$ records reflect changes in the strength of the biological pump (Shackleton et al. 1983a; Shackleton and Pisias 1985; Curry and Crowley 1987; Shackleton et al. 1992). If planktics alone require a correction for higher glacial carbonate ion, the actual surface - deep $\delta^{13}C$ difference during glacial episodes was significantly larger (~0.4‰) than calculated from the foraminiferal shell $\delta^{13}C$ differences. If benthic shell $\delta^{13}C$ is also affected by carbonate ion concentration, some or all of the negative carbon isotope shift during glacial episodes is likely to be due to a whole-ocean carbonate ion increase. This attribution reduces the actual mean ocean $\delta^{13}C$ shift and therefore diminishes the inferred amount of terrestrial carbon transferred to the ocean during the LGM. This change further enlarges the difference between pollen-based and ocean $\delta^{13}C$-based estimates of the amount of carbon transferred from the terrestrial biosphere to the ocean during glacial episodes (Shackleton 1977; Crowley 1995). Because the carbonate ion effect appears to be a major factor influencing the foraminiferal isotope record, calibration of the response in each of the major paleoceanographic planktic and benthic species is a necessary next step towards fully understanding and utilizing the oceanic isotopic record.

Acknowledgments

The senior author would like to thank the Department of Geophysical Sciences, University of Chicago, for a Visiting Professorship, support, and facilities, while undertaking this research. Thanks go to Alan Mix, Brad Linsley, Chris Charles, Tom Crowley, Lloyd Keigwin and Michael Sarnthein for sharing isotope data and to Jim Kennett and Nick Shackleton for comments on the ms. Reviews by W. Berger and an anonymous reviewer improved the manuscript. This research was supported by the US National Science Foundation (DWL and HJS) and by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 261 at Bremen University, Contribution no. 204) and the Program for the Advancement of Special Research Projects at the Alfred Wegener Institute, Germany (JB).

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