Carbon isotopic disequilibrium in polar planktonic foraminifera and its impact on modern and Last Glacial Maximum reconstructions

K. E. Kohfeld, R. F. Anderson, and J. Lynch Stieglitz
Lamont-Doherty Earth Observatory and Department of Earth and Environmental Sciences, Columbia University
Palisades, New York

Abstract. Calibration studies of Neogloboquadrina pachyderma (sinistral coiling, hereinafter referred to as N. pachyderma (s.)) in the South Atlantic raise questions about the interpretation of this species’ carbon isotope composition as a paleoceanographic tracer of Southern Ocean surface nutrient contents. Carbon isotope disequilibrium between δ13C of total CO2 (TCO2) of seawater and δ13C of N. pachyderma (s.) increases systematically between 70°S and 40°S. Several effects could cause the observed carbon isotopic disequilibrium, including a combination of foraminiferal diet, calcification temperature, and carbonate ion chemistry. Combining these corrections to the δ13C of N. pachyderma (s.) improves the reconstruction of the δ13C of seawater TCO2 between 0 and 200 m in the modern South Atlantic. With these corrections applied, the δ13C for equilibrium calcite reconstructed from N. pachyderma (s.) at the Last Glacial Maximum is very similar to preindustrial values, suggesting that one cannot rule out the possibility that surface nutrient concentrations in the South Atlantic Ocean were comparable to today. However, the magnitude of the uncertainties associated with these corrections make it difficult to assess absolute palaeonutrient concentrations with much confidence.

1. Introduction

Previous studies have reached different conclusions about the use of the δ13C of Neogloboquadrina pachyderma (sinistral coiling, hereinafter referred to as N. pachyderma (s.)) as a proxy for surface ocean chemistry. Keigwin and Boyle [1989] attempted to correlate the δ13C of N. pachyderma (s.) from core top sediments with the δ13C of total CO2 (TCO2) and PO4 from high-latitude surface waters and concluded that no relationship existed. In contrast, Charles and Fairbanks [1990] argued that the δ13C of core top N. pachyderma (s.) shows a reasonable correspondence with surface water δ13C of TCO2 with biological processes causing N. pachyderma (s.) δ13C to be ~1% depleted compared with δ13C of TCO2. Using more data, Lynch-Stieglitz et al. [1994] demonstrated that the δ13C of N. pachyderma (s.) follows the surface ocean trend of δ13C of TCO2 south of the Antarctic Polar Front (APF), with N. pachyderma (s.) exhibiting an average “vital effect” offset of 0.75‰ compared with δ13C of TCO2. However, north of the APF at ~50°S, the oceanic and foraminiferal values diverge. While the δ13C values of core top N. pachyderma (s.) decrease with latitude north of the APF, implying higher nutrients, the δ13C of surface water TCO2 increases northward, reflecting the progressive depletion of nutrients. Thus the δ13C of N. pachyderma (s.) from surface sediments does not follow a consistent relationship with surface water nutrient concentration or with the δ13C of TCO2 in surface water.

Lynch-Stieglitz et al. [1994] initially hypothesized that the decrease in δ13C of N. pachyderma (s.) north of the APF might result from deeper calcification depths. If the depth at which the δ18O of N. pachyderma (s.) is approximately equal to the δ18O predicted for calcite formed in equilibrium with seawater (δ18Ocalc) defines the apparent calcification depth, then N. pachyderma (s.) seems to calcify between 0 and 300 m (Figure 1b). However, when the apparent calcification depth is estimated comparing the δ13C of N. pachyderma (s.) with δ13C of calcite formed in equilibrium with seawater TCO2 (δ13Ceq), the apparent calcification depths occur below 4000 m (Figure 1b). Even if a constant 1.0‰ “vital offset” is added to the δ13C of N. pachyderma (s.), the estimated calcification depths still extend below 1000 m north of 48°S. The apparent calcification depths of N. pachyderma (s.) determined using δ18O are consistent with the relatively near-surface distribution of N. pachyderma (s.) in plankton tows in the South Atlantic Ocean, in which maximum abundances occur above 300 m in all cases (Figure 2). Thus, some other processes must cause N. pachyderma (s.) to calcify out of equilibrium with the δ13C of TCO2.

Recent plankton tow and laboratory culture studies have suggested that carbon isotopic disequilibrium between foraminiferal calcite and seawater TCO2 may result from the effects of several environmental variables upon the calcification process in planktonic foraminifera. These effects include (1) temperature [e.g., Ortiz et al., 1996; B. E. Bemis et al., Temperature influence on the carbon isotopic composition of Orbulina universa and Globigerina bulloides (planktonic foraminifera) submitted to Marine Micropaleontology, 1999, (hereinafter referred to as Bemis et al., submitted manuscript, 1999)], (2) carbonate chemistry of seawater [e.g., Spero et al., 1997]; (3) foraminiferal shell size [e.g., Ravelo and Fairbanks, 1995; Spero and Lea, 1996]; and (4) the isotopic composition of the foraminiferal diet [e.g., Spero and Lea, 1996; Bijma et al.,...
Figure 1. Oxygen and carbon isotopes of Neogloboquadrina pachyderma (s.) and equilibrium calcite versus latitude. Solid circles show δ¹⁸O and δ¹³C of N. pachyderma (s.) recovered from sediment traps and surface marine sediments (Tables A1-A3). (a) δ¹⁸O of calcite (per mil, relative to Pee Dee Belemnite standard) versus latitude (°S) in the South Atlantic. Solid and dashed lines show δ¹⁸O predicted for calcite formed in equilibrium with the seawater (δ¹⁸Oₗₗ) at 100 m depth intervals between 0 and 500 m and at 1000 m. (b) Solid lines show δ¹³C predicted for calcite formed in equilibrium with seawater (δ¹³Cₗₗ) at 1000 m depth intervals between 0 and 4000 m. Open circles show δ¹³C of N. pachyderma (s.) from surface sediments with a 1% "vital offset" added. Apparent calcification depths estimated from the δ¹³C of N. pachyderma (s.) are unrealistic in either case north of 48°S.

This study evaluates the controls on the isotopic composition of N. pachyderma (s.) from surface sediments in the South Atlantic Ocean. First, the spatial changes in carbon isotope disequilibrium of N. pachyderma (s.) are quantified by comparing the δ¹³C of N. pachyderma (s.) with a best approximation of the δ¹³C of calcite formed in equilibrium with preindustrial modern seawater TCO₂. Second, the correction factors for three carbon isotope fractionation effects are determined and applied to the δ¹³C of N. pachyderma (s.). Correcting for these effects produces an improved relationship between the δ¹³C of foraminiferal calcite and that of surface water TCO₂ in the modern ocean and opens a means for improved interpretation of the δ¹³C of glacial age N. pachyderma (s.).

2. Methods

2.1. Compilation of Data

2.1.1. Core tops. The δ¹⁸O and δ¹³C of N. pachyderma (s.) measured from sediment traps and surface marine sediments were compiled from the literature (Figure 3) [Charles, 1991; Charles and Fairbanks, 1990; Charles et al., 1996; Donner and Wefer, 1994; Grobe and Mackensen, 1992; Grobe et al., 1990; Hodell, 1993; Keigwin and Boyle, 1989; Mackensen et al., 1989, 1994; Niebler, 1995; Wefer et al., 1982] (Tables A1-A3). Only surface sediment and sediment trap samples from the South Atlantic basin are included in the compilation. Sites excluded from this analysis follow the same rationale as applied by Lynch-Stieglitz et al. [1994].

2.1.2. Oceanographic data. Values for δ¹⁸Oeq were determined using February temperature and salinity data from Levitus and Boyer [1994] along 2.5°E. The δ¹⁸Oeq was determined after Kim and O’Neil [1997]:

\[
\delta^{18}O_{eq}(\%e, \text{PDB}) = 3.276 - T(°C) \times 0.97 + (0.99973 \times \delta^{18}O_{SMOW} - 0.27),
\]

where δ¹⁸Oeq is relative to the Pee Dee Belemnite (PDB) standard, and δ¹⁸O of water is relative to Standard Mean Ocean Water (SMOW).

The δ¹⁸O-Salinity (S) relationship:

\[
\delta^{18}O_{water} = 0.58 \times S \times 19.79
\]

was determined from Geochemical Ocean Sections Study (GEOSECS) archived at the National Oceanographic Data Center, available on the World Wide Web at http://www.nodc.noaa.gov) using samples from 35° to 65°S and 0 to 500 m.

The δ¹⁴C of TCO₂ data were compiled from Mackensen et al. [1993; 1996]. Between 70° and 40°S, these data were contoured to estimate δ¹³C of TCO₂ profiles between 0 and 4000 m. Values for δ¹³Ceq were determined after Romanek et al. [1992]:

\[
\delta^{13}C_{eq}(\%e, \text{PDB}) = \delta^{13}C_{TCO₂} + 1.0.
\]

2.2. Correcting for Anthropogenic Effects on the δ¹³C of TCO₂

Before the δ¹³C of seawater TCO₂ can be compared with the δ¹³C of N. pachyderma (s.) from surface marine sediments, the effects of the invasion of anthropogenic carbon upon the isotopic composition of surface water TCO₂ must be considered. In modern surface water the δ¹³C of TCO₂ is affected by gas exchange with isotopically light CO₂ in the atmosphere, added during fossil fuel burning. However, surface sediment samples from the South Atlantic most likely represent preindustrial conditions.

Estimates of the oceanic uptake of anthropogenic carbon dioxide suggest that the invasion of anthropogenic CO₂ has increased the TCO₂ of South Atlantic waters (~100 m) by ~20 to 40 μmol kg⁻¹ between 70° and 40°S [Grobner, 1998]. Model simulations have also predicted a first-order relationship between the anthropogenic change in the δ¹³C of TCO₂ and the amount of anthropogenic CO₂ in seawater (C₅₆(N. Grober, personal communication, 1997)):

\[
\Delta \delta^{13}C(\%e) = 0.00095 - 0.012 (\%e \text{ μmol}^{-1} \text{ kg}^{-1}) C_{anth}(\text{μmol kg}^{-1})
\]

\[C_{anth} < 35 \text{ μmol kg}^{-1}\]

Supporting tables are available electronically at World Data Center-A for Paleoclimatology, NOAA/NGDC, 325 Broadway, Boulder, Colorado (e-mail: paleo@mail.ngdc.noaa.gov; URL: http://ngdc.noaa.gov/paleo).
Drake Passage Transect, Multinet Plankton Tows
ANT X/5, Aug-Sept, 1992

Figure 2. Depth distribution of planktonic foraminifera in the Drake Passage. Abundances of total foraminifera (number per meter$^3$) versus depth (m), collected from six stations of vertically stratified plankton tows, across the Drake Passage (Table A3). Maximum abundances are always found between 0 and 300 m. Plankton tow samples were collected from ANT X/5, August to September, 1992 on board the R.V. Polarstern. SAFZ, Sub-Antarctic Front Zone; APFZ, Antarctic Polar Front Zone; CWB, Continental Water Boundary.

Figure 3. Locations of sediment and sediment trap samples used in this study (Table A1). Open circles show locations of sediment traps, and solid circles indicate sediment samples.
\[ \Delta \delta^{13}C (\%e) = 0.3\%e - 0.020 (\%e \ mu mol^{-1} kg^{-1}) C_{\text{mer}} (\mu mol kg^{-1}) \]

\[ C_{\text{mer}} > 35 \mu mol kg^{-1}. \] (5)

Using the above relationships, the uptake of anthropogenic CO\textsubscript{2} has decreased the \( \delta^{13}C \) of TCO\textsubscript{2} between 0 and 200 m by \(-0.15\) to 0.65\%e since preindustrial times. These values are consistent with the modeling study of Lynch-Stieglitz et al. [1995], which suggested a +0.2\%e correction for Antarctic Surface Water (\(-70^\circ S\)), increasing to +0.8\%e at \(-40^\circ S\). These anthropogenic corrections are used to estimate preindustrial values of \( \delta^{13}C \) of TCO\textsubscript{2} to determine carbon isotope disequilibrium for core top \textit{N. pachyderma} (s.). The anthropogenic correction is not applied when using the \( \delta^{13}C \) of \textit{N. pachyderma} (s.) from sediment traps, which are assumed to reflect modern \( \delta^{13}C \) of TCO\textsubscript{2}.

3. Rationale: Correcting for Carbon Isotope Disequilibrium in \textit{N. pachyderma} (s.)

The carbon isotope composition of a foraminiferal shell \( \delta^{13}C_{\text{shell}} \) will be a function of the \( \delta^{13}C \) of ambient seawater TCO\textsubscript{2} \( \delta^{13}C_{\text{TCO}_2} \), the fractionation predicted for inorganic calcite formed in equilibrium with seawater \( \Delta_{\text{eq}} \) and the sum of all effects causing the \( \delta^{13}C_{\text{shell}} \) to deviate from equilibrium \( \Delta_{\text{diseq}} \):

\[ \delta^{13}C_{\text{shell}} = \delta^{13}C_{\text{TCO}_2} + \Delta_{\text{eq}} + \Delta_{\text{diseq}}. \] (6)

Throughout this investigation we compare the \( \delta^{13}C_{\text{shell}} \) with the \( \delta^{13}C \) of calcite formed in equilibrium with seawater TCO\textsubscript{2} \( \delta^{13}C_{\text{eq}} \), using a constant \( \Delta_{\text{eq}} \) of 1\%e [Romanek et al., 1992]. Equation (6) can be rewritten as

\[ \delta^{13}C_{\text{shell}} = \delta^{13}C_{\text{eq}} + \Delta_{\text{diseq}} \text{ or } \Delta_{\text{diseq}} = \delta^{13}C_{\text{eq}} - \delta^{13}C_{\text{shell}}. \] (7)

Several effects could contribute to the increase in carbon isotope disequilibrium between \( \delta^{13}C \) of \textit{N. pachyderma} (s.) and \( \delta^{13}C_{\text{eq}} \) north of the APF. These effects include (1) effect of dietary \( \delta^{13}C \) on shell composition \( \Delta_{\text{det}} \) [Spero and Lea, 1996; Bijma et al., 1999], (2) changes in the carbonate ion concentration \( \Delta_{\text{carb}} \) [Spero et al., 1997], (3) temperature-dependent changes in metabolic rate \( \Delta_{\text{T}} \) [Ortiz et al., 1996], and (4) size-dependent changes in either metabolic activity or growth rate, causing carbon isotope fractionation of the shell \( \Delta_{\text{size}} \) [e.g., Kohfeld, 1998]. Thus it is likely that \( \Delta_{\text{diseq}} \) will result from a combination of these effects.

\[ \delta^{13}C_{\text{eq}} - \delta^{13}C_{\text{shell}} = \Delta_{\text{diseq}} = \Delta_{\text{det}} + \Delta_{\text{carb}} + \Delta_{\text{T}} + \Delta_{\text{size}}. \] (8)

While the \( \delta^{13}C \) of planktonic foraminifera has been shown to be dependent on shell size [e.g., Curry and Matthews, 1981; Oppo and Fairbanks, 1989; Donner and Wefer, 1994; Ravelo and Fairbanks, 1995; Spero and Lea, 1996; Kohfeld, 1998], establishing \( \Delta_{\text{det}} \) for this study using core top samples is complicated: (1) in some cases the size fraction of \textit{N. pachyderma} (s.) analyzed was not recorded; and (2) measurements were made on pooled shells of foraminifera from a wide size range (e.g., 150 to 325 \( \mu m \)). Thus, in this study, we must assume that a consistent size range of \textit{N. pachyderma} (s.) was sampled across the study area.

Evaluating the carbon isotope disequilibrium \( \Delta \) for any environmental factor involves three parameters: (1) a sensitivity coefficient \( M \), (2) the magnitude of the parameter expressing the environmental factor \( X \), and (3) an offset \( B \) that includes the effects of all other environmental parameters that affect \( \Delta_{\text{diseq}} \). That is, for each parameter \( i \), \( \Delta_{\text{i}} = M_{\text{i}}X_{\text{i}} + B_{\text{i}} \):

\[ \delta^{13}C_{\text{shell}} - \delta^{13}C_{\text{eq}} = (MX)_{\text{det}} + (MX)_{\text{carb}} + (MX)_{\text{T}} + R_{\text{det}}. \] (9)

where \( R_{\text{det}} \) is the combination of offsets from all of the factors \( (R_{\text{det}} + R_{\text{carb}} + R_{\text{T}}) \) and is considered constant over the South Atlantic region.

Values for \( M \) and \( B \) for each environmental parameter have been determined in a variety of manners using field, core top, and culture studies. In culture studies, slopes are determined by holding all but one environmental variable constant. Thus the offset \( R \) will incorporate the disequilibrium effects of those environmental conditions that are held constant and will undoubtedly vary from study to study. In field studies using either surface sediment or plankton tow samples, the environmental conditions affecting \( \Delta_{\text{diseq}} \) are not held constant. Thus, in field studies, multiple environmental factors can contribute both to \( M \) and to \( B \).

It is important to emphasize that the offset \( B \) determined for each environmental parameter in previous studies will be arbitrary, depending on the ambient conditions of the study. The important element for this comparison is the slope \( M \) determined for each environmental parameter and how it can be applied to correct the \( \delta^{13}C \) of \textit{N. pachyderma} (s.), regardless of the value chosen for \( B \). For this study, we somewhat arbitrarily establish that \( \delta^{13}C_{\text{eq}} \) at 43\%e is the reference level. In other words, for each correction procedure, values of \( B \) are chosen so that the corrected \( \delta^{13}C \) of \textit{N. pachyderma} (s.) will equal \( \delta^{13}C_{\text{eq}} \) at 43\%e. We have chosen to align the \( \delta^{13}C \) of \textit{N. pachyderma} (s.) with the \( \delta^{13}C_{\text{eq}} \) here because at this latitude we have several consistent measurements of both the \( \delta^{13}C \) of \textit{N. pachyderma} (s.) and the \( \delta^{13}C \) of TCO\textsubscript{2}. Choosing a different reference level would not affect the slope of each disequilibrium effect, only the offset \( B \). Here we discuss each effect individually before examining the cumulative effect of the corrections.

3.1. Dietary Effects

Culture experiments using the symbiotic species \textit{Globigerina bulloides} suggest a 0.084\%e change in the foraminiferal shell composition for each 1\%e change in dietary carbon isotope composition [Spero and Lea, 1996].

\[ \Delta_{\text{det}} (\%e) = -0.084 (\delta^{13}C_{\text{org}}) + 1.07. \] (10)

where \( \Delta_{\text{det}} \) is the carbon isotope disequilibrium between \( \delta^{13}C_{\text{eq}} \) and \( \delta^{13}C_{\text{shell}} \) due to changes in dietary \( \delta^{13}C \), \( \delta^{13}C_{\text{org}} \) is the carbon isotope composition of the food source, and 1.07\%e is the experiment-specific offset.

Given this relationship, explaining the entire decrease in the \( \delta^{13}C \) of \textit{N. pachyderma} (s.) north of the APF in terms of food source changes would require that the \( \delta^{13}C \) of marine phytoplankton decrease by \(-10\%e \) from 51\%e to 41\%e. On the contrary, the \( \delta^{13}C \) of phytoplankton and particulate organic matter show an increase by \(-9\%e \) between 70\%e and 40\%e [Rau et al., 1991; Sackett et al., 1974], which would result in a 0.76\%e increase in the \( \delta^{13}C \) of \textit{N. pachyderma} (s.) between 70\%e and 40\%e. Thus the dietary \( \delta^{13}C \) correction is insufficient to account for the observed \( \Delta_{\text{diseq}} \) and, in fact, takes the corrected \( \delta^{13}C_{\text{shell}} \) in the
3.2. Effect of Carbonate Ion Concentrations

An increase in the carbonate ion concentration of seawater also explains some of the observed disequilibrium between the δ13C of core top N. pachyderma (s) and δ13Ceq. For every 10 μmol kg⁻¹ increase in seawater [CO₃²⁻] the δ13C and δ18O of G. bulloides decrease by 0.13‰ and 0.045‰, respectively [Spero et al., 1997]:

\[ \Delta_{\text{arb}} = 0.013 \ [\text{CO}_3^{2-}] + 1.27. \]  (11)

While the exact mechanism for this effect is unknown, the authors hypothesize that the pH dependence of the CO₂ hydration and hydroxylation reactions may be responsible for the kinetic discrimination against ¹⁸O and ¹³C during calcification. A recent modeling study suggests that the dependence of shell δ¹⁸O on the carbonate chemistry can be explained in terms of equilibrium fractionation in Orbifera universals, but species with steeper slopes (such as G. bulloides) require additional kinetic effects [Zeebe, 1999]. The dependence of shell δ¹³C on the carbonate chemistry, however, can only be explained in terms of kinetic effects [Björne et al., 1999, Wolf-Gladrow et al., 1999, Zeebe et al., 1999].

In the modern South Atlantic, measured [CO₃²⁻] between 50 and 150 m range from 90 to 175 μmol kg⁻¹ between 60° and 38°S during austral summer (Figure 4) [GEOSECS, data archived at NODC, Chipman et al., 1994]. However, surface ocean [CO₃²⁻] will also be affected by anthropogenic changes in atmospheric pCO₂, and so preindustrial values of [CO₃²⁻] must be estimated. Assuming equilibrium between the atmosphere and the surface ocean and that all other variables in the carbon system are approximately the same as today, then preindustrial pCO₂ levels of 150 ppm result in carbonate ion concentrations of -120 to 180 μmol kg⁻¹ between 70° and 40°S (Figure 4). This meridional gradient in [CO₃²⁻] should result in a decrease (from south to north) in the δ¹³C of N. pachyderma (s) by 1.2‰ and by <0.3‰ in δ¹⁸O across the same latitudinal band.

We can apply the carbonate ion correction to the δ¹³C of N. pachyderma (s) to arrive at an estimate for δ¹³Ceq in the following way:

\[ \delta^{13}C_{\text{eq}} = \delta^{13}C_{\text{shell}} + 0.013 \ [\text{CO}_3^{2-}] + B, \]  (12)

where a value of 0.5‰ was arbitrarily chosen for B such that the corrected δ¹³Cshell is equal to δ¹³Ceq at 43°S. Applying only the carbonate ion correction to the δ¹³C of N. pachyderma (s) is not sufficient to reproduce the observed latitudinal distribution of the predicted preindustrial δ¹³Ceq between 0 and 200 m (Figure 5). The situation is worse once the dietary δ¹³C effect is included:

\[ \delta^{13}C_{\text{eq}} = \delta^{13}C_{\text{shell}} + 0.013 \ [\text{CO}_3^{2-}] + \Delta_{\text{diet}} + B, \]  (13)

where -1.3‰ was arbitrarily chosen for B (Figure 5). The effects of Δdiet and Δarb tend to offset each other. Thus, when these two corrections are combined, there remains a substantial difference between δ¹³Ceq and the corrected δ¹³Cshell. This difference implies that at least one more correction must be made.
In this instance, a value of −2.8 for $B_{\text{tot}}$ aligns the corrected $N. pachyderma$ (s.) δ¹³C with the predicted preindustrial δ¹³C(eq) between 0 and 200 m at 43°S (Figure 5).

Calcification temperature $T$ can be taken as the ambient seawater temperature found at the apparent calcification depth determined from the δ¹⁸O of the shells. Estimating $T$ in this way assumes that δ¹⁸O of $N. pachyderma$ (s.) is found in isotopic equilibrium with the water column. As mentioned previously, while changes in carbonate ion concentration are expected to affect the δ¹⁸O of $N. pachyderma$ (s.), we estimate that this effect will be <0.3‰ across the transect on the basis of culture sensitivities of $G. bulloides$ [Spetro et al., 1997].

4. Results: Summary of Effects

Figure 5 suggests that to first order, the observed carbon isotope composition of $N. pachyderma$ (s.) deviates from equilibrium on the basis of the additive combination of three fractionation effects (Table 1). The relative magnitudes of these effects between 70° and 40°S can be compared (Table 1). The maximum carbon isotope disequilibrium attributable to temperature across the transect is 1.96‰, with 1.17‰ attributable to meridional changes in carbonate ion concentrations. The dietary δ¹³C effect is approximately one third that of the temperature effect, acting in a competing direction.

The difference between the corrected δ¹³C of $N. pachyderma$ (s.) and the predicted preindustrial δ¹³C(eq) increases slightly with increasing δ¹³C(eq) $R^2 = 0.41$ and $N = 50$ (Figure 6). The slight trend seems to suggest that these three correction factors do not account for all of the observed carbon isotope disequilibrium in $N. pachyderma$ (s.). Nevertheless, these three corrections to the δ¹³C of $N. pachyderma$ allow for a reasonable representation of modern δ¹³C(eq) between 0 and 200 m in the South Atlantic. This reflects that carbon isotope disequilibrium in $N. pachyderma$ (s.) is systematic and can be attributed to variations in environmental parameters.

5. Discussion

5.1. Assumptions and Caveats

The fact that the three correction factors do not account for all of the carbon isotope disequilibrium could be the result of either uncertainties in the field data or the result of the assumptions that we have made in this analysis. First, there are uncertainties in our abilities to estimate both the δ¹³C(eq) predicted for preindustrial waters between 0 and 200 m, as well as uncertainties associated with core top sediment ages. Furthermore, the application of these corrections to $N. pachyderma$ (s.) makes several assumptions: (1) the slopes for $G. bulloides$ can be applied to $N. pachyderma$ (s.), (2) the environmental parameters ($T$, $CO_2$, and diet) are independent, (3) the empirical relationships determined for the temperature, carbonate ion, and diet corrections are independent, and (4) no other fractionation process (in particular, size) is contributing to carbon isotope disequilibrium and varying systematically.

We assume that relationships determined on $G. bulloides$ can be extended to $N. pachyderma$ (s.), but it is quite possible that each species will have a different physiological response to environmental parameters. For example, in the culture dietary
**Table 1. Summary of Relationships Between Carbon Isotope Disequilibrium and Environmental Variables as Determined in Culture Experiments**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Slope $M$</th>
<th>Offset $B$</th>
<th>$R^2$</th>
<th>Species</th>
<th>Reference</th>
<th>South Atlantic Latitudinal Range</th>
<th>$\delta^{13}\text{C}$ Sensitivity, † %e</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{13}\text{C}_{\text{org}, \text{%e}}$</td>
<td>0.084</td>
<td>1.07</td>
<td>0.84</td>
<td>G. bull.</td>
<td>Spero and Lea [1996]</td>
<td>-21 to -30%</td>
<td>0.76</td>
</tr>
<tr>
<td>[CO$_3^{2-}$], μmol kg$^{-1}$</td>
<td>+0.013</td>
<td>1.27</td>
<td>0.94</td>
<td>G. bull</td>
<td>Spero et al. [1997]</td>
<td>120 to 210 μmol kg$^{-1}$</td>
<td>-1.17</td>
</tr>
<tr>
<td>$T$, °C</td>
<td>+0.13</td>
<td>-1.47</td>
<td>0.99</td>
<td>G. bull</td>
<td>Bemis et al., (submitted manuscript, 1999)</td>
<td>-2 to 13°C</td>
<td>-1.96</td>
</tr>
</tbody>
</table>

*G. bull. is Globigerinoides bulloides.*

*Observed range in the environmental parameter between 70° and 40°S in the South Atlantic Ocean.

†Expected change in carbon isotope composition from 70° to 40°S, resulting from changes in environmental parameter (e.g., $\delta^{13}\text{C}$ of planktonic foraminifera is expected to decrease by 1.96% as a result of increasing temperatures across this latitudinal range).

$\delta^{13}\text{C}$ experiments, G. bulloides were fed brine shrimp of varying isotopic compositions. However, N. pachyderma (s.) is believed to be herbivorous [Gowing, 1989; Hemleben et al., 1989]. While the metabolic CO$_2$ contributing to the isotopic composition of the foraminiferal calcite may respond similarly in both species, these types of interspecific differences could make a difference. The residual disequilibrium found in the field data (Figure 6) suggest that either the temperature sensitivity, the carbonate ion sensitivity, or both sensitivities for N. pachyderma (s.) must be somewhat larger than culture-determined sensitivities for G. bulloides. This also assumes that there are no additional fractionation processes contributing the $\delta^{13}\text{C}$ of N. pachyderma (s.).

A second complication is that the environmental parameters themselves are not independent. Carbonate ion concentrations and ambient seawater temperatures are highly correlated in the GEOSECS, World Ocean Circulation Experiment (WOCE), North Atlantic, and German Joint Global Ocean Flux Study (JGOFS) data (Figure 7; 0 to 150 m). Thus, it is not surprising that both show a high correlation with carbon isotope disequilibrium, which also increases more or less linearly north of the APF. Because of this high correlation between temperature and carbonate ion concentrations it is not possible to isolate a unique solution for the N. pachyderma (s.) sensitivities using the field data, further emphasizing the need for culture studies on N. pachyderma (s.).

Finally, this analysis assumes that each process affecting carbon isotope fractionation can be treated independently, and therefore the effects are additive. It is quite possible that each effect may be interdependent, and the slopes for one parameter

![Figure 6. Residuals $e$ versus preindustrial $\delta^{13}\text{C}_{\text{eq}}$, where $e = \delta^{13}\text{C}_{\text{eq}} - \delta^{13}\text{C}_{\text{org}} - \delta^{13}\text{C}_{\text{sh}} - M_{\text{dis}} - M_{\text{carb}} - M_{\text{f}} - B_{\text{rot}}$.](image)

![Figure 7. Carbonate ion concentration versus temperature for the North and South Atlantic regions. North Atlantic data are included to demonstrate that empirical field relationship between [CO$_3^{2-}$] and temperature is essentially the same in both regions. Carbonate ion concentrations and temperatures are taken from the same sources as found in Figure 4 plus data from the Transient Tracers in the Oceans/North Atlantic Study [Takahashi and Brewer, 1986].](image)
may vary depending on other environmental conditions. For example, Spero and Iea [1996] suggest that the relationship between δ13C and size in *G. bulloides* may be temperature-dependent. Additionally, an increase in shell size decreases the amount of metabolic CO₂ incorporated into the calcite lattice [Hemleben and Bijma, 1994; Kohfeld, 1998], so one would expect the dietary δ13C effect to decrease with increasing shell size. This synergism, which may occur when two (or more) disequilibrium effects interact, could explain the residual disequilibrium not accounted for by a strict additive combination of effects shown in Figure 5. More culture studies are needed to quantify the specific relationships and offsets for *N. pachyderma* (s.), and to determine how these effects may interact when more than one environmental parameter is varied.

5.2. Implications for Paleoceanographic Reconstructions: A Sensitivity Analysis

One logical extension of this analysis is to reconstruct the δ13C in the South Atlantic Ocean during the Last Glacial Maximum (LGM). The glacial δ13C values of *N. pachyderma* (s.) in South Atlantic sediments were ~0.2 to 1.25‰ lower than in surface sediments (Figure 8). However, in order to arrive at an estimate of the δ13C at the LGM the δ13C of *N. pachyderma* (s.) (δ13Cshell) must be corrected for global reservoir changes and the various disequilibrium effects. Here we attempt to estimate how the glacial-interglacial variability in each environmental parameter might affect the glacial-interglacial change in the δ13C of *N. pachyderma* (s.) (Table 2).

To reconstruct δ13Ceq for the LGM, we apply the corrections developed for the modern ocean:

\[
\delta^{13}C_{\text{eq,LGM}} = \delta^{13}C_{\text{shell,LGM}} + \Delta_{\text{res}} + (MX)_{\text{det,LGM}} + (MX)_{\text{carb,LGM}} + (MX)_{\text{det,LGM}} + B_{\text{res}}.
\]  

where values for *Mdet*, *MF*, and *Mcarb* are found in Table 1. On the assumption that *Bres* will not vary significantly through time, we use the value of -2.8‰ for *Bres* established in Figure 5. Furthermore, we will use the sensitivities determined on *G. bulloides* in culture studies (Table 1). The new term in Equation 16 is Δres, which represents the global ocean reservoir decrease of 0.4‰ in the carbon isotopic composition of benthic foraminifera [Shackleton, 1977; Curry et al., 1988; Duplessy et al., 1988]. The environmental parameters *Xdet*, *Xf*, and *Xcarb* must be estimated for the LGM.

Glacial-interglacial changes in the dietary δ13C (\(X_{\text{diet}}\)) can be estimated from the δ13C of organic material isolated from diatom frustules recovered from sediments (Figure 9a), assuming that the δ13C of organic matter in marine sediments is a proxy for dietary δ13C. South of the modern-day APF (~50°S) in the South Atlantic, the δ13C of diatom organic matter in glacial sediments is lower than modern values by ~3.6‰ [Shemesh et al., 1993], with the LGM/Holocene difference decreasing to zero at 48°S [Rosenthal and Shemesh, 1998]. On the basis of these estimates the glacial-interglacial difference in the dietary δ13C correction is relatively small, accounting for 0.0 to 0.3‰ of the glacial-interglacial change in δ13C of *N. pachyderma* (s.). This estimation assumes that the feeding rates of *N. pachyderma* (s.), which can also affect the δ13C fractionation [e.g., Hemleben and Bijma, 1994], remain constant on glacial-interglacial timescales.

South Atlantic glacial sea surface temperatures (\(X_f\)) were ~2 to 3°C cooler than modern SSTs [Figure 9b; Climate: Long-Range Investigation, Mapping, and Prediction (CLIMAP],
1981], with the major difference being the apparent position of the APT. To circumvent the problem of no data between 50° and 70°S, we assume a SST value of 1.8°C at 70°S and linearly interpolate as a function of latitude to the CLMAP SST value at 50°S. Given this average temperature decrease, the temperature effect on the δ¹³C of N. pachyderma (s.) during the LGM was ~0.25 to 0.4‰ lower than today. Thus, while the temperature effect is dominant meridionally, the glacial-interglacial change is relatively small.

In the absence of paleoceanographic data an indirect estimate of glacial [CO₃²⁻] (X_{CO₃}) is required to evaluate the carbonate ion effect upon the δ¹³C of N. pachyderma (s.) (Figure 9c). If values for pCO₂ and temperature and one other major variable of the seawater carbon system are known, then we can calculate [CO₃²⁻]. For estimation of glacial [CO₃²⁻] we use sea surface temperatures from CLIMP [CLIMP, 1981] and an atmospheric pCO₂ value of 200 ppm from ice cores [Barnola et al., 1987]. Equilibrium between the atmosphere and surface ocean is assumed. We assume that regional patterns of salinity and alkalinity [Chipman et al., 1994] are unchanged from today but adjust these values upward by 3% to account for the drop in global sea level. Implicit in this calculation is the assumption that the mechanism responsible for the lower glacial CO₂ involved only the redistribution of carbon within the ocean atmosphere system by biological cycling and that there was no whole ocean change in alkalinity [e.g. Broecker, 1982]. This calculation suggests that [CO₃²⁻] were 30 to 46 μmol kg⁻¹ higher than preindustrial values at the LGM. As a result, the total amplitude of the carbonate ion correction to the δ¹³C of N. pachyderma (s.) is 0.4 to 0.6‰ greater during the LGM. If, on the other extreme,
we assume that the scenario for lower glacial pCO$_2$ involved primarily the addition of CaCO$_3$ to the ocean (e.g., changes in rain ratio [Archer and Maier-Reimer, 1994; Lea et al., 1999]), then the increase in glacial [CO$_2$] would result in a 0.9 to 1.0$\%$ correction to the $\delta^{13}$C of N. pachyderma (s).

When the combined corrections are added to the glacial $\delta^{13}$C of N. pachyderma (s) (Equation 16), the $\delta^{13}$C$_{org}$ values are more similar to the modern $\delta^{13}$C$_{org}$ between 30$^\circ$ and 38$^\circ$S than the uncorrected $\delta^{13}$C of N. pachyderma (s) and are significantly higher than modern $\delta^{13}$C$_{org}$ at 70$^\circ$S (Figure 10). For both the carbonate addition and biological cycling mechanisms the LGM reconstructed $\delta^{13}$C$_{org}$ is equal to or greater than today (Table 7), particularly north of 47$^\circ$S (Figure 10).

The magnitude of the total correction to the $\delta^{13}$C of N. pachyderma (s) at the LGM is 2.1 to 4.6$\%$, increasing from south to north, -4 to 8 times the total glacial-interglacial change in the uncorrected $\delta^{13}$C of N. pachyderma (s). The large uncertainties associated with this estimation make quantitative and robust reconstructions of nutrient concentrations from the $\delta^{13}$C of N. pachyderma (s) difficult, particularly because the sensitivities coefficients for N. pachyderma (s) have not been well constrained in culture experiments

In both of these scenarios the reconstruction of LGM carbon isotope in the South Atlantic provides a very different picture from previous interpretations, which suggest that low glacial $\delta^{13}$C values of N. pachyderma (s) indicate higher glacial surface nutrients compared to today. This result suggests that the $\delta^{13}$C of TCO$_2$ in the glacial South Atlantic may not have been that different from modern conditions in the Sub-Antarctic regions. Similar conclusions have been drawn from a study on the basis of one site in the South Atlantic [Lea et al., 1999], in which the $\delta^{13}$C of G. bulloides and N. pachyderma (s) were corrected for modeled changes in carbonate ion concentrations, in response to CaCO$_3$ addition. Clearly, some combination of nutrient concentrations and air-sea gas exchange rates are required to create the observed distribution of carbon isotopes in the near-surface waters. However, simply interpreted, the corrected $\delta^{13}$C results from this study suggest that one cannot rule out the possibility that nutrient concentrations in the South Atlantic Ocean were comparable to today. Furthermore, this interpretation would reconcile the $\delta^{13}$C record of N. pachyderma (s) with new, temperature-corrected Cd/Ca records in South Atlantic planktonic foraminifera, which also suggest little or no glacial-interglacial change in nutrient concentrations [Rickaby and Elderfield, 1999].

6. Conclusions

The observed carbon isotopic disequilibrium between N. pachyderma (s) and TCO$_2$ of surface seawater can be accounted for by correcting for changes in (1) dietary $\delta^{13}$C, (2) calcification temperature, and (3) carbonate ion concentration. However, because ambient [CO$_2$]$_2$ and temperatures are strongly correlated in the South and North Atlantic Ocean, it is difficult to resolve the relative importance of these two factors by empirical correlations of field data. The large corrections required in the $\delta^{13}$C of N. pachyderma (s) make it difficult to reliably reconstruct the $\delta^{13}$C$_{org}$ under past conditions from down-core records of $\delta^{13}$C of N. pachyderma (s), at least until the variable parameters involved in the corrections have been thoroughly evaluated with laboratory culture experiments. The total magnitude of the corrections to N. pachyderma (s) is 4 to 8 times greater than the glacial-interglacial change in the uncorrected $\delta^{13}$C of N. pachyderma (s), making it difficult to reconstruct nutrient concentration from N. pachyderma (s) with any confidence. However, it is likely that the glacial Southern Ocean surface water $\delta^{13}$C was not as low as suggested by the down-core decrease in the $\delta^{13}$C of N. pachyderma (s) in this region.

Acknowledgements: We thank J. Bijma, R. Rickaby, and one anonymous reviewer for their constructive suggestions, and S. Rubin and J. Ortiz for helpful discussions. We thank B. Bemis for access to unpublished data from laboratory culture experiments and N. Gruber for access to results of model simulations. Y. Rosenthal (Rutgers University) provided unpublished $\delta^{13}$C diatom data, S. Schiel (AWI-Bremenhaven, Germany) provided plankton tow samples collected on board the R/V Polarstern; the CO$_2$ laboratory of T. Takahashi (LDDE) provided computer programs to estimate carbonate chemistry. This work was supported by a NASA Global Change Research Fellowship to K.E.K. and by NSF Grant OCE-9314654 to R.F.A. This is LDDE Publication 6006.

References

Bijma, J., H.J. Spero, and D.W. Lea, Reassessing

Figure 10. Combined corrections to the $\delta^{13}$C of N. pachyderma (s) from the LGM. Solid lines and shaded regions show $\delta^{13}$C from 0 and 200 m for modern and preindustrial modern water column, respectively. The $\delta^{13}$C of N. pachyderma (s) are corrected using temperature, dietary $\delta^{13}$C, carbonate ion concentrations, and global reservoir changes, assuming either carbonate addition (solid circles) mechanism or the biological cycling (triangles) mechanism. Open circles are uncorrected glacial values.
KOHLE ET AL.: CARBON ISOTOPE DISEQUILIBRIUM

63

foraminiferal stable isotope geochemistry: Impact of the oceanic carbonate system (experi-
mental results), in Use of Proxies in Paleo-

Brockeler, W.S., Ocean chemistry during Holocene time, Geochem. Cosmochim. Acta, 46, 1689-
1705, 1982.


Lee, D.W., D. Bijma, H.J. Spero, and D. Archer, Implications of the effect on shelf carbon and oxygen isotopes for glacial ocean conditions, in Use of Proxies in Paleo-
ceanography: Examples from the South Atlantic edited by G. Fischer and G. Wefer, pp. 513-


Lynch-Stieglitz, J., R.G. Fairbanks, and C.D. Charles, Glacial interhemispheric history of Antar-

Mackensen, A., H. Grobe, H.W. Hubberten, V. Spiess, and D.K. Fütterer, Stable isotope stratigraphy from the Antarctic continental margin during the last one million years, Mar. Geol., 87, 315-331, 1990.


Lee, D.W., D. Bijma, H.J. Spero, and D. Archer, Implications of the effect on shelf carbon and oxygen isotopes for glacial ocean conditions, in Use of Proxies in Paleo-
ceanography: Examples from the South Atlantic edited by G. Fischer and G. Wefer, pp. 513-


Lynch-Stieglitz, J., R.G. Fairbanks, and C.D. Charles, Glacial interhemispheric history of Antar-

Mackensen, A., H. Grobe, H.W. Hubberten, V. Spiess, and D.K. Fütterer, Stable isotope stratigraphy from the Antarctic continental margin during the last one million years, Mar. Geol., 87, 315-331, 1990.


Wefer, G., E. Suess, W. Balzar, G. Liebezeit, P.J. Mueller, C.A. Ungerer, and W. Zenk, Fluxes of
biogenic components from sediment trap deployment in circum polar waters of the Drake
Wolf-Gladrow, D.A., T. Bijma, and J. B. Zeebe, Model simulation of the carbonate chemistry in
Zeebe, R., An explanation of the effect of seawater carbonate concentration on foraminiferal oxygen

R. F. Anderson and J. Lynch-Staiglitz, Lamont-Doherty Earth Observatory, Department of Earth and Environmental Sciences, Columbia University, Box 1000, Palisades, NY 10964.
(boba@ldco.columbia.edu; jean@ldco.
columbia.edu)
K. E. Kohfeld, Max Planck Institute for Biogeochemistry, Postfach 100164, D-07701 Jena, Germany. (kek@bge-jena.mpg.de)

(Received February 10, 1999; revised September 27, 1999; accepted September 30, 1999.)