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Calculating surface water pCO_2 from foraminiferal organic $\delta^{13}C$

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Abstract—The $\delta^{13}C$ of organic matter bound within the crystal lattice of foraminiferal calcite tests may provide a potential tracer of the isotopic composition of the surface water primary photosynthate. Using $\delta^{13}C$ of the organic matter extracted from the crystal lattice and the calcite test, it is theoretically possible to estimate the paleo-surface water pCO_2. We have tailored this technique initially for the subpolar planktonic foraminifera species *Globigerina bulloides*. Initial surface water pCO_2 estimates from deep-sea core BOFS 5K (50°41.3′N, 21°51.9′W, water depth 3547 m) indicate that the northeast Atlantic Ocean may have been a greater sink for CO_2 during the last glacial than during the Holocene. Greatly reduced benthic foraminifera abundances, especially phytodetritus feeders, in BOFS 5K during the last glacial indicates low surface productivity. This rules out a productivity-driven CO_2 sink. The enhanced glacial CO_2 sink must, therefore, have results from a southwards shift of the centre of deep water formation.

1. INTRODUCTION

Past fluctuations in atmospheric CO_2 are an essential concern of paleoclimatic studies because of their relevance to understanding the anthropogenic-induced greenhouse effect. Ice core records have demonstrated that atmospheric CO_2 was at least 80 ppm lower during the last glacial than in preindustrial times (Barnola et al., 1987). Deep-sea sediments provide an insight into the global carbon cycle as they contain over 60 times more carbon than the preindustrial atmosphere (Sundquist, 1985). It has been proposed that the ocean system may drive changes in atmospheric CO_2 (Broecker and Peng, 1982, 1989). It is the aim of this study to improve on a method of estimating the surface water dissolved CO_2 content, using carbon isotope measurements of the organic and calcite components of planktonic foraminiferal tests.

The deep-sea sedimentary record has been used not only to estimate the changes in atmospheric CO_2 (Shackleton and Pisias, 1985; Jasper and Hayes, 1990), but also to investigate possible driving forces, such as changes in productivity, ocean chemistry, and/or circulation. The interpretation of carbon isotopic analyses of foraminifera calcite tests is limited by the difficulty to deconvolve the effects of surface water productivity, upwelling, circulation, and global carbon storage. Alternative approaches using the analysis of carbon isotopes of organic matter have been developed to further understand the changes in the oceanic carbon cycle. Sackett (1974) and Rau et al. (1989) demonstrated a strong link between the amount of dissolved CO_2 in surface waters and the carbon isotopic characteristics of phytoplankton (Fig. 1). Organic matter isotopic records, therefore, enable the reconstruction of surface water pCO_2 (e.g., Sackett et al., 1968; Fontugne and Duplessy, 1986; Jasper and Gagosian, 1990; Hayes et al., 1990; Hayes, 1993; Jasper et al., 1995). There are at present three main approaches to measuring changes in the oceanic organic carbon cycle, (1) analysis of bulk organic matter (Fontugne, 1978), (2) analysis of specific groups of organic molecules or "biomarkers" (Jasper and Hayes, 1990; Hayes et al., 1990; Hayes, 1993), and (3) extraction of organic matter contained in tests of foraminifera or diatoms (Stott, 1992; Maslin, 1993; Shemesh et al., 1993).

The first of these involves measuring the ^{12}C:^{13}C ratio of all the organic matter extracted from a core sample (Fontugne, 1978; Chasselet et al., 1981; Müller et al., 1983; Fontugne and Duplessy, 1978, 1986; Sarnthein et al., 1988; Jasper and Gagosian, 1990). This extraction is done by decarbonating the sample with acid. Burning the sample then liberates the carbon dioxide which is analysed in a mass-spectrometer (Fontugne and Duplessy, 1978). However, the interpretation of bulk organic matter $\delta^{13}C$ data is limited, because the organic matter may be a mixture of terrestrial and marine components and may have been affected by surface water conditions and fractionation during deposition and diagenesis.

The second approach to understanding the oceanic carbon cycle has been based on isolating individual organic molecules (i.e., biomarkers) from the sediment. This circumvents the problem of the unknown origin of the bulk organic matter, because the biomarkers are selected on their restricted occurrence. The role and the effects of marine phytoplankton on pCO_2 in the surface water and thus, atmospheric CO_2 can be studied directly (Shackleton, 1990; Jasper and Hayes, 1990). If the right biomarkers are chosen, terrestrial and marine environments can be studied, because, for instance, the source region of both aeolian and other terrestrial organic matter can be determined, along with paleoclimatic data such as wind direction, wind intensity, and sea surface temperatures (Brassell, 1993; Killops and Killops, 1993). Biomarker study, however, requires a sophisticated combination of equipment and

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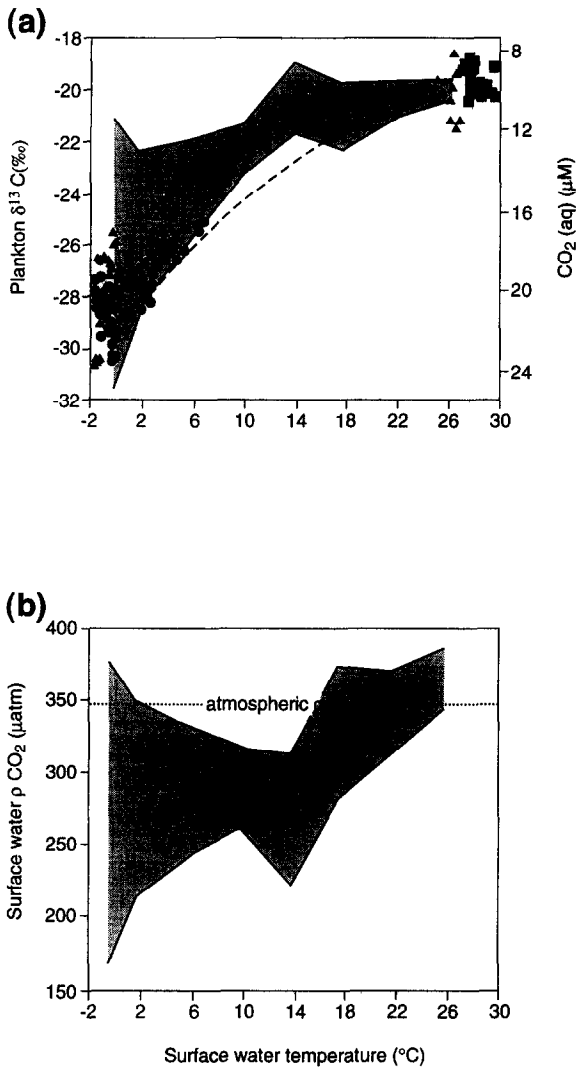

FIG. 1. (a) Planktonic $\delta^{13}C$ and dissolved CO_2 as a function of sea surface temperature (SST) in the South Atlantic, Southern Ocean, and the Weddell Sea, from data from a number of sources. Shaded region is the range of dissolved CO_2 in the surface waters as a function of SST calculated from pCO_2 data shown in (b). The dashed line represents surface water equilibrium values under an atmospheric pCO_2 of 340 ppm. The apparent relationship between planktonic $\delta^{13}C$ and dissolved CO_2 is that the extent of fractionation is linked to the availability of CO_2. In warm waters, because of the inverse relationship between temperature and CO_2 solubility, the availability of CO_2 is limited (Kroopnick, 1974) and there is very little fractionation, typical values being −13‰. In colder waters, solubility is higher and there is a net CO_2 invasion; isotopic fractionation is greater as the competition for $^{12}CO_2$ (which is "cheap" in energy costs for phytoplankton to incorporate) is reduced because of the increased abundance of CO_2, typical values may be up to −32‰. Redrawn from Rau et al. (1989) (b) Comparison of surface water pCO_2 at ambient temperature with SST in the South Atlantic, Southern Ocean, and the Weddell Sea. Redrawn from Rau et al. (1989)

relies on the assumption that there is no diagenesis of the individual molecules. Moreover, there can be difficulties comparing molecular results and those of the larger size fractions in the sediment (e.g., foraminifera stable isotopes) because of differential bioturbation (McCave, 1995).

A third approach has been to extract organic matter from within the walls of diatoms (Shemesh et al., 1993; Singer and Shemesh, 1995) or planktonic foraminifera (Stott, 1992; Maslin, 1993). This approach has the advantage that the organic matter within the test is protected from diagenesis (Stott, 1992; Shemesh et al., 1993; Singer and Shemesh, 1995). The measurements can be directly related to complementary measurements such as $\delta^{18}O$ of diatoms or $\delta^{18}O$ and $\delta^{13}C$ of foraminifera, without the problem of differential bioturbation rates (McCave, 1995).

In this study, we have developed the extraction and measurement of the carbon isotopic composition of the organic component of planktonic foraminiferal tests based on the method outlined by Stott (1992). We have assumed that the $\delta^{13}C$ of this organic matter reflects changes in the $\delta^{13}C$ of the phytoplankton ingested by the foraminifera (DeNiro and Epstein, 1976; Rau et al., 1989). We have, thus, been able to estimate the dissolved CO_2 content for the surface waters of the northeast Atlantic Ocean. An advantage of this method is that it is much simpler than the biomarker techniques, requiring only minor alterations, i.e., addition of a cracker, to a standard mass-spectrometer.

2. NATURE AND FORMATION OF THE ORGANIC MATTER WITHIN THE CRYSTAL LATTICE OF THE FORAMINIFERA CALCITE TEST

To be able to extract the organic matter in the crystal lattice of foraminifera and interpret the measurements, we must understand the nature and formation of this organic matter. The formation occurs in two stages: the absorption of organic matter into the cytoplasm, and the building of new chambers with an organic matrix. There are two possible major contributors to the organic matter which is absorbed in to the cytoplasm: food and from symbionts photosynthetic products (Fig. 2). The foraminifera species *Globigerina bulloides* and *Neogloboquadrina pachyderma* (*s*) which have been used in this study have not been documented as utilizing symbionts (Hemleben et al., 1988); thus, diet is the primary control on the type of carbon incorporated into the test. This assumption can not be made when bulk foraminifera samples have been used, as they may include species which do utilize symbionts. The foraminiferal diet is species-dependent (e.g., Anderson et al., 1979; Spindler et al., 1984; Hemleben et al., 1988). Hemleben et al. (1988) divided foraminifera into two groups using the convention of Murray (1887) spinose (e.g., *Globigerina bulloides*) and nonspinose (e.g., *Neogloboquadrina pachyderma*), based on the three-dimensional microstructure and ultra-structure features of the test/shell. From observation and examination of the digestive vacuoles of captured and laboratory-grown foraminifera, it has been determined that foraminifera are omnivorous, although a clear preference for a diet of "animals" exists among the spinose species (Anderson et al., 1979; Spindler et al., 1984), whereas nonspinose species are largely herbivorous (Anderson et al., 1979; Hemleben and Auras, 1984; Hemleben et al., 1985). This generalisation is true for the nonspinose *N. pachyderma* (*s*), as evidence from transmission electron microscopy of the contents of their food vacuoles showed that the dominant prey was phytoplankton, i.e., diatoms and eukaryotic algae (Anderson et al., 1979). *G. bulloides* has been shown to have a more varied diet including both zooplankton and phytoplankton (Lee et al., 1965). The omnivorous diet could cause more noise in the $\delta^{13}C$ record as the photosynthesis signal will have passed through one or more stages in the food chain, and each additional step will have had its own fractionation effect on the carbon (Sackett, 1974), see Figs. 2 and 3.

Once the food is absorbed into the food vacuole and broken down it has three possible fates: (1) it may be oxidised by respiration to release energy, (2) it may be used to build larger chambers and to expand the cytoplasm, and (3) it may be excreted as waste from

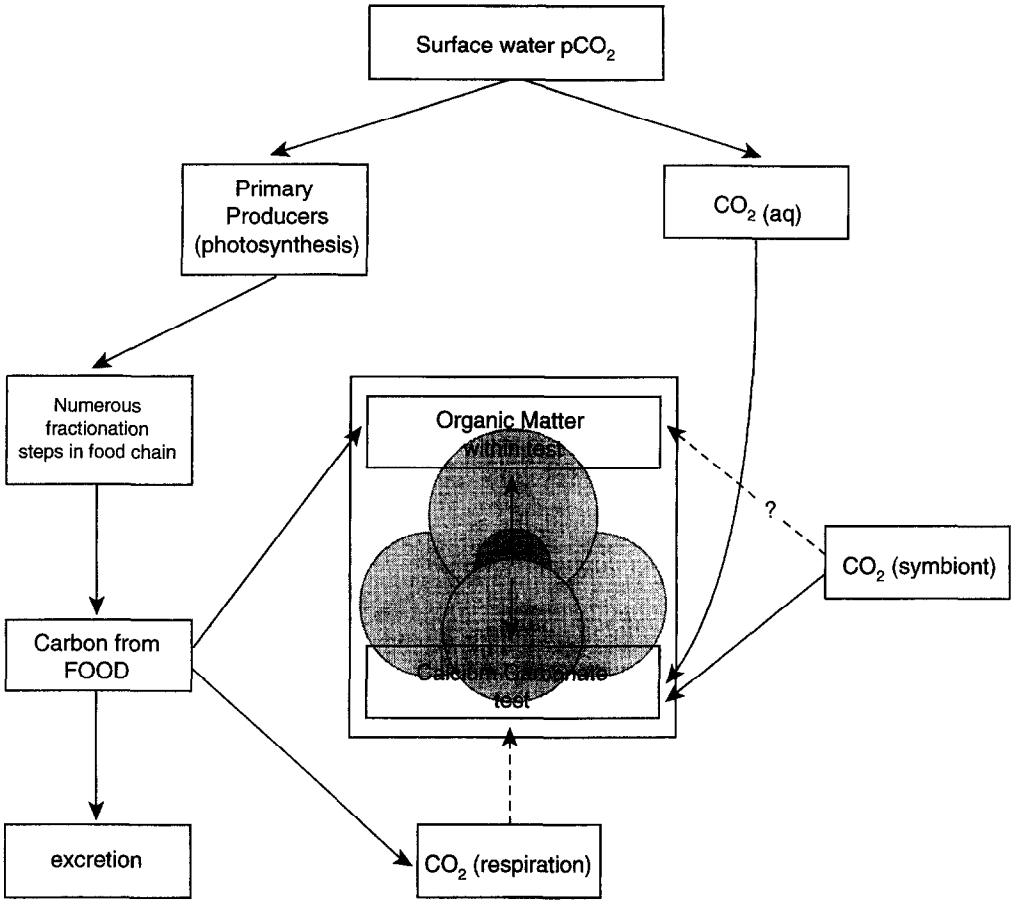

FIG. 2. Simplification of the possible origins of carbon incorporated in to both the calcite and organic matter parts of the foraminiferal test.

the foraminifera. The key process is the transference of organic matter within the cell's cytoplasm from the food vacuole to the test structure, but very little is known of this process. It has also never been confirmed whether ingested food is the sole contributor to the organic matter of the wall structure, or whether carbon dioxide absorbed from the surrounding seawater primarily to produce $CaCO_3$, is also incorporated. Foraminifera in the sediment are predominantly at the adult or terminal stage (Brummer, 1987), and it is the processes at these stages which we are most concerned about. Chamber formation is very similar in spinose and nonspinose species (Bé, 1985; Hemleben et al., 1985, 1988) and the structure of the test wall as envisaged by Bé (1980) has been redrawn in Fig. 4.

Confirmation of the proteinaceous composition of organic matter in foraminifera calcite tests has been found by many researchers (Lee et al., 1965; King and Hare, 1972; Robbins, 1987; Robbins and Healy-Williams, 1990; Robbins and Brew, 1990). The relative abundance of certain amino acids in the hydrolysed test has, moreover, provided evidence for a classification system. Using the Q-mode factor analysis, King and Hare (1972) classified sixteen species into three factorial groups, those rich in: (1) alanine, proline, and valine, (2) asparic acid and threonine, and (3) glycine, serine, and glutamic acid. Robbins and Brew (1990) extracted protein and amino acids from planktonic foraminifera from two samples dated 2–4 kyrs BP and 300 kyrs BP, confirming the range of amino acids and species diversity of King and Hare (1972). Robbins and Brew (1990) also found that most of the polypeptides were present in both samples, with the loss of only a few of the more soluble acidic polypeptides in the older sample. The approximate weight of the two major fossil proteins ranged from 50,000–70,000 daltons. This suggest that the proteinaceous material in the crystal lattice is unaffected by diagenesis, and that the molecules are large enough to be recoverable. They have also shown as do King and Hare (1972) that each species has a different set of proteins. This may mean that they have different $\delta^{13}C$ records as the different protein structures may cause different amounts of fractionation.

3. EXPERIMENTAL METHODS

The major problems with extracting organic matter from the crystal lattice which must be eliminated or addressed are:

1) Preventing contamination of the sample from organic matter within the sediment and remains of the cytoplasm which will have been affected by diagenesis, leaving the primary organic membrane, inner organic layer, outer organic layer, and inner pore lining (see Fig. 4) to be sampled. In addition, as the amount of organic matter within the crystal lattice of the foraminifera test is very small, the samples are very sensitive to any organic contamination and are thus difficult to handle.

2) Removal of the tightly bound calcium carbonate crystal lattice, which has a substantially different $\delta^{13}C$ values (over 20‰ heavier).

3) Releasing the carbon bound in the proteins/amino acids and analysing it in the mass spectrometer.

4) Estimation of the amount of hydrolyzation of proteins/amino acids due to aging and the implications for the carbon isotopic results.

Samples consisted of weighed bulk foraminiferal material or picked set numbers of individual foraminifera of a particular species (e.g., 50 *G. bulloides*). The samples were treated with bleach (5 mL of $NaOCl_{(aq)}$) for 3 h to remove organic matter contamination on the outer and inner surfaces of the tests. The $NaOCl_{(aq)}$ was then pipetted off and the samples rinsed in distilled water. The calcite test was removed by adding 3 mL of 20% $HCl_{(aq)}$. The samples

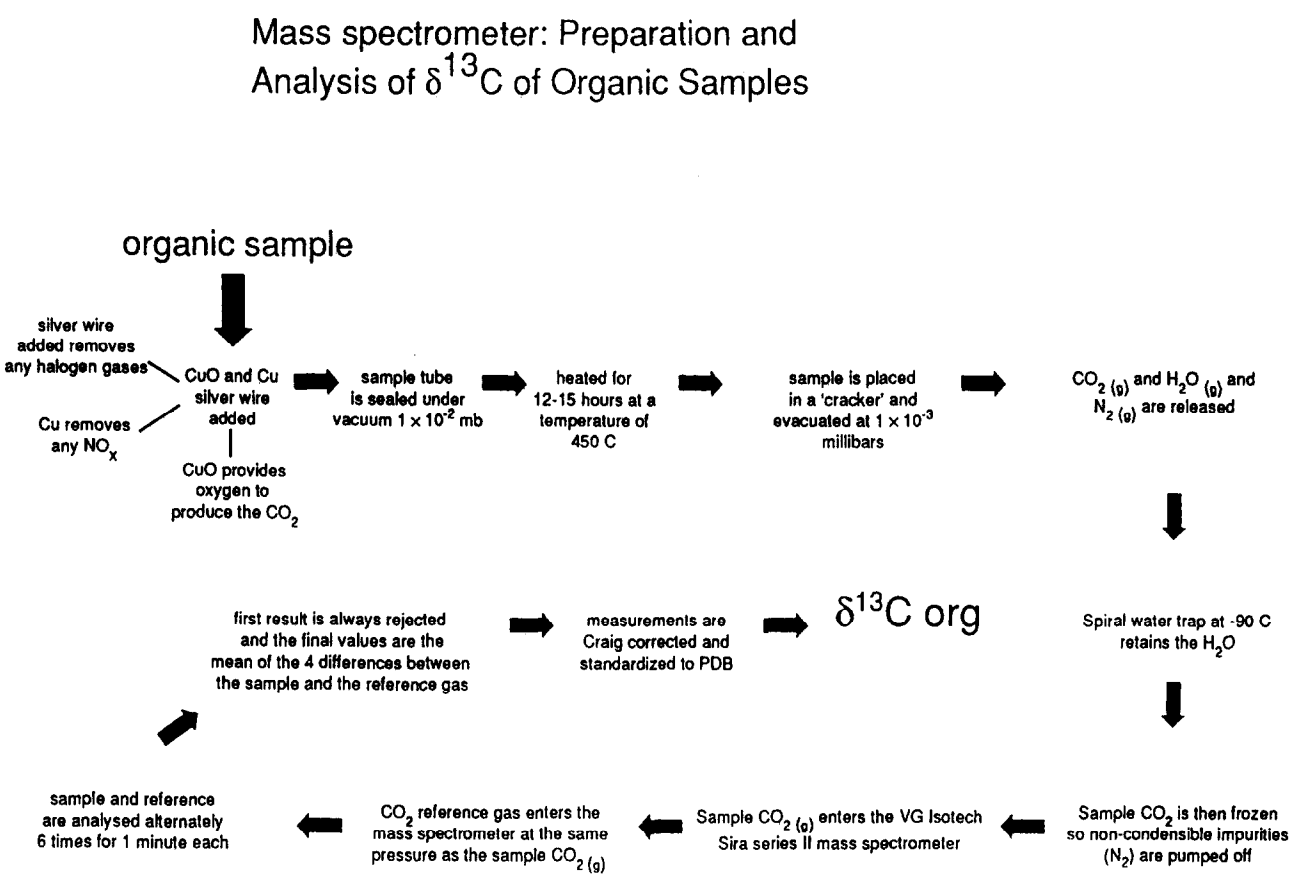

FIG. 3. Mass-spectrometer: Preparation and analysis of organic matter $\delta^{13}C$.

were then placed in an ultrasonic bath for 5 min to aid in the removal of the liberated CO_2 from solution. The acidified sample solution was then dialysed through 500 Molecular Weight Cut Off (MWCO) tubing to exchange the remaining acid for distilled water. Before using the dialysis tubing it is rinsed continuously both inside and outside, with distilled water overnight to remove trace amounts of cellulose, glycerene, and sulphur compounds. Once the pH of the distilled water reservoir remains unchanged for more than three hours the sample solution was transferred into Chromic acid washed Pyrex sample tubes (diameter 9 mm, length 15 cm) and centrifuged at 10,000 rpm for 5 h. The sample was frozen overnight and dried in a vacuum oven at room temperature (25°C), leaving the organic residue.

Copper oxide (to react with the organic carbon to produce CO_2), Ag wire (to remove possible halogens), and Cu (to remove any NO_x products) were added to the dry organic residue (Fig. 3). The glass sample tubes were then vacuum sealed, and baked at 450°C. The sealed sample tubes were then broken in a vacuum line using a stainless steel "cracker". Water condensed on the spiral cold trap, liquid nitrogen was placed round the U-trap to freeze out the carbon dioxide, and the noncondensible gases are pumped off. The carbon dioxide was transferred into the inlet system of a V. G. Isotech SIRA series II mass spectrometer where it is calibrated against a carbon dioxide reference gas which was continually calibrated to PDB using the NBS oxalic acid standard (see Fig. 3). Over 450 individual experiments were made in the development of this method. More details of the development process can be found in Maslin (1993).

4. DEVELOPMENT OF THE ORGANIC $\delta^{13}C$ METHOD

The most significant problems in developing this method were retaining the organic sample and preventing contamination. It was found that the major control on the recovery of the organic matter is the molecular weight cut off (MWCO) of the dialysis tubing (Craig and Chen, 1969). Robbins and Brew (1990) showed that using dialysis tubing of 6000–8000 MWCO caused the loss of up to a third of the proteineous material in planktonic foraminifera and that this loss was not equally divided between the different amino acid groups, for example, 86% of aspartic acid was lost, while glycine actually showed a slight increase after dialysis. Initially, a MWCO of 3500 was used, but after erratic results the fractionation of the 3500 MWCO dialysis tubing was tested with a wheat flour standard and found to be 0.51‰ ± 0.11‰ ($N = 20$). Because of these findings the MWCO of the dialysis tubing was reduced to 500. Amino acids molecular weights vary from 100–1000 (Norman and Waddington, 1983); the lower weights are unlikely to occur, as our samples were not completely hydrolysed. The 500 MWCO, therefore, retained most of the organic matter while allowing relatively rapid dialysis of any excess acid, the calcium chloride, and any bicarbonate which may have formed. When the 500 MWCO dialysis tubing was tested with the wheat flour standard the reproducibility was reduced to 0.17 ± 0.11‰ ($N = 20$). To reduce the risk of contamination plastic gloves were worn when handling the samples, all the glassware was washed in Decon 90 (a strong surface active agent), and the sample gas was mass-scanned in the mass-spectrometer between 28 and 55. Contamination was

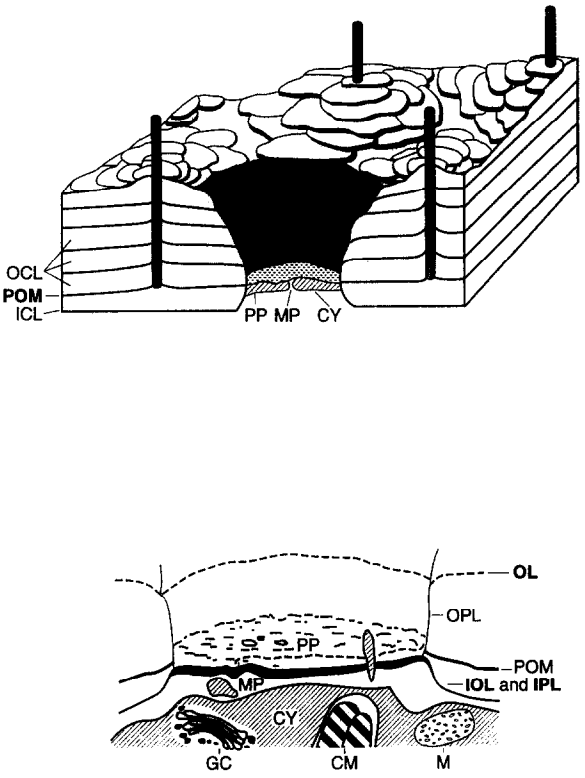

FIG. 4. Schematic block diagram and cross-section structures of pores in Spinouse planktonic foraminifera (redrawn from Be et al., 1980). CM = copepod muscle within the digestive vacuole, CY = cytoplasm, GC = Golgi complex, ICL = inner calcite layer, IOL = inner organic layer, IPL = inner pore lining, M = mitochondrium, MP = micropore, OCL = outer calcite layer, OL = outer organic layer, OPL = outer pore lining, POM = primary organic membrane, and PP = pore plate. The organic parts in bold are those which the extraction method aims to separate and analysis.

found in some samples between 44–46 of the mass spectra. This was due to NO_x products and these were removed by adding Cu to the sample tubes before sealing. Occasionally, samples were up to 4‰ lighter than the reproducible samples but no source of contamination has yet been found to account for this.

Problems also arose when deacidifying the samples, which is essential for the protection of the mass-spectrometer, this was exacerbated by reducing the MWCO to 500. The rate and efficiency of the dialyses were investigated by measuring the changes in pH both in the dialysis tubing and in the surrounding distilled water reservoir. As the most extreme case, acid (20% HCl_{aq}) was placed into all ten of the dialysis tubes. In one of the ten acid samples a Russel fine pH probe (CMAWL-R-2893/1) was placed and sealed, while a Whatman pH μ-sensor was placed into the surrounding 1.5 L distilled water reservoir. The sensors were calibrated using buffer solutions of pH 4 and 7. It was found that regular (every hour) changes of the distilled water reservoir most important, maintaining a strong gradient, and at least eight changes were made before the samples are left overnight. The samples were only removed once the pH of the distilled water reservoir remain constant for over 3 h.

We also tested the use of both quartz or Pyrex glass sample tubes. Quartz has the advantage of a higher melting point, which allows the samples to be heated to 850°C, ensuring all the organic matter decomposes, while Pyrex is limited to 450°C. However, we found that quartz was more porous to gases than Pyrex, which caused additional fractionation when samples were left for more than 24 h. The advantages of Pyrex is that it is easier to manipulate, due to its lower melting point; it is also cheaper. Experiments using reference gas has shown that there is little fractionation of $\delta^{13}C$ in either quartz or Pyrex glass tubes. Using the mass spectra scan showed that there are more contaminates between masses 38–43, associated with water, in quartz tubes than Pyrex; thus, for our methodology, Pyrex tubes were used.

5. DISCUSSION

Deep-sea core BOFS 5K (McCave, 1990) was recovered from the East Thulean Rise in the North East Atlantic (50°41.3′N, 21°51.9′W, water depth 3547 m). The BOFS 5K organic *G. bulloides* $\delta^{13}C$ and calcite test $\delta^{18}O$ and $\delta^{13}C$ of *G. bulloides* and *N. pachyderma* (*s*) records are shown in Fig. 5. The mean value for the whole of the *G. bulloides* organic $\delta^{13}C$ record is −26.7‰, with an overall range of 1.3‰ and with individual standard deviations for five replicates ranging from ±0.1‰ to ±0.45‰ (compared to the reproducibility of foraminifera calcite test $\delta^{13}C$ of ±0.09‰). The BOFS organic $\delta^{13}C$ record and the calcite $\delta^{13}C$ record of *G. bulloides* (Fig. 5) appear to vary independently. This suggests that there is no significant link between the metabolic systems absorbing dissolved CO_2 from the surrounding waters to construct the calcite test and the digestion of food to provide the framework for the test.

One major problem with the BOFS 5K foraminiferal organic $\delta^{13}C$ record is whether or not the organic matter recovered has been affected by diagenesis, in particular, progressive hydrolyzation of the proteins with increasing age of the samples. Robbins and Brew (1990) have shown that planktonic foraminifera protein and amino acids were very similar in samples dated as 2–4 kyrs BP and 300 kyrs BP. Robbins and Brew (1990) also found that most of the polypeptides were present in both samples, with the loss of only a few of the more soluble acidic polypeptides in the older sample. However, significant hydrolysis of amino acids recovered from deep-sea sediments and foraminifera test has been shown (Bada and Man, 1980; Müller, 1984; J. L. Bada, pers. commun., 1995). Bada and Man (1980) demonstrated that the approximately hydrolysis half-life in calcareous rich sediments was 1–2 million years. Despite being much longer than the timescale investigated in this study, hydrolysis could still be an important factor, as even a small amount may have a significant influence on the $\delta^{13}C$ value. To estimate whether there was any hydrolysis and thus, loss of the lighter organic molecules, either from the lattice itself or during the extraction process, the BOFS 5K organic samples were weighed and the resultant CO_2 gas pressures in the mass-spectrometer measured. Both these estimates confirmed that very similar yields were obtained for each sample, moreover there was no trend in these estimates with increasing age of the sample (Maslin, 1993). This, however, does not remove the fact that there could be significant fractionation during

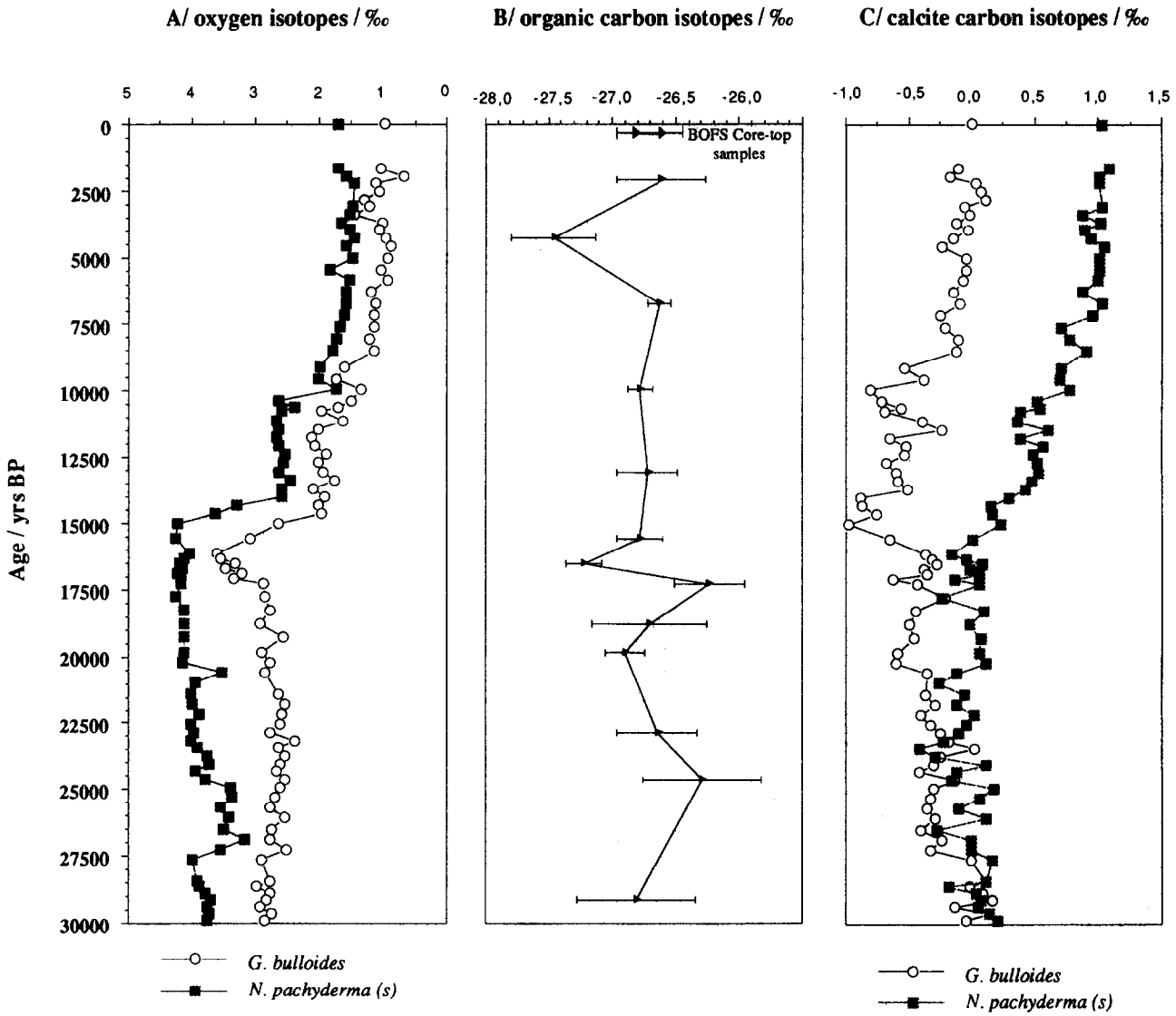

FIG. 5. Comparison of the *G. bulloides* $\delta^{18}O$ and $\delta^{13}C$ of the calcite test and $\delta^{13}C$ of the organic matter extracted from within the calcite test records for BOFS 5K (50°41.3′N, 21°51.9′W, water depth 3547 m). Experimental error bars on the organic $\delta^{13}C$ record were calculated as ± one standard deviation from five replicate experiments. NBS Oxalic acid (Ethanedioxic acid HO_2C-CO_2H) was used to calibrate the mass spectrometer, but, due to its very low molecular weight, it was heavily fractionated by both the dialysis and the evaporation stages (Maslin, 1993). Ordinary pure wheat flour was found to be an excellent alternative standard to test the method having a $\delta^{13}C$ signal of −25.21 ± 0.06‰, it has the added advantage of being similar in both composition and $\delta^{13}C$ value to the foraminifera organic matter.

peptide bond hydrolysis, but no major loss of organic material.

Another approach to try and validate the BOFS 5K down core record, is by comparing the results with core top data and other organic $\delta^{13}C$ proxies. The core top data was measured on box core samples, dated between 0–500 y, from five BOFS cores in a rough profile along 20°W ranging from 50–60°N (Maslin, 1993). The range of these results are shown in Fig. 5; however, there was no obvious North-South pattern, due to the pervasive effect of the northeast Atlantic Ocean spring productivity blooms. It is interesting and important to note that most of the BOFS 5K Holocene results have similar values to the box core results.

The second comparison which is possible is with the work of Singer and Shemesh (1995); they found in the Southern Ocean glacial diatom organic $\delta^{13}C$ values of −26.5‰, compared to an glacial average of −26.4‰ for BOFS 5K. Their core locations (about 52°S and 63°S) had a very similar glacial SST to that of BOFS 5K (50°N) (CLIMAP Group, 1982), the closeness of the organic results may suggest that the surface water productivity and pCO_2 conditions may have been similar in the Southern Ocean and the North Atlantic during the last glacial.

These comparisons do suggest that the organic values obtained for BOFS 5K are consistent with other work. They do not, however, remove the possibility that the organic

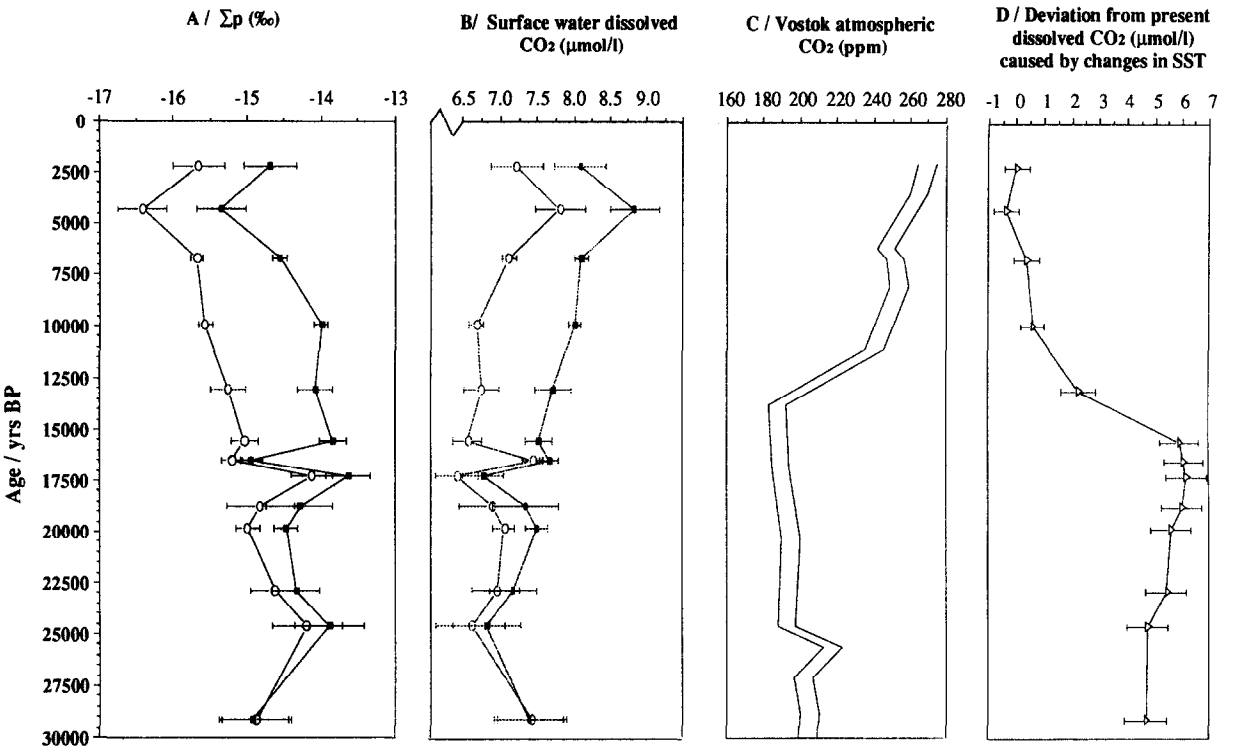

FIG. 6. Comparison of the (A) the isotopic effect of fixation of CO_2 (Σp) and (B) the calculated surface water dissolved CO_2 of BOFS 5K with the (C) Vostok atmospheric CO_2 record (Barnola et al., 1987) for the last 30,000 years. Note that open circles indicate when the calcite $\delta^{13}C$ values of *G. bulloides* were used in the calculation of Σp and dissolved CO_2 while closed squares indicate the use of *N. pachyderma(s)* calcite $\delta^{13}C$ (see text).

matter within the foraminifera crystal lattice could have been altered as the foraminifera test sinks from the surface. Work done comparing $\delta^{13}C$ of specific biomarker compounds in *E. huxleyi* in cultures, surface sediment, and surface waters to water column particular organic matter suggests there is a fractionation affect; however, it is constant. Therefore, it is possible to assume that the organic matter within the much thicker test walls of planktonic foraminifera may also be protected from water column diagenetic affects. To confirm this, however, organic $\delta^{13}C$ results using the method out line above are required on foraminifera recovered from plankton tows and this could then be compared to the $\delta^{13}C$ of the primary photosynthate.

Assuming the organic $\delta^{13}C$ record does represent the isotopic composition of the surface water primary photosynthate, it is possible to estimate the surface water dissolved CO_2 content from the organic and calcite $\delta^{13}C$. Jasper and Hayes (1990), by utilizing the theoretical models linking isotopic fractionation associated with photosynthetic fixation of carbon and the surface water pCO_2 calculated by Popp et al. (1989) and Hayes et al. (1990), were able to estimate the surface water pCO_2. Two empirical relationships linking the two factors have been suggested;

$$\epsilon_p = a \log C + b \quad \text{Popp et al. (1989)} \qquad (1)$$

or

$$\epsilon_p = a + b/C_e \quad \text{Jasper et al. (1995)}, \qquad (2)$$

where ϵ_p is the isotopic effect (‰) associated with the fixation of carbon, C is the surface water concentration of dissolved CO_2 (μM), C_e is the surface water concentration of dissolved CO_2 (μM) (where the e specifies the concentration external to a photosynthetic cell), and a and b are constants. The constants a and b are representative of the physiological, ecological, and environmental factors which influence the ϵ_p-CO_2 relationship. Equation 2 of Jasper et al. (1995) and their prescribed constants were also used to calculate the BOFS 5K pCO_2, but very little difference was found between the two solutions.

Farquhar et al. (1982) and Popp et al. (1989) derive another estimate of the ϵ_p by assuming the processes involved in photosynthetic fixation of carbon are: (1) the transport of inorganic carbon to C-fixing enzymes ("mass-transport") and (2) the formation of chemical bonds ("fixation"). By assuming a steady state, mass-balancing allows the determination of the following equation;

$$\epsilon_p \equiv ([(\delta_P + 1000)/(\delta_d + 1000)] - 1)\ 1000, \qquad (3)$$

where δ_P is the isotopic composition of the total biomass of the primary photosynthate and δ_d is the isotopic composition of the dissolved CO_2.

Jasper and Hayes (1990) assumed that in surface waters the dissolved CO_2 is depleted in ^{13}C relative to the TDC by 8.8‰ (T = 24°C, pH = 8.2). They measured the isotopic composition of the calcite test of the planktonic foraminifera *Globigerinoides ruber* and assumed that it was depleted in ^{13}C by an average of 0.5‰ in comparison to the TDC. So the isotopic composition of the δ_d is estimated by correcting

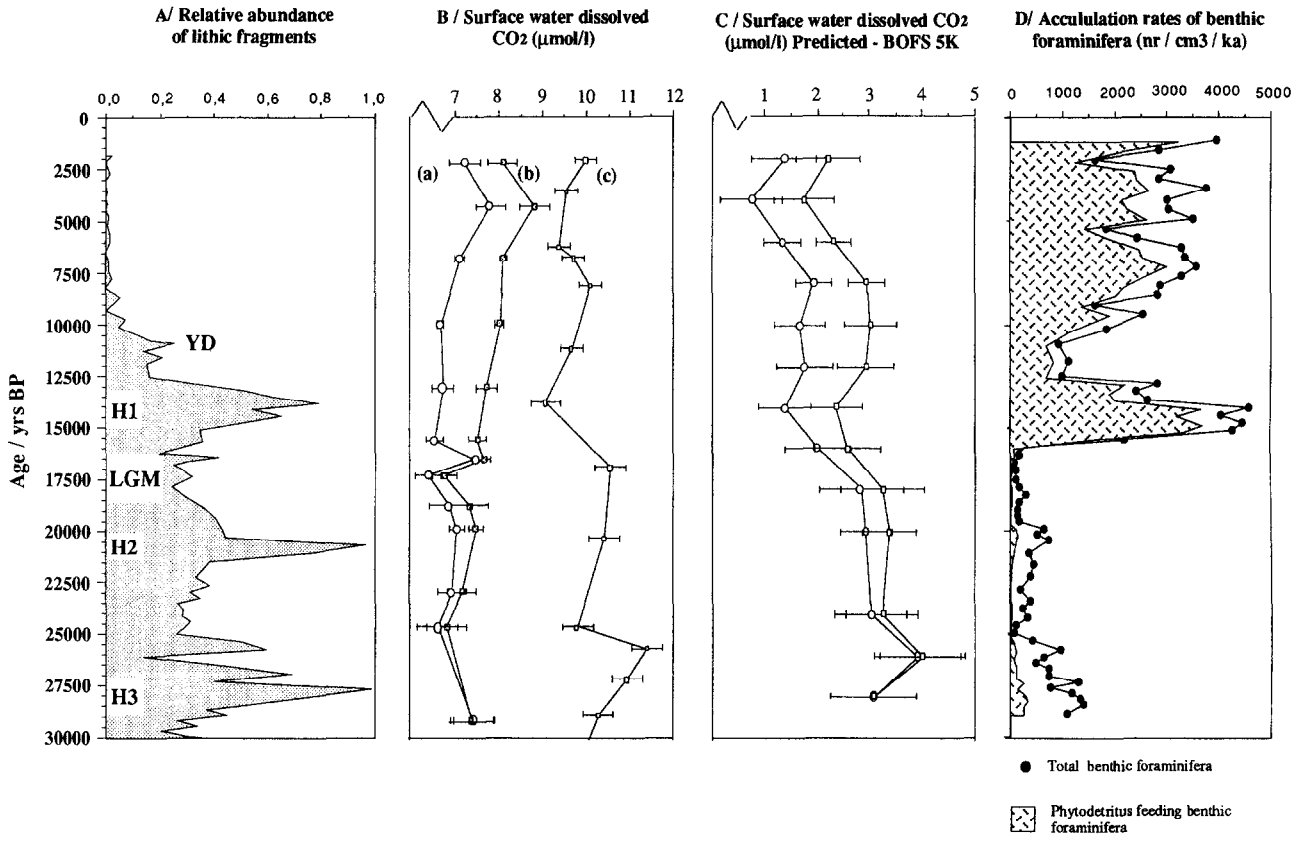

FIG. 7. The comparison of the "estimated" and "predicted" surface water dissolved carbon dioxide at the BOFS 5K site (50°41.3′N, 21°51.9′W, water depth 3547 m). (A) Changes in amount of carbon dioxide dissolved in the surface water at BOFS 5K due to changing sea surface temperatures. The error bars are calculated assuming an error range of ±1°C in the EPOCH SIMMAX SST estimates (Pflaumann et al., 1992; Maslin, 1993). (B) (a) + (b) Dissolved CO_2 estimates calculated from the foraminifera calcite and organic $\delta^{13}C$ records. Note that open circles indicate when the calcite $\delta^{13}C$ values of *G. bulloides* were used to calculate dissolved CO_2, while closed squares indicate the use of *N. pachyderma(s)* calcite $\delta^{13}C$. (c) Predicted dissolved CO_2 for the BOFS 5K site for the last 30,000 years based on the Vostok atmospheric CO_2 record and the EPOCH SIMMAX SST estimates of BOFS 5K. (C) The difference between the isotopically estimated dissolved CO_2 record and that predicted by the Vostok atmospheric CO_2 and BOFS 5K EPOCH SIMMAX SST records. Note error bars are calculated as the sum total of the errors on both the estimated and predicted dissolved CO_2 records.

the *G. ruber* $\delta^{13}C$ record ($\delta_{G.ruber}$) by a factor of −8.3‰. This correction has been revised to a variable one by Jasper et al. (1995) to take into account the temperature effect on the calcite-CO_2 and the vital effects of the individual species. Jasper and Hayes (1990) determined the δ_p by using a gas chromatograph/mass-spectroscopy technique to determine the isotopic composition of C_{37} alkadienones ($\delta_{37:2}$). Having analysed the isotopic composition of the total algal cell material and that of the isolated alkenones they estimated that there was a correction of 3.8‰ between the $\delta_{37:2}$ and the isotopic ratio of the primary photosynthate, represented by the total algal cell material. This assumes a constant isotopic relationship between the algal cell material and the alkenones. It also assumes that the total algal cell material represents the total biomass of the primary photosythate.

The major problem with using the Popp et al. (1989) and Hayes et al. (1990) equations is the determination of the constants quantifying three very different effects: physiological, ecological, and environmental changes. Jasper and Hayes (1990) determined the constants a and b in Eqn. 1, using two approaches. They first used the Vostok ice core record of atmospheric CO_2 (Barnola et al., 1987) to estimate values of C, assuming there was equilibrium with the atmosphere at 25°C during the Holocene and at 23°C during the glacial interval. A regression of ϵ_p on log C gave the estimate of the constants $a = -32.9$ and $b = 14.3$. This approach precludes an independent record of atmospheric and surface water CO_2, and there is also the problem of comparing the Vostok ice core and marine records, as there can be errors in the dating of up to ±2,000 y. For the second approach they used data reported by Sackett (1974) and Rau et al. (1989) for lacustrine and marine phytoplankton $\delta^{13}C$ and temperature (Fig. 1). From this Jasper and Hayes (1990) estimated that a varied between −17 and −21; they used $a = -20$ which favoured marine systems. Using both of these estimates Jasper and Hayes (1990) estimated the surface water pCO_2 and atmospheric CO_2, and achieved records similar to the Vostok ice core record of atmospheric CO_2. See Jasper et al. (1995) for a description of how they estimated the constants a and b for Eqn. 2 ($a = -27$‰ and $b = -130$‰ µM).

The isotopic effect associated with the fixation of carbon (ϵ_P) can be calculated using the $\delta^{13}C$ of the foraminifera organic matter to represent changes in the isotopic composition of the total biomass of primary photosynthate (δ_p) and the calcite $\delta^{13}C$ to represent the isotopic composition of the total dissolved CO_2 (δ_d) (see Eqn. 3). Two estimates of ϵ_P were calculated, using the calcite $\delta^{13}C$ of *G. bulloides* and *N. pachyderma* (*s*). This is because it has been shown that the calcite $\delta^{13}C$ record of *G. bulloides* may not reflect the average isotopic composition of the surface water as the $\delta^{13}C$ can be affected by upwelling and blooms (Ganssen, 1983; Ganssen and Sarnthein, 1983; Reynolds and Thunell, 1985), whereas the deeper-living, earlier-blooming *N. pachyderma* (*s*) seems to be less influenced by rapid changes in surface water productivity (Duplessy et al., 1988; Maslin, 1993). The difference in the calcite $\delta^{13}C$ of *G. bulloides* and *N. pachyderma* (*s*) is small during the last glacial (<0.4‰), due to the cessation of the spring blooms. However, the difference in the records is very apparent in the Holocene sections, and causes a maximum difference in the dissolved CO_2 values of 1 μmol/L. We calibrated the calcite $\delta^{13}C$ to δ_p by using (1) the equations defining the temperature-dependent fractionation of Jasper et al. (1995) by using the Simmax sea surface temperatures estimates (Maslin et al., 1995) and (2) the vital effects of *G. bulliodes* estimated by Ganssen (1983). Unfortunately, we do not have a calibration of δ_d in modern waters; therefore, the organic $\delta^{13}C$ record was adjusted by a factor of +3.8‰ (Jasper and Hayes, 1990; Jasper et al., 1995). To calculate the surface water dissolved CO_2 content from the ϵ_P the constants *a* and *b* in Eqn. 1 have to be estimated. In our calculations we used $a = -20$ and $b = 2.5$, from the study of Rau et al. (1989), which was made over a wide range of SSTs and are, therefore, more comparative with BOFS 5K "temperate" location than that of the tropical study of Jasper and Hayes (1990). Using Eqn. 2 (Jasper et al., 1995) we used the constants $a = -27$‰ and $b = -130$‰ μM. When the ϵ_P and the surface water dissolved CO_2 were calculated using both Eqns. 1 and 2, very little difference between the two solutions. The ϵ_P and the surface water dissolved CO_2 shown against age with 1 s.d. error bars in Figs. 5–7 are from the original solution using Eqn. 1.

Jasper and Hayes (1990) and Jasper et al. (1995) demonstrated that surface water pCO_2 can be estimated from foraminifera calcite $\delta^{13}C$ and organic estimates of the photosynthate $\delta^{13}C$. However, the estimation of pCO_2 from foraminiferal organic matter $\delta^{13}C$ should be viewed with caution: first, because of the problems of calibrating foraminiferal organic matter $\delta^{13}C$ and calcite $\delta^{13}C$ to pCO_2, and second, Laws et al. (1995) have indicated from laboratory culture experiments that, at least in diatoms, the growth rate, as well as the ϵ_P are required to accurately estimate ancient pCO_2. It is not yet known whether this is also true of foraminifera and if so, we at present have no way of estimating fossil growth rates. We, however, believe that taking into account these drawbacks, general conclusions can be drawn from our foraminifera based estimates of paleo-pCO_2.

To predict the surface water dissolved CO_2 at the BOFS 5K site both the change in the atmospheric CO_2 and the SST must be considered. The atmospheric CO_2 and the surface water dissolved CO_2, assuming equilibrium conditions are linked by the constant α (Weiss, 1974; Broecker and Peng, 1982, page 150).

$$pCO_2 = [CO_2]/\alpha \quad (4)$$

when pCO_2 = atmospheric CO_2 content (ppm) and $[CO_2]$ = surface water dissolved CO_2 content (μmol/L).

Weiss (1974) measured α and found that it was temperature dependent. Using the results of Weiss (1974) the relationship between temperature and α was estimated (Maslin, 1993)

$$\alpha = 6.24 \times 10^{-2} - 2.11 \times 10^{-3}\, T + 2.95 \times 10^{-5}\, T^2 \quad (5)$$

when T = temperature (°C).

Because of the large glacial-interglacial shifts in SST at BOFS 5K, its effect on dissolved CO_2 is significant. Using the EPOCH SIMMAX (Pflaumann et al., 1996) summer sea-surface temperature (SST) estimates of BOFS 5K (Maslin, 1993; Maslin et al., 1995), α was calculated using Eqn. 5 and applied to the Vostok atmospheric pCO_2 (Fig. 6C; Barnola et al., 1987) to obtain an estimate of the "predicted" surface water dissolved CO_2 for the last 30 ka at the BOFS 5K site. The magnitude of the SST effect on dissolved pCO_2 is shown in Fig. 6D. Figure 7B shows the comparison of the "estimated" surface water pCO_2 from the $\delta^{13}C$ records with the "predicted" surface water dissolved CO_2. A gaussian interpolation using weighted duplicates (sample spacing of 2,000 yrs and a window size of 4,000 y) was performed so that the two chronologies were compatible.

Figure 7C shows the difference between the isotopically estimated dissolved CO_2 and the prediction dissolved CO_2, based on the Vostok ice core and the SST records. Because of the problems of calibrating the BOFS 5K isotope estimate it is not known how large the present-day offset is between the predicted and the estimated dissolved CO_2 contents. The results of Tans et al. (1990) do suggest that at present the northeast Atlantic Ocean is a sink of CO_2 but the exact scale of draw-down is still not known. The comparison between the predicted and estimated dissolved CO_2 content suggests that the difference was greatest during the Last Glacial Maximum (LGM). The largest change occurs between 18,000 and 14,000 y BP, when there is a reduction of the difference between the prediction and the estimate of between 1 and 1.5 μmol/L. These results suggest that during the last glacial in the northeast Atlantic Ocean may have been a stronger "sink" for atmospheric CO_2 than at the present-day. Surface water sinks are usually caused by high surface water productivity or areas of deep water formation (Tans et al., 1990; Siegenthaler and Sarmiento, 1993).

Figure 7 also shows the comparison of the CO_2 estimates with the relative abundance of lithic fragments in BOFS 5K deposited primarily by ice-rafting. From this record it is possible to identify the Heinrich events (Bond et al., 1992; Maslin, 1993; Maslin et al., 1995). Because of the extremely low absolute abundances of planktonic foraminifera in the Heinrich layers in BOFS 5K (Maslin, 1993) it has not yet been possible to obtain reliable organic $\delta^{13}C$ measurements.

Sancetta (1992), having studied the modern and fossil assemblages of diatoms, suggested that there was enhanced

productivity in the north Atlantic Ocean during the last glacial possible due to nutrient input from icebergs. However, this runs counter to most other evidence that suggests that at least the northeast Atlantic Ocean had very low productivity during the last glacial (e.g., Bond et al., 1992; Maslin, 1993; Thomas et al., 1995; Jasper et al., 1996). Figure 7D shows the absolute abundance of benthic foraminifera in the BOFS 5K sediment; the most striking feature is the extremely low abundances during the last glacial. This is primarily caused by the drastic reduction in the numbers of the phytodetritus feeding benthics (Fig. 7D; Thomas et al., 1995) which thrive when there are huge spring blooms in the northeast Atlantic Ocean (Gooday, 1988; Gooday and Turley, 1990; Gooday et al., 1992). This suggests that high surface water productivity of the northeast Atlantic Ocean, which is primarily driven by the spring blooms, ceased almost completely during the last glacial (Thomas et al., 1995). Therefore, we suggest that the enhanced down-draw observed at BOFS 5K is due to glacial deep water formation in the northeast Atlantic Ocean. It has been suggested that during the last glacial, because of extensive sea ice in the Nordic Seas, deep water formation occurred further south (Duplessy et al., 1988; Labeyrie et al., 1992; Sarnthein et al., 1994; Seidov and Maslin, 1996). This is supported by results from the northeast Atlantic Ocean showing the similarity between the deep-living planktonic foraminifera *N. pachyderma* (*s*) calcite $\delta^{13}C$ and benthic foraminifera calcite $\delta^{13}C$, suggesting a link between the surface and deep waters (Duplessy et al., 1988, Curry et al., 1988; Jansen and Veum, 1990; Maslin, 1993; BOFS, unpub. data).

6. CONCLUSIONS

This study has shown that it is possible to extract organic matter from within foraminifera tests and to obtain reasonable $\delta^{13}C$ reproducibility. The foraminifera organic $\delta^{13}C$ values obtained from North East Atlantic core tops are very similar to the Holocene values of BOFS 5K and the glacial values of BOFS 5K are similar to the glacial diatom organic $\delta^{13}C$ of Singer and Shemesh (1995). This comparative evidence, and the fact that the yields of organic matter from each BOFS 5K samples were similar, leads us to believe that the foraminifera organic $\delta^{13}C$ record is reliable estimate of the isotopic composition of the surface water primary photosynthate. We were able to estimate the surface water dissolved CO_2 using the method of Jasper and Hayes (1990). This method is still in the development stage and key areas that need to be improved are:

1) Modern calibration (e.g., from plankton tows) of the organic $\delta^{13}C$ of each foraminifera species to the isotopic composition of the total biomass of the primary photosynthate (δ_p) would remove the reliance and possible bias of the Jasper and Hayes (1990) calibration.

2) SST has a significant effect on the dissolved CO_2 content of the surface waters, thus, reliable SST estimates are essential if conclusions are to be drawn from about glacial-interglacial changes in dissolved CO_2 in temperate and subpolar regions. It is also important to test this method in tropical regions where the glacial-interglacial variation in SST is minimal.

The initial results of this method are encouraging, suggesting North East Atlantic during the last glacial may have been a stronger "sink" of CO_2 than during the Holocene and this may be due to southward migration of deep water formation.

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REFERENCES

Anderson O. R., Spindler M., Bé A. W. H., and Hemleben Ch. (1979) Trophic activity of planktonic foraminifera. *J. Mar. Bio. Assoc. UK* **59,** 791–799.

Bada J. L. and Man E. H. (1980) Amino acid diagenesis in Deep Sea Drilling Project cores: Kenetics and mechanisms of some reactions and their applications in geochronology and in paleotemperature and heat flow determinations. *Earth-Sci. Rev.* **16,** 21–55.

Barnola J., Raynaud D., Korothevich Y. S., and Lorius C. (1987) Vostok ice core provides 160,000 yrs record of atmospheric CO_2. *Nature* **329,** 408–413.

Bé A. W. H. (1980) Gametogenic calcification in the spinose planktonic foraminifera, *Globigerinoides sacculifer* (Brady). *Marine Micropalontol.* **5,** 283–306.

Bond G. et al. (1992) Evidence for massive discharges of icebergs into the North Atlantic ocean during the last glacial. *Nature* **360,** 245–249.

Brassell S. C. (1993) Application of biomarkers for delineating marine paleoclimatic fluctuations during the Pleistocene. In *Organic Geochemistry: Principles and Applications* (ed. M. H. Engles and S. A. Macko), pp. 699–738. Plenum.

Broecker W. S. and Peng T.-H. (1982) *Tracers in the Sea.* Eldigio Press.

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

Brummer G. J. A., Hemleben Ch., and Spindler M. (1987) Ontogency of extant globerinid planktonic foraminifera: a concept exemplified by *Globigerinoides sacculifer* (Brady) and *G. ruber* (d'Orbigny). *Marine Micropaleontol.* **12,** 357–381.

Chasselet R., Fontugne M., Buat-Menard P., Ezat U., and Lambert C. (1981) The origin of particulate organic matter in the marine atmosphere as indicated by its stable carbon isotope composition. *Geophys. Res. Lett.* **8,** 345–348.

Craig L. and Chen H.-C. (1969) On rapid laboratory dialysis. *Anal. Chem.* **41,** 590–612.

Curry W. B., Duplessy J.-C., Labeyrie L., and Shackleton N. (1988) Change in the distribution of $\delta^{13}C$ of deep water ΣCO_2 between the last glaciation and the Holcene. *Paleoceanography* **3,** 317–341.

DeNiro M. J. and Epstein S. (1976) You are what you eat (plus a few ‰): the carbon isotope cycle in food chains-abstract. *GSA Abstr. Progr.* **8,** 834–835 (abstr.).

Duplessy J.-C., Shackleton N., Fairbanks R., Labeyrie L., Oppo D., and Kallel N. (1988) Deepwater source variation during the last climatic cycle and their impact on global deepwater circulation. *Paleoceanography* **3,** 343–360.

Farquhar G. D., O'Leary H., and Berry J. A. (1982) On the relationship between carbon isotope discrimination and the intercellular carbon dioxide concentration in leaves. *Aust. J. Plant Phys.* **9,** 121–137.

Fontugne M. R. (1978) Etude de la composition isotopique du car-

bon organique du plancton. Application a la paléocéanographie. PhD thesis, Univ. Bordeaux, France.
Fontugne M. R. and Duplessy J.-C. (1978) Carbon isotope ratio of marine plankton related to surface water masses. *Earth Planet. Sci. Lett.* **41,** 365–371.
Fontugne M. R. and Duplessy J.-C. (1986) Variations of the Monsoon regime during the upper Quaternary: Evidence from carbon isotopic record of organic matter in North Indian Ocean sediment cores. *Palaeogeogr., Palaeoclimtol., Palaeoecol.* **56,** 69–88.
Ganssen G. (1983) Dokumentation von Köstennahem Auftrients anhand stabiler Isotope in rezenten Foraminiferen vor Nordwest-Afrika. *"Meteor" Forsch-Ergeb., Reihe C* **37,** pp. 1–23.
Ganssen G. and Sarnthein M. (1983) Stable isotope composition of foraminifera: the surface and bottom waters record of coastal upwelling. In *Coastal Upwelling: Sediment Record, Part A* (ed. A. E. Suess and J. Thiede), pp. 21–35. Plenum.
Gooday A. J. (1988) A response by benthic foraminifera to the deposition of phytodetritus in the deep sea. *Nature* **332,** 70–73.
Gooday A. J. and Turley C. M. (1990) Responses by benthic organisms to inputs of organic material to the ocean floor: a review. *Phil. Trans Roy. Soc. London, A* **331,** 119–138.
Gooday A. J., Levin L., Linke P., and Heeger T. (1992) The role of benthic foraminifera in deep sea food webs and carbon cycling. In *Deep Sea Food Chains and the Global Carbon Cycle* (ed. G. T. Rowe and V. Pariente), pp. 63–91. Kluwer.
Hayes J. M. (1993) Factors controlling ^{13}C contents of sedimentary organic compounds: principles and evidence. *Marine Geol.* **113,** 111–125.
Hayes J. M., Freeman K. H., Popp B. N., and Hoham C. H. (1990) Compound-specific isotopic analyses: a novel tool for reconstruction of ancient biogeochemical processes. *Organic Geochem.* **16,** 1115–1128.
Hemleben Ch. and Auras A. (1984) Variations in the calcite dissolution pattern on the Barbados ridge complex at Sites 541 and 543. In *Initial Rept. of the DSDP Leg 78* (ed. B. Biju-Duval and J. C. Moore), pp. 471–497.
Hemleben Ch., Bé A. W. H., Anderson O. R., and Tuntivate-Choy S. (1977) Test morphology, organic layers and chamber foramation of planktonic foraminifera *Glogorotalia menardii* (d'Orbingy). *J. Foram. Res.* **7,** 1–25.
Hemleben Ch., Spindler M., Breitinger I., and Deuser W. (1985) Field and laboratory studies on the ontogeny and ecology of some glodorotaliid species from the Sargasso Sea off Bermuda. *J. Foram. Res.* **15,** 254–272.
Hemleben Ch., Spindler M., and Anderson O. (1988) *Modern Planktonic Foraminifera.* Springer-Verlag.
Jansen E. and Veum T. (1990) Evidence for two step deglaciation and its impact on North Atlantic deep water circulation. *Nature* **343,** 612–616.
Jasper J. P. and Gagosian R. B. (1990) The sources and deposition of organic matter in Late Quaternary Pigmy Basin, Gulf of Mexico. *Geochim. Cosmochim. Acta* **54,** 1117–1132.
Jasper J. P. and Hayes J. (1990) A carbon isotope record of CO_2 level during the late Quaternary. *Nature* **347,** 462–464.
Jasper J. P., Hayes J. M., Mix A. C., and Prahl F. G. (1995) Photosynthetic fractionation of ^{13}C and concentrations of dissolved CO_2 in the central equatorial Pacific during the last 255,000 years. *Paleoceanography* **9,** 781–798.
Jasper J. P., Hayes J. M., and Sikes E. L. (1996) Transfer of CO_2 from equatorial latitudes during the late Quaternary. In *Air-Water Gas Transfer* (ed. B. Jahne and E. Monahan). AEON Verlag (in press).
Killops S. D. and Killops V. J. (1993) *An Introduction to Organic Geochemistry.* Longman Scientific and Technical.
King K. and Hare P. (1972) Amino acid composition of planktonic foraminifera: a paleobiochemical approach to evolution. *Science* **175,** 1461–1463.
Kroopnick P. (1974) Correlation between $\delta^{13}C$ and ΣCO_2 in surface water and atmosphere CO_2. *Earth Planet. Sci. Lett.* **22,** 217–240.
Labeyrie L. D. et al. (1992) Changes in the vertical structure of the North Atlantic Ocean between Glacial and Modern times. *Quat. Sci. Rev.* **11,** 401–414.
Laws E., Popp B., Bidigare R., Kennicutt M., and Macko S. (1995) Dependence of phytoplankton carbon isotopic composition on growth rate and $(CO_2)aq$: Theoretical considerations and experimental results. *Geochim. Cosmochim. Acta* **59,** 1131–1138.
Lee J. J., McEnery M. E., Pierce S., Freudebthal H. D., and Muller W. A. (1965) Tracer experiments in feeding littoral foraminifera. *J. Protozool.* **13,** 659–670.
Maslin M. A. (1993) A study of the palaeoceanography of the North East Atlantic in the late Pleistocene. PhD thesis, Cambridge Univ., UK.
Maslin M. A., Shackleton N., and Pflaumann U. (1995) Surface water temperature, salinity and density changes in the North East Atlantic during the last 45,000 years: Heinrich events, deep water formation and climatic rebounds. *Paleoceanography* **10,** 527–544.
McCave I. N. (1989) *RRS Discovery 184 BOFS 1989 Leg 3 Cruise Report.* Cambridge Univ.
McCave I. N. (1995) Sedimentary processes and the creation of the straigraphic record in the late Quaternary North Atlantic Ocean. *Philos. Trans. Roy. Soc. London, B* **348,** 229–241.
Müller P. (1984) Isoleucine epimerization in Quaternary planktonic foraminifera: Effects of diagenetic hydrolysis and leaching, and Atlantic-Pacific intercore correlation. *"Meteor" Forsch-Ergeb., Reihe C,* **38,** 25–47.
Müller P., Erlenkevser H., and von Grafenstein R. (1983) Glacial to interglacial changes in oceanic productivity inferred from organic carbon cycles in Eastern North Atlantic sediment cores. In *Coastal Upwelling; Sediment Record, Part B* (ed. J. Thiede and E. Suess), pp. 365–398. Plenum.
Murray J. (1887) On the distribution of the pelagic foraminifera at the surface and on the floor of the ocean. *Nat. Sci.* **11,** 17–27.
Norman R. O. C. and Waddington D. J. (1983) *Modern Organic Chemistry.* Bell and Hyman.
Pflaumann U., Duprat M., Pujol C., and Labeyrie L. (1992) SIMMAX, A modem analog technique to deduce Atlantic sea surface temperatures from planktonic foraminifera in deep sea sediment. *Paleoceanography* **11,** 15–36.
Popp B., Takigiku R., Hayes J., Louda J., and Baker E. (1989) The past paleozoic chronolgy and mechanism of ^{13}C depletion in primary marine organic matter. *Amer. J. Sci.* **289,** 436–454.
Rau G. H., Takahashi T., and Des Marais D. (1989) Latitudinal variation in plankton $\delta^{13}C$: implications for CO_2 and productivity in past oceans. *Nature* **341,** 516–518.
Reynolds L. and Thunell R. (1985) Seasonal succession of planktonic foraminifera in the subpolar north Pacific. *J. Foram. Res.* **15,** 282–301.
Robbins L. (1987) The morphologic varibility and protein isolation and characterization of recent planktonic foraminifera. PhD thesis, Univ. Miami.
Robbins L. and Brew K. (1990) Proteins from the organic matrix of core top and fossil planktonic foraminifera. *Geochim. Cosmochim. Acta* **54,** 2285–2292.
Robbins L. and Healy-Williams N. (1990) Towards a classification of planktonic foraminifera based on biochemical, geochemical and morphological criteria. *J. Foram. Res.* **20,** 333–354.
Sackett W. M. (1974) The depositional history and isotope organic composition of marine sediments. *Mar. Geol.* **2,** 173–185.
Sackett W. H., Eckelmann W., Bender M., and Bé A. W. H. (1968) Temperature dependance of carbon isotopic composition in marine plankton and sediments. *Science* **148,** 235–237.
Sancetta C. (1992) Primary productivity in the glacial North Atlantic and North Pacific oceans. *Nature* **360,** 249–251.
Sarnthein M., Winn K., Duplessy J.-C., and Fontugne M. (1988) Global variations of surface ocean productivity in low and mid latitudes: Influences on CO_2 reservoirs of the deep ocean and atmosphere during the last 21,000 years. *Paleoceanography* **3,** 361–399.
Sarnthein M. et al. (1994) Changes in east Atlantic deepwater circulation over the last 30,000 years: Eight time slice reconstructions. *Paleoceanography* **9,** 209–268.
Shackleton N. J. (1990) Estimating atmospheric CO_2. *Nature* **347,** 427–428.
Shackleton N. J. and Pisias N. (1985) Atmospheric carbon dioxide, orbital forcing and climate. *Geophys. Mono.* **32,** 303–317.

Shemesh A., Charles C., and Fairbanks R. (1993) Oxygen isotopes in biogenic silica: global changes in ocean temperature and isotopic composition. *Science* **262,** 407–410.

Seidov D. and Maslin M. A. (1996) Seasonally ice-free glacial Nordic Seas without deep water ventilation. *Terra Nova* **8,** 245–254.

Siegenthaler U. and Sarmiento J. (1993) Atmospheric carbon dioxide and the ocean. *Nature* **365,** 119–124.

Singer A., and Shemesh A. (1995) Climatically linked carbon isotope variations during the past 430,000 years in Southern Ocean sediments. *Paleoceanography* **10,** 171–177.

Spindler M., Hemleben Ch., Salomow J., and Smit L. (1984) Feeding behavior of some planktonic foraminifera in laboratory cultures. *J. Foram. Res.* **14,** 237–249.

Stott L. (1992) Higher temperatures and lower pCO_2: A climate enigma at the end of the Paleocene Epoch. *Paleoceanography* **7,** 395–404.

Sundquist E. T. (1985) Geological perspective on carbon dioxide and carbon cycle. *Geophys. Mono.* **32,** 5–60.

Tans P., Fung I., and Takahashi T. (1990) Estimating atmospheric carbon dioxide. *Science* **247,** 1431–1438.

Thomas E., Booth L., Maslin M., and Shackleton N. (1995) Northeastern Atlantic benthic foraminifera: the last 45,000 years: Changes in productivity seen from the bottom up. *Paleoceangraphy* **10,** 545–562.

Weiss R. F. (1974) Carbon dioxide in water and sea water: The solubility of a non-ideal gas. *Mar. Chem.* **2,** 203–215.