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Glacial northeast Atlantic surface water p_{CO_2}: Productivity and deep-water formation

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Abstract

The carbon isotopic composition of bound organic material within the crystal lattice of planktonic foraminiferal calcite is a valuable proxy for the isotopic composition of primary photosynthate in surface waters. This proxy can be used to estimate p_{CO_2} in the surface waters of the northeast Atlantic during the last glacial period, if combined with data on the carbon isotopic composition of foraminiferal calcite. Our first estimates of surface water p_{CO_2} at the location of Biogeochemical Ocean Flux Studies Core 5K (50°41.3'N, 21°51.9'W) indicate that this region was probably a more important sink for CO_2 during the glacial than during the Holocene. This increased sink could not have been caused by local high primary productivity, because glacial primary productivity as estimated from benthic foraminiferal data was extremely low at 5K. We thus conclude that the enhanced sink at these latitudes resulted from increased convection of surface water to intermediate or greater depths, i.e. from the southward shift of an important centre of deep-intermediate water formation, as confirmed by computer simulation. © 1997 Elsevier Science B.V.

Keywords: paleoceanography; North East Atlantic; last glacial period; foraminifera; organic matter; carbon isotopes

1. Introduction

1.1. Glacial–interglacial p_{CO_2} differences

Atmospheric p_{CO_2} was at least 80 ppm lower during the last glacial than in the pre-industrial Holocene, as shown by ice core data (e.g. Barnola, 1989). It has been proposed that the oceans, which contain about 60 times as much CO_2 as the atmosphere, drive the atmospheric p_{CO_2} changes (Broecker and Peng, 1982, 1989; Sundquist, 1985). Therefore the deep-sea record has been used to estimate the p_{CO_2} changes at glacial–interglacial time scales, but also to investigate possible driving forces, such as changes in oceanic productivity, chemistry, and circulation (e.g. Shackleton and Pisias, 1985; Jasper and Hayes, 1990).

Increased glacial productivity at low latitudes in the Atlantic and Pacific oceans (e.g. Sarnthein et al., 1988; Herguera and Berger, 1991; Murray et al., 1993) resulted in decreased surface water

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p_{CO_2}, thus increased draw-down of atmospheric CO_2. The global effects of this increased low-latitude productivity have not been established precisely, because we do not yet have precise estimates of the overall area in which this higher productivity occurred: at some high- and mid-latitude regions productivity probably decreased (e.g. Kumar et al., 1993; Thomas et al., 1995).

In addition, changes in sea-surface temperature and ocean circulation may influence atmospheric p_{CO_2}. For instance, during the glacial, the low temperatures at high latitudes resulted in increased carbonate dissolution, and thus may have been partially responsible for the glacial drop in p_{CO_2} (Chester, 1990). Presently, however, oceanic uptake of CO_2 occurs over a small part of the total ocean surface (Toggweiler and Sarmiento, 1985), so that this temperature effect occurs in a small region only and cannot have been responsible for the full decrease in p_{CO_2} unless major changes in ocean circulation and ventilation also occurred. Therefore many numerical models have been used to explore the links between ocean circulation and the short-term carbon cycle (e.g. Keir, 1988; Heinze et al., 1991; Lautenschlager et al., 1992; Paillard et al., 1993; Rahmstorf, 1994; Fichefet et al., 1994; Stocker et al., 1994; Weaver and Hughes, 1994; LeGrand and Wunsch, 1995; Winguth et al., 1996; Seidov and Maslin, 1996). These studies indicate that the major changes between glacial and modern North Atlantic circulation are decreased meridional overturning and North Atlantic Deep Water (NADW) production during glacial times, which had a profound impact on the CO_2 budget.

1.2. Carbon isotopes as a tool to investigate the oceanic carbon system

The interpretation of carbon isotope data on foraminiferal calcite is extremely complex, because of the need for deconvolution of the effects of local and global surface water productivity, upwelling patterns and intensity, global carbon storage, and deep-water circulation and aging patterns. Therefore carbon isotope data on organic matter have been used as an additional proxy to try to unravel the complexities of the oceanic carbon cycle; there is a strong correlation between the p_{CO_2} in surface waters and the carbon isotope composition of phytoplankton (Sackett et al., 1968; Sackett, 1974; Rau et al., 1989). Records of the carbon isotopic composition of organic material can thus assist in the reconstruction of surface water p_{CO_2} (e.g. Sackett, 1974; Fontugne and Duplessy, 1986; Jasper and Gagosian, 1990; Hayes et al., 1990; Hayes, 1993; Brassell, 1993). Presently, there are three approaches in the use of organic matter in carbon isotope studies: (1) analysis of bulk organic matter (Fontugne, 1978; Fontugne and Duplessy, 1978); (2) analysis of specific groups of organic molecules or 'biomarkers' (Hayes et al., 1990; Hayes, 1993); and (3) the extraction of organic matter contained within the tests of foraminifera or diatoms (Stott, 1992; Shemesh et al., 1993; Maslin et al., 1996). All three methods have their advantages and disadvantages (see Maslin et al., 1996 for a review).

We chose the third method because the 'foundation' organic matter trapped within the calcite of the test is protected against diagenesis, and the measurements can be directly related to complementary measurements such as $\delta^{18}O$ and $\delta^{13}C$ in foraminiferal calcite, without problems related to bioturbation rates which vary according to the size fraction of the material (McCave, 1995). In this paper we present our data on the carbon isotopic record of organic matter within calcite of planktonic foraminiferal tests (Maslin et al., 1996), and use these data to interpret the concentration of dissolved CO_2 in glacial North Atlantic surface waters. We then interpret this record, in combination with data on $\delta^{18}O$ and $\delta^{13}C$ in foraminiferal calcite, sea surface temperature records based on foraminiferal transfer functions (Maslin et al., 1995), and benthic foraminiferal faunal records (Thomas et al., 1995), and combine the data with circulation modelling in order to gain increased understanding of northeast Atlantic glacial oceanographic processes.

2. Material and methods

Core BOFS 5K was recovered from the east Thulean Rise in the northeast Atlantic at

50°41.3'N, 21°51.9'W, water depth 3547 m (McCave, 1989), presently in contact with southern-source deep water, derived from Antarctic Bottom water (Manighetti and McCave, 1995). Several proxies were measured on the core (Elderfield and Thomas, 1995). We used 50 specimens of *G. bulloides* for each experiment in which we tried measuring the carbon isotopic composition of organic matter in foraminiferal tests; overall, we conducted more than 450 of these experiments (Maslin et al., 1996). Samples were treated with 5 ml $NaCl_{(aq)}$ (bleach) for 3 h to remove organic contamination from the test surface. The liquid was then pipetted off and the material rinsed in distilled water. The calcite tests were dissolved in 3 ml 20% $HCl_{(aq)}$, while the samples were placed in an ultrasonic bath (5 min) to assist in removing CO_2 from the solution. The acidified samples solution was then dialysed through 500 molecular weight cut off (MWCO) tubing to exchange the remaining acid with distilled water. When the pH of the distilled water reservoir remained unchanged for 3 h, the solution was transferred into Pyrex sample tubes which had been washed in chromic acid, and centrifuged at 10,000 rpm for 5 h. The samples were then frozen and dried in a vacuum oven at 25°C.

We added copper oxide, silver wire and copper to the dry organic residue, and the samples tubes were vacuum sealed and baked at 450°C. The sealed tubes were then broken in a vacuum line, water condensed on the cold trap, and liquid nitrogen placed round the u-trap to freeze out the CO_2, while non-condensable gases were pumped off. The CO_2 was then transferred into the inlet of a VG Isotech SIRA Series II mass spectrometer (see Maslin et al., 1996, for more details).

For determination of oxygen and carbon isotope composition of planktonic foraminiferal calcite, we analyzed tests of *G. bulloides* (300–350 μm) and *N. pachyderma* (s) (250–300 μm) in a VG PRISM mass-spectrometer using a VG ISOCARB automatic common acid bath containing 100% orthophosphoric acid at 90°C. The CO_2 and reference gases then were admitted to the mass-spectrometer for analysis, alternating between sample and reference gas 12 times. The results were then corrected for instrumental effects, and calibrated to TDB using standard NBS 19. We used the same procedure for analysis of benthic foraminiferal tests, for which we used specimens larger than 125 μm of *Cibicidoides wuellerstorfi* and species of *Pullenia* and *Oridorsalis*, specimens of *Epistominella exigua* larger than 63 μm. Data on planktonic foraminifera are given in Maslin (1993). The age models of both BOFS 5K and 14K are described in Maslin (1993) and Manighetti et al. (1995).

3. Results

The organic $\delta^{13}C$ record (Fig. 1) for core 5K has a mean value of −26.7‰, with an overall range of 1.3‰, and with individual standard deviations for five replicate analyses ranging between ±0.1 and ±0.45‰, which can be compared to a reproducibility of ±0.09‰ of $\delta^{13}C$ measurements in carbonate. There is no simple correlation between the $\delta^{13}C$ record of the organic material and the content of organic matter of the sediment, or between the organic $\delta^{13}C$ record and the records of $\delta^{13}C$ in the calcite of *G. bulloides* tests. The latter indicates that the metabolic systems absorbing dissolved CO_2 from the water to construct the test, and those systems which digest food to provide the organic framework for the test, operate independently.

Core top data (Fig. 1C) are fully within the range of Holocene data for core 5K, and the results are consistent with data from other researchers (Singer and Shemesh, 1995). We therefore do not consider hydrolization of proteins with increasing age of the samples as an important problem with the 5K record, as discussed in more detail by Maslin et al. (1996). We therefore assumed that the organic $\delta^{13}C$ record represents the isotopic composition of primary photosynthate in the surface waters, and used the record to estimate the surface water dissolved CO_2 content (Appendix A; Maslin et al., 1996).

The effect of the temperature changes between glacial and interglacial times on dissolved CO_2 is significant at the location of core 5K, because these changes are very large (Maslin et al., 1995). We thus used the sea surface temperature (SST) estimates for 5K (Fig. 1E) as derived by using the

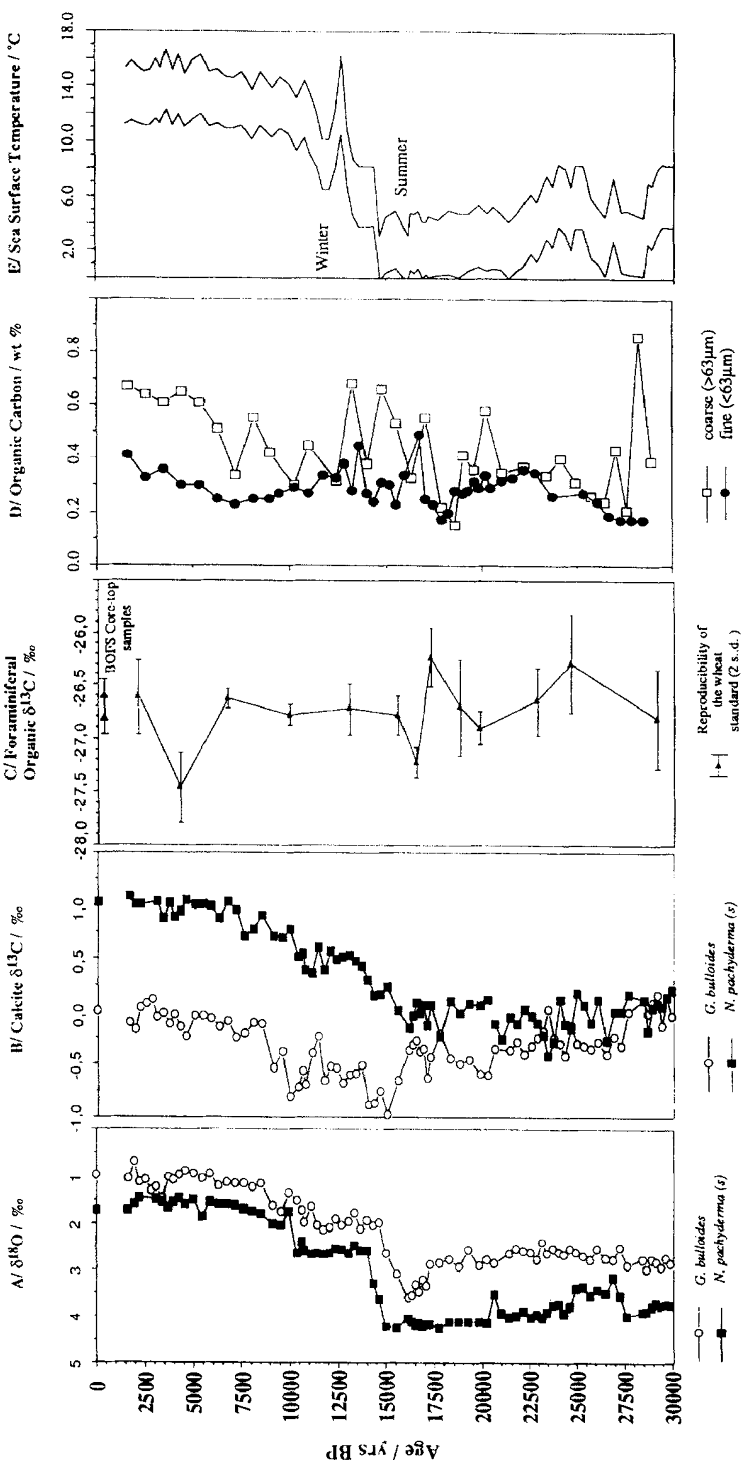


Fig. 1. BOFS 5K (50°41.3'N, 21°51.9'W, water depth 3547 m) records: (A) $\delta^{18}O$ records of the calcite tests of *G. bulloides* and *N. pachyderma* (s); (B) $\delta^{13}C$ records of the calcite tests of *G. bulloides* and *N. pachyderma* (s); (C) $\delta^{13}C$ record of the organic matter extracted from within the calcite test of *G. bulloides*, note that the error bars of the organic $\delta^{13}C$ record are the 1 s.d. calculated from five repeat measurements at each depth; (D) weight percentage of organic carbon; (E) sea surface temperature estimated using planktonic foraminifera relative species abundances and the SIMMAX modern analog techniques (Pflaumann et al., 1996).

EPOCH SIMMAX equation (Pflaumann et al., 1996) in order to calculate this effect (Fig. 2D), and thus derived the estimated surface water p_{CO_2}, as estimated from our records, and compared this with the 'expected' p_{CO_2} record, derived from the data for the Vostok ice core (Barnola et al., 1989; see Fig. 2E.)

This comparison of estimated and expected surface water p_{CO_2} is made difficult because we do not know the present off set between these two records. Tans et al. (1990) suggest that the northeast Atlantic presently is a sink, but we do not know to which magnitude. Our comparison, however, shows that the difference was maximal during the last glacial maximum. The largest change occurred between 18 and 15 ka, when the difference between 'expected' and 'estimated' values decreased by 1 to 1.5 μmol/l. These data suggest that the North Atlantic may have been a stronger 'sink' for atmospheric CO_2 than it was during the Holocene. Large surface water 'sinks' usually indicate the locations of regions of high surface primary productivity, or areas of deep-water formation, where sinking cold waters carry dissolved CO_2 away from the atmosphere (Tans et al., 1990; Siegenthaler and Sarmiento, 1993).

There have been some suggestions that the North Atlantic was indeed a location of high productivity during the last glacial, possibly as a result of nutrient input from melting icebergs (Sancetta, 1992). This is, however, in disagreement with evidence from planktonic foraminifera (Bond et al., 1992; Maslin, 1993), benthic foraminifera (Thomas et al., 1995) and organic matter isotopic records (Jasper et al., 1997) that primary productivity was very low in the northeast Atlantic during the last glacial, when the Polar Front was to the south of core 5K.

Benthic foraminiferal accumulation rates have been related to surface primary productivity (Herguera and Berger, 1991). Data for core 5K show extremely low values for the last glacial compared with both the Holocene record at 5K and the glacial record of 14K, a core much further to the north (see Fig. 3). This extreme and unusually low value is mainly caused by the similarly low accumulation rates of species that in the present ocean feed on 'phytodetrital material', which originates in the mixed layer during the well-documented northeast Atlantic spring blooms (Gooday, 1988; Gooday and Turley, 1990; Gooday et al., 1992). The present high surface water productivity in the northeast Atlantic is primarily driven by these spring blooms, as shown for instance in satellite (Coastal Zone Colour Scanner, CZCS) images (Antoine et al., 1996). The benthic foraminifera suggest that such blooms did not occur to the north of the glacial Polar Front, which may have been located at about 40°N (Robinson et al., 1995).

We therefore suggest that the increased drawdown of atmospheric CO_2 during the last glacial at the location of 5K did not result from increased productivity, but from the formation of glacial intermediate waters in the northeast Atlantic (the glacial equivalent of NADW, sinking to shallower levels than its present counterpart), as had been proposed by Duplessy et al. (1988), Labeyrie et al. (1992), Sarnthein et al. (1994); see also Imbrie et al. (1992, fig. 3). This model of more southerly intermediate water formation is supported by the similarity between the $\delta^{13}C$ values of the deep-dwelling planktonic foraminifera *N. pachyderma* (s) and of benthic foraminifera, which suggests that surface and deep waters in the area were coupled (e.g. Duplessy et al., 1988; Curry et al., 1988; Jansen and Veum, 1990; Maslin, 1993).

4. Discussion

We need to consider the reconstruction of glacial North Atlantic surface circulation (Fig. 4), in order to gain insight into the glacial–interglacial surface water p_{CO_2} history. Our surface p_{CO_2} reconstructions and those of Jasper et al. (1997) suggest that during the last glacial the area of core 5K was an increased sink for CO_2 (Fig. 4B), whereas this was not so in the area to the west of Scotland (Fig. 4C). Computer reconstructions of North Atlantic circulation during glacial periods indicate that the North Atlantic Drift was extremely zonal, with an almost meridional, weak, warm northward current near 20°W (Fig. 4), i.e. the site of BOFS 5K. The Labrador Current may have been

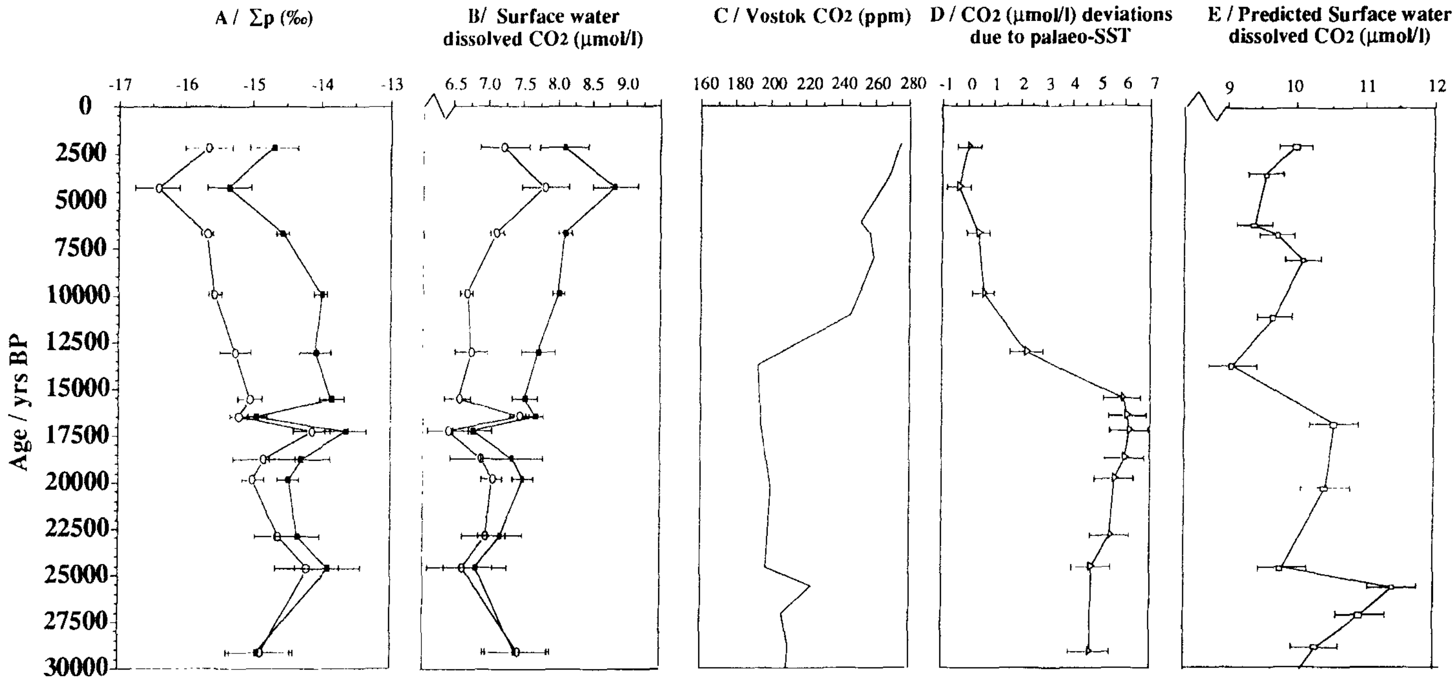


Fig. 2. Comparison of: (A) the isotopic effect of fixation of CO_2 (ϵ_p) and (B) the calculated surface water dissolved CO_2 of BOFS 5K (the error bars are calculated from the 1 s.d. errors indicated in Fig. 1); circles indicate when calcite $\delta^{13}C$ values of *G. bulloides* and squares when *N. pachyderma* (s) calcite $\delta^{13}C$ were used to calculate ϵ_p and dissolved CO_2; (C) Vostok atmospheric CO_2 record (Barnola et al., 1989); (D) the effect on surface water dissolved CO_2 at the BOFS 5K site due to changing sea surface temperatures (see Appendix A), error bars calculated assuming a ±1°C error (Pflaumann et al., 1996); (E) the predicted dissolved CO_2 for the BOFS 5K site was calculated using the EPOCH SIMMAX summer sea surface temperature estimates at BOFS 5K (Maslin, 1993; Maslin et al., 1995), to estimate α which was applied to the Vostok atmospheric p_{CO_2} (see Appendix A) to obtain an estimate of the 'predicted' surface water dissolved CO_2. A gaussian interpolation using weighted duplicates (sample spacing of 2000 years and window size of 4000 years) was performed so that the two chronologies were compatible.

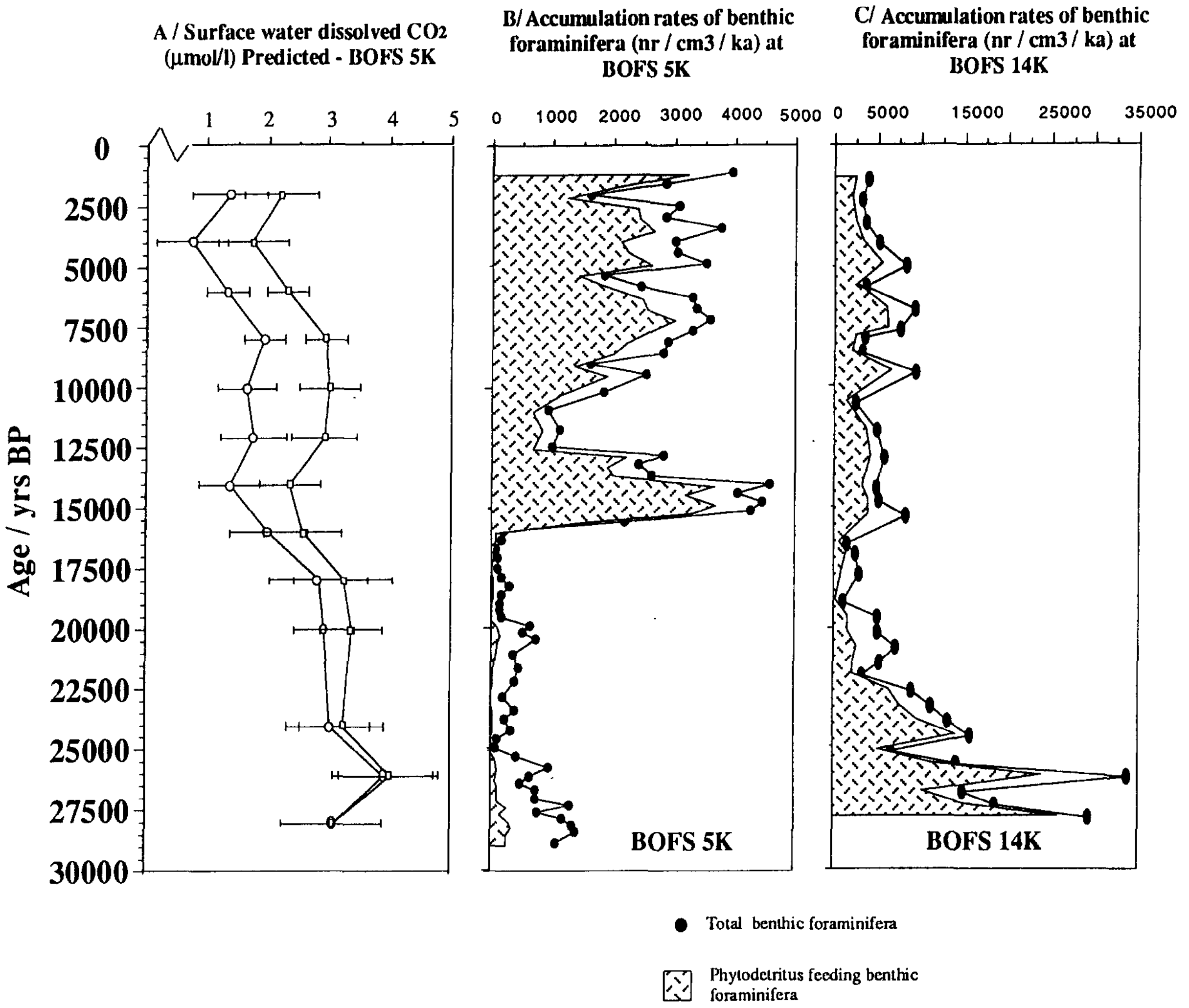
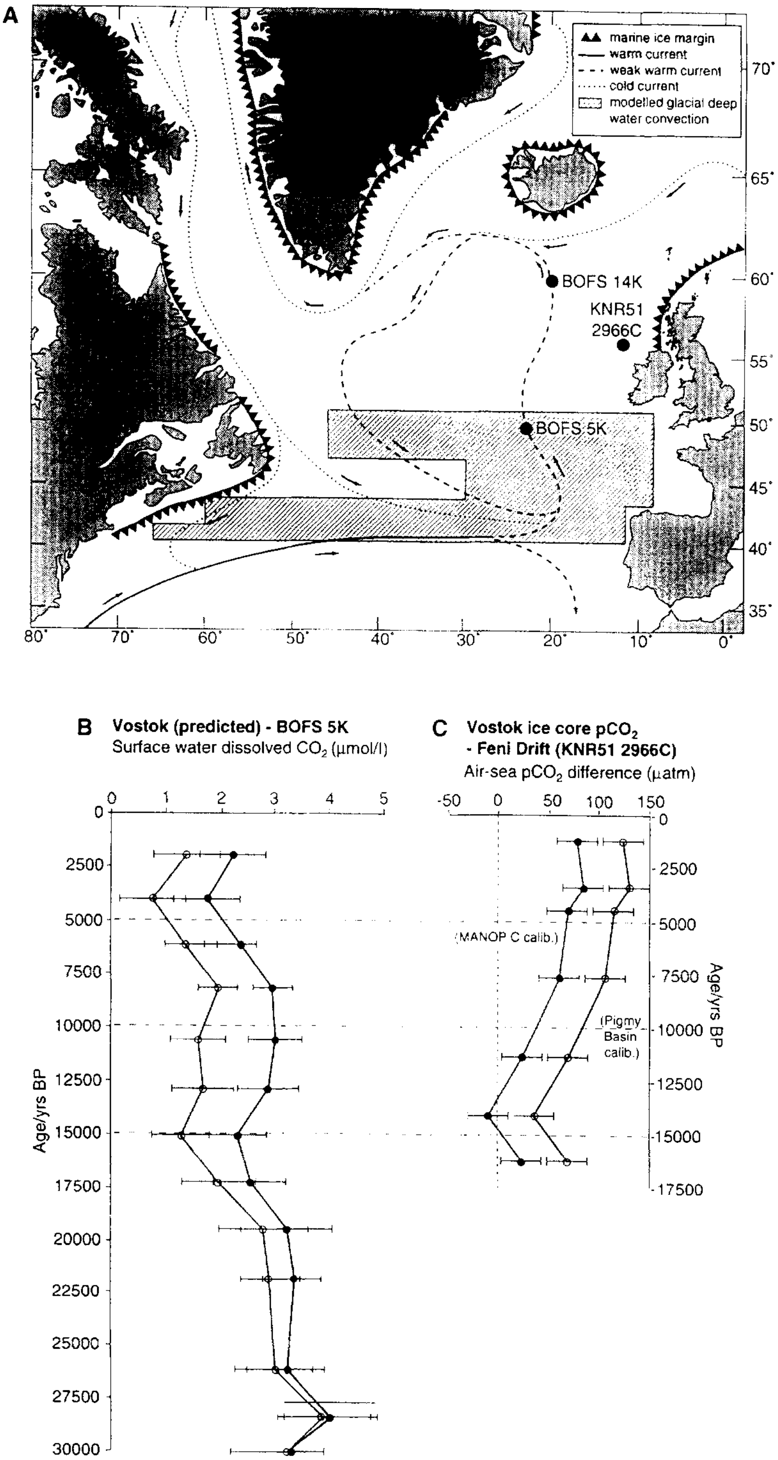


Fig. 3. Comparison of the following records: (A) the difference between the isotopically estimated and the predicted dissolved CO_2 record (see Fig. 2); note error bars are calculated as the sum total of the errors on both the estimated and predicted dissolved CO_2 records; (B) the absolute abundance of benthic foraminifera indicating the surface water productivity at BOFS 5K (Thomas et al., 1995); (C) the absolute abundance of benthic foraminifera indicating the surface water productivity at BOFS 14K. Note scale difference between (B) and (C).

stronger, and carried cold water southeastward to the Polar Front.

This different pattern of surface circulation during the last glacial led to different ventilation patterns of the deep oceans. The surface water moving to the north did not penetrate into the Nordic Seas as the present Gulf Stream does, thus there was greatly reduced or no convection there. But the northward flowing water cooled on its travel northward, and may have cooled enough to form the glacial equivalent of upper North Atlantic Deep Water in the middle of the sub-polar gyre (Seidov et al., 1996; Seidov and Maslin, 1996; Yu et al., 1996). This glacial equivalent of upper North Atlantic Deep Water was not as dense as the present NADW which is derived from the cold Nordic Seas, and it did therefore not ventilate the deeper North Atlantic. This model of glacial ventilation thus implies that the deep Atlantic was less ventilated during the last glacial maximum,


A
marine ice margin
warm current
weak warm current
cold current
modelled glacial deep water convection
70°
65°
60°
55°
50°
45°
40°
35°
80°
70°
60°
50°
40°
30°
20°
10°
0°
BOFS 14K
KNR51 2966C
BOFS 5K
B Vostok (predicted) - BOFS 5K
Surface water dissolved CO2 (μmol/l)
0 1 2 3 4 5
Age/yrs BP
0
2500
5000
7500
10000
12500
15000
17500
20000
22500
25000
27500
30000
C Vostok ice core pCO2 - Feni Drift (KNR51 2966C)
Air-sea pCO2 difference (μatm)
-50 0 50 100 150
(MANOP C calib.)
(Pigmy Basin calib.)
Age/yrs BP
0
2500
5000
7500
10000
12500
15000
17500

whereas the intermediate-depth waters were much more intensely ventilated, in agreement with reconstructions of ventilation using carbon isotope values and Cd/Ca ratios (Labeyrie et al., 1992; Bertram et al., 1995; Sarnthein et al., 1995). A simplified model of glacial ocean ventilation suggests that the glacial convection to intermediate depths shifted to the south by more than 10° (Seidov and Maslin, 1996; see Fig. 4A), which agrees qualitatively with Imbrie et al. (1992). Seidov et al. (1996) demonstrated that this glacial mid-Atlantic convection had its maximum ventilation depth close to the location of core site 5K, in the centre of the cyclonic gyre.

A more intense ventilation at mid-depths and lesser ventilation in the glacial deep North Atlantic implies that there was a strong outflow of upper NADW from the North Atlantic at depths of about 2 km, which was far shallower than the present outflow (2.5–3.0 km). The shallower, but more vigorous outflow from the North Atlantic could have transported dissolved CO_2 southward as effectively as the present outflow, and the simulated glacial upper NADW at 30°N was almost as strong as the present outflow, in agreement with the reconstructions models developed using radiochemical data (Yu et al., 1996).

5. Conclusions

Our data on the carbon isotope composition of organic matter in planktonic foraminiferal tests, combined with earlier published data on the carbon isotope composition of the calcareous tests, suggest that the northeast Atlantic Ocean at about 50°N, 20°W was a stronger sink for CO_2 during the last glacial maximum than it is presently. Our data on benthic foraminiferal accumulation rates indicate that this increased sink was not caused by local high surface water productivity. We therefore suggest that a glacial equivalent of upper North Atlantic Deep Water, which ventilated the North Atlantic to intermediate depths only, formed close to the location of core site BOFS 5K, i.e. much further to the south than the regions where NADW forms presently. This circulation pattern is supported by circulation modelling.

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Appendix A

Calculating palaeo-surface water p_{CO_2}

Details of the development of the extraction method and the p_{CO_2} calculation can be found in (Maslin et al., 1996). The key steps in the Palaeo-Surface Water p_{CO_2} calculation are given in this Appendix.

It is possible to estimate the surface water dissolved CO_2 content from the organic and calcite $\delta^{13}C$ by assuming that the organic $\delta^{13}C$ record represents the isotopic composition of the surface water primary photosynthate. Jasper and Hayes (1990), by utilizing the theoretical models linking

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Fig. 4. (A) Summarized glacial North Atlantic upper ocean circulation (Maslin, 1993; Robinson et al., 1995) showing the locations of cores BOFS 5K, BOFS 14K, KNR51 2966C and indicating the key region of glacial deep water convection from the surface identified by circulation models of Seidov et al. (1996) and Seidov and Maslin (1996). (B) The estimated surface water dissolved CO_2 contents by taking the difference between the isotopically estimated dissolved CO_2 record and that predicted by the Vostok atmospheric CO_2 combined with the BOFS 5K EPOCH SIMMAX SST records. (C) The estimated air–sea p_{CO_2} difference for the Feni Drift (core KNR51 2966C) reconstructed by Jasper et al. (1997).

isotopic fractionation associated with photosynthetic fixation of carbon and the surface water p_{CO_2} calculated by Popp et al. (1989) and Hayes et al. (1989), were able to estimate the surface water p_{CO_2}. Two empirical relationship linking the two factors have been suggested:

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

or

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

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 surface water concentration of dissolved CO_2 (μM) (where the subscript '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. Eq. (2) of Jasper et al. (1995) and their prescribed constants were also used to calculate the BOFS 5K p_{CO_2}, but very little difference was found between the two solutions.

Farquhar et al. (1982) and Popp et al. (1989) derived another estimate of the ϵ_p by assuming that 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:

$$\epsilon_p = \{[(\delta_p + 1000)/(\delta_d + 1000)] - 1\}\ 1000 \tag{3}$$

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 foraminifer *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 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. (1989) 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 Eq. (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 ±2000 years. 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. From this Jasper and Hayes (1990) estimated that a varied between −17 and −21; they used $a = -20$ which favoured marine systems. Using both these estimates Jasper and Hayes (1990) estimated the surface water p_{CO_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 how they estimated the constants a and b for Eq. (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 foraminiferal 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 Eq. (3)). Two estimates of ϵ_p were calculated the 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) was 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. bulloides* 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 Eq. (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 Eq. (2) (Jasper et al., 1995) we used the constants $a=-27‰$ and $b=-130‰\ \mu M$. When the ϵ_p and the surface water dissolved CO_2 were calculated using both Eq. (1) and Eq. (2), very little difference between the two solutions was shown. The ϵ_p and the surface water dissolved CO_2 shown against age with 1 s.d. error bars in Fig. 2 are from the original solution using Eq. (1).

Jasper and Hayes (1990) and Jasper et al. (1995) demonstrated that surface water p_{CO_2} can be estimated from foraminiferal calcite $\delta^{13}C$ and organic estimates of the photosynthate $\delta^{13}C$. However, the estimation of p_{CO_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 p_{CO_2}. Second Laws et al. (1995) 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 p_{CO_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 foraminifer-based estimates of palaeo-p_{CO_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, p. 150).

$$p_{CO_2}=[CO_2]/\alpha \qquad (4)$$

when p_{CO_2} = atmospheric CO_2 content (ppm), $[CO_2]$ = 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):

$$\alpha=6.24\times10^{-2}-2.11\times10^{-3}T+2.95\times10^{-5}T^2 \qquad (5)$$

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 Eq. (5) and applied to the Vostok atmospheric

p_{CO_2} (Fig. 2C; Barnola et al., 1989) to obtain an estimates 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 p_{CO_2} is shown in Fig. 2D. Fig. 2E shows the comparison of the 'estimated' surface water p_{CO_2} from the $\delta^{13}C$ records with the 'predicted' surface water dissolved CO_2. Note that a gaussian interpolation using weighted duplicates (sample spacing of 2000 years and a window size of 4000 years) was performed so that the two chronologies were compatible.

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