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Mid-depth South Atlantic ocean circulation and chemical stratification during MIS-10 to 12: implications for atmospheric CO₂

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Abstract

A detailed record of benthic foraminifera carbon isotopes from the South East Atlantic margin shows little glacial-interglacial variability between MIS-12 to MIS-10, suggesting that Glacial North Atlantic Intermediate Water (GNAIW) consistently penetrated to at least 30° S. Millennial-scale increases in either the mass or flux of GNAIW over the core site occur alongside reductions in Lower North Atlantic Deep Water recorded in North Atlantic sediment cores and show that the lower and intermediate limb of the Atlantic deepwater convective cell oscillated in anti-phase during previous glacial periods. In addition, a 500 yr resolution record of the Cape Basin intermediate-deep $\delta^{13}\text{C}$ gradient shows that a reduction in deep Southern Ocean ventilation at the end of MIS-11 was consistent with a modelled CO_2 drawdown of $\sim 21\text{--}30$ ppm. Further increases in the Southern Ocean chemical divide during the transition into MIS-10 were completed before minimum CO_2 levels were reached, suggesting that other mechanisms such as alkalinity changes were responsible for the remaining ~ 45 ppm drawdown.

1 Introduction

A number of mechanisms within the earth-ocean-atmosphere system have the potential to exert a positive or negative feedback on orbitally forced climate variability. Changes in ocean circulation can have an impact on climate changes over timescales ranging from decades to millennia, by altering the distribution of alkalinity in the oceans, and thus changing atmospheric CO_2 (e.g. Boyle, 1988; Toggweiler et al., 1999; Sigman and Boyle, 2000), or by changing the distribution of surface heat transported by ocean currents (Clark et al., 2002). Glacial-interglacial changes in ocean circulation have been reconstructed in a number of studies, traditionally using changes in the carbon isotope ratios of benthic foraminifera (e.g. Curry and Lohmann, 1983; Shackleton et al., 1983; Boyle and Keigwin, 1985/86; Boyle and Keigwin, 1987; Oppo and Fairbanks, 1987; Curry et al., 1988; Duplessy et al., 1988; Oppo et al., 1990; Raymo et al., 1990;

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Charles et al., 1996; Yu et al., 1996; Lynch-Stieglitz et al., 2007; Martinez-Mendez et al., 2008) and have consistently shown that the production of Lower North Atlantic Deep Water (LNADW) decreased during the cold climates of the Last Glacial Maximum (LGM) and during Heinrich events and was replaced by southern sourced deepwaters that expanded into the Northern Atlantic below ~2000 m. At the same time, Glacial North Atlantic Intermediate Water (GNAIW) spread southwards at depths shallower than 2000 m to at least 30° S (Duplessy et al., 1988; Oppo and Lehman, 1993; Oppo and Horowitz, 2000; Curry and Oppo, 2005).

Marine Isotope Stage (MIS) 11, the most recent interglacial period to occur under a similar pattern of orbital forcing to the Holocene (Loutre and Berger, 2003) has the potential to provide information on the type and magnitude of climate variability that could be expected under “baseline” (i.e. non-anthropogenic) conditions. However, few detailed records of deepwater variability during the middle Brunhes period have been produced, and those that do are predominantly located in the North Atlantic Ocean (e.g. Oppo et al., 1998; Poli et al., 2000; Thunell et al., 2002; McManus et al., 2003; Hall and Becker, 2007; Martrat et al., 2007).

Here we present a new ~450 yr resolution benthic foraminifera $\delta^{13}\text{C}$ record from ODP-1085 in the South Eastern Atlantic Ocean (Table 1 and Fig. 1) that extends between 480–330 ka. The data show that the increased advection of GNAIW to intermediate depths in the South East Atlantic Ocean at millennial-timescales was coincident with a reduced production of LNADW, possibly in response to the delivery of meltwater to sites of deepwater production in the North Atlantic. Furthermore, similarities between the structure of the Cape Basin vertical $\delta^{13}\text{C}$ gradient and the spliced EPICA Dome C (EDC)/Vostok atmospheric CO_2 record supports previous suggestions of a close link between ventilation of the deep ocean and changes in atmospheric greenhouse gas concentrations.

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2 Modern deepwater hydrography at ODP-1085

The structure of the South Atlantic water column has been discussed in detail by McCartney (1977), Saunders and King (1994), and Siedler et al. (1996), and is shown in Fig. 2 with profiles of dissolved oxygen, phosphate and $\delta^{13}\text{C}$ CO_2 from GEOSECS Station 102 (Kroopnick, 1980). NADW flows southwards in the Western Atlantic between 1200–4000 m, and is marked by dissolved O_2 concentrations of $\sim 230 \mu\text{mol kg}^{-1}$ and PO_4 concentrations of $\sim 1.6 \mu\text{mol kg}^{-1}$. South of the equator, this flow branches into two components and enters the South East Atlantic, where it can be identified between 2000–3500 m (Fig. 2a and b). Northwards-flowing Circumpolar Deep Water (CDW) is intersected by NADW east of Drake Passage, and bifurcates into an upper and lower branch (UCDW and LCDW respectively). UCDW can be identified by low dissolved oxygen ($< 200 \mu\text{mol kg}^{-1}$) and high phosphate ($\sim 2 \mu\text{mol kg}^{-1}$) concentrations, which are derived from its origins in Indian and Pacific waters (Whitworth and Nowlin Jr., 1987). These properties are modified slightly by mixing with underlying NADW and are identifiable in the GEOSECS 102 data between ~ 1100 m and 2000 m. LCDW occupies the bottom of the Cape Basin below 3500 m (Siedler et al., 1996) where it can be distinguished from NADW by comparatively higher phosphate and lower oxygen concentrations. Antarctic Intermediate Water (AAIW) is formed by the subduction of upwelled CDW at the sub-Antarctic front (McCartney, 1977), and fills much of the South Atlantic at depths between 700–1000 m.

Modern ΣCO_2 $\delta^{13}\text{C}$ profiles in the South Eastern Atlantic are clearly related to the distribution of these water masses (Kroopnick, 1980; Bickert and Wefer, 1999). In Fig. 2c, NADW is clearly distinguished by high $\delta^{13}\text{C}$ values of $+0.8\text{‰}$, while values for AAIW, UCDW and LCDW are $< +0.5\text{‰}$. ODP-1085 is currently located within the NADW/UCDW mixing boundary, where T-S data suggests that it is influenced by a respective 60/40 mixture of each water mass.

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3 Methods

Benthic foraminifera samples from ODP-1085 were picked from the $>250\ \mu\text{m}$ fraction at 2 cm intervals between 11.00–17.50 mbsf. Measurements were performed on the epibenthic species *Cibicidoides wuellerstorfi* and the infaunal species *Uvigerina* spp. where *C. wuellerstorfi* was absent. Each sample was reacted at 90°C in a VG IsoCarb common acid bath system attached to an Optima mass spectrometer. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values are expressed relative to the Vienna PDB scale by reference to an internal laboratory working standard (KCM) calibrated against NBS-19. Internal precision was monitored with repeat measurements of KCM and was 0.09‰ for $\delta^{18}\text{O}$ and 0.06‰ for $\delta^{13}\text{C}$ over the period of analysis. $\delta^{18}\text{O}$ values of *C. wuellerstorfi* have been corrected by $+0.64\text{‰}$ and $\delta^{13}\text{C}$ values of *Uvigerina* spp. have been corrected by $+0.90\text{‰}$ to correct for offset from isotopic equilibrium (Duplessy et al., 1984).

Foraminifera fragments $>150\ \mu\text{m}$ have also been counted as a qualitative measure of carbonate dissolution (e.g. Le and Shackleton, 1992). In order to account for changes in the abundance of foraminifera through time, the abundance of fragments is expressed relative to the mass of sand-sized material ($>63\ \mu\text{m}$), which is dominated by planktonic foraminifera. An age-model for ODP-1085B has been generated through visual correlation to the LR04 benthic oxygen isotope stack (Lisiecki and Raymo, 2005). This approach yields a study section extending between 330–480 ka, at an average temporal resolution of 450 years. Tie points are shown in Table 1.

4 Results

The *C. wuellerstorfi/Uvigerina* spp. $\delta^{18}\text{O}/\delta^{13}\text{C}$ data from ODP-1085 are shown in Fig. 3, along with foraminifera fragment abundances and accumulation rates. The $\delta^{18}\text{O}$ record shows the most obvious features of MIS-11, in particular the long deglaciation during termination 5 and a decrease in the rate of $\delta^{18}\text{O}$ change in the early part of the interglacial from ~ 420 ka. Along with several $\delta^{18}\text{O}$ minima during MIS-12 and late

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MIS-10, these features permitted the transfer of the LR04 chronology to the studied section of ODP-1085. $\delta^{13}\text{C}$ values of individual data points range from 0 to +1‰. However, the average glacial-interglacial change in $\delta^{13}\text{C}$ is close to the mean-ocean changes found for the last deglaciation (Curry et al., 1988; Duplessy et al., 1988, see discussion below). Several short-term $\delta^{13}\text{C}$ increases are superimposed on this long-term trend. These increases are defined as periods when $\delta^{13}\text{C}$ values rise abruptly by +0.1 to +0.3‰, and are maintained for several adjacent data points before decreasing again to pre-excursion values (shaded bands in Figs. 3 and 4). Foraminifera fragments indicate varying levels of carbonate preservation through the study interval. Highest abundances/accumulation rates occur at the beginning of MIS-12, during the climate optimum of MIS-11 (424–390 ka), towards the end of MIS-11 (383–370 ka) and during MIS-10 (355–345 ka). The intervening intervals are characterised by relatively low amounts of fragmentation.

5 Discussion

5.1 Effects of organic matter on benthic foraminifera $\delta^{13}\text{C}$ in ODP-1085

The release of ^{12}C into bottom waters during organic matter breakdown may cause locally lowered $\delta^{13}\text{C}$ values in benthic foraminifera. Although *C. wuellerstorfi* has been demonstrated to calcify close to bottom-water carbon isotopic equilibrium (Graham et al., 1980; Belanger et al., 1981; Duplessy et al., 1984), a highly seasonal flux of organic matter to the seafloor can generate *C. wuellerstorfi* blooms whose $\delta^{13}\text{C}$ is offset from bottom water $\sum\text{CO}_2$ by -0.4 to -0.6 ‰ (Mackensen et al., 1993; Bickert and Wefer, 1999). A number of lines of evidence suggest that this “photodetritus” effect does not unreasonably compromise the *C. wuellerstorfi* $\delta^{13}\text{C}$ data from ODP-1085. Firstly, highly pulsed seasonal organic matter production does not occur over the study site, although there is a small peak in organic matter flux during summer (Romero et al., 2002; Muller and Fischer, 2003). Secondly, core-top *C. wuellerstorfi* $\delta^{13}\text{C}$ val-

ues of nearby cores GeoB-1721-5, GeoB1719-4, GeoB-1729-2 and GeoB-1720-3 are within 0.15‰ of bottom water $\delta^{13}\text{C} \sum\text{CO}_2$, suggesting that unlike sites closer to the coastal upwelling cells, a photodetritus effect does not arise from enhanced productivity in more open-ocean locations (Bickert and Wefer, 1999; Dickson et al., in prep.).

5 *Uvigerina* spp. calcify within sediment porewaters and thus may be biased by low $\delta^{13}\text{C}$ metabolic carbon during organic matter oxidation (Zahn et al., 1986). However, 43 paired measurements of *C. wuellerstorfi* and *Uvigerina* spp. from ODP-1085 and GeoB-17202/3 give a $\delta^{13}\text{C}$ difference of +0.96‰ which is close to the Duplessy et al. (1984) +0.90‰ correction, and is also constant downcore. Additionally, *C. wuellerstorfi* $\delta^{13}\text{C}$ in nearby ODP-1088 (Pierre et al., 2001) (41.8° S, 13.3° E, 2082 m) (Fig. 3b) are extremely similar to *Uvigerina* spp. during MIS-12 in ODP-1085, suggesting that these values may be reliably interpreted in terms of bottom water $\delta^{13}\text{C}$.

5.2 Glacial-interglacial changes in benthic $\delta^{13}\text{C}$

15 Deep sites within the Cape Basin have more negative benthic foraminifera $\delta^{13}\text{C}$ values than the deep Pacific Ocean during late Pleistocene glacials (Raymo et al., 1990; Oppo and Horowitz, 2000; Ninnemann and Charles, 2002; Hodell et al., 2003a). In contrast, benthic $\delta^{13}\text{C}$ in ODP-1085 reaches +0.8–0.9‰ during MIS-11 and +0.1–0.2‰ during MIS-10 and 12, and never falls below the deep Pacific $\delta^{13}\text{C}$ values recorded at ODP-849 (Mix et al., 1995) (Fig. 3b). The average glacial-interglacial $\delta^{13}\text{C}$ change between the MIS-11 climate optimum (424–397 ka) and MIS-10 (360–340 ka) is –0.34‰, which is similar in amplitude to the 0.32‰ glacial-interglacial change in whole-ocean $\delta^{13}\text{C}$ due to expansions and contractions of the terrestrial biosphere seen over the MIS-2/1 transition (Curry et al., 1988), but less than the 0.95‰ proposed for the MIS-12/11 boundary (Thunell et al., 2002). Consequently, it may be surmised that a low-nutrient water mass with similar $\delta^{13}\text{C} \sum\text{CO}_2$ values to the present NADW/UCDW mixture must have been present at ~1700 m depth during glacial stages MIS-10 and 12 in the South East Atlantic Ocean at 30° S. Slightly higher $\delta^{13}\text{C}$ values at ODP-1088 between 360–340 ka (Pierre et al., 2001) probably reflect increased mixing with underlying CDW

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during full glacial conditions (Fig. 3b).

The source of the low-nutrient water mass that overlay ODP-1085 during MIS-10 and 12 may be sought through a comparison to several studies that have shown the presence of a sharp chemocline in the South Atlantic and adjacent Southern Ocean during glacial periods (Ninnemann and Charles, 2002; Hodell et al., 2003a). This chemocline separated low-nutrient (high $\delta^{13}\text{C}$) water above 2100 m from high-nutrient (low $\delta^{13}\text{C}$) water below. The presence of a low-nutrient water mass at intermediate depths <2100 m can also be traced along the African continental slope (Pierre et al., 2001; Mackensen et al., 2001) and into the western South Atlantic Ocean, where it has been identified as a water mass with $\delta^{13}\text{C}$ values $>+0.8\text{‰}$ centred at ~ 1500 m depth and bounded above and below by higher-nutrient water masses (Oppo and Horowitz, 2000; Curry and Oppo, 2005). A glacial chemocline at 2000 m depth has also been identified in the North Atlantic (Oppo and Lehmann, 1993), and is related to the production of GNAIW and the northwards spread of low $\delta^{13}\text{C}$ southern sourced deepwaters below the minimum depth of the mid-Atlantic ridge (Curry and Oppo, 2005). Based on the similarity of $\delta^{13}\text{C}$ values, the consistency with existing reconstructions of glacial water mass geometry, and the consistency with modern oceanographic observations of a divergence of NADW flow from the western to the eastern South Atlantic south of the equator, bottom waters over ODP-1085 during MIS-10 and 12 were likely influenced by GNAIW, and not the SAMW suggested by Hodell et al. (2003a).

5.3 Millennial-scale changes in benthic $\delta^{13}\text{C}$

The temporal resolution of the ODP-1085 dataset allows millennial-scale changes in deepwater $\delta^{13}\text{C}$ to be identified (shaded bands in Fig. 3). These events are most pronounced during the transition from MIS-11 into MIS-10 (397–340 ka), when their amplitude ranges from $+0.1$ to $+0.3\text{‰}$. Each event is superimposed onto the glacial-interglacial $\delta^{13}\text{C}$ trend, over timescales that are too short to be explained by terrestrial biosphere expansions. Supplementary information about the balance between CDW and northern-sourced waters (either NADW in the modern sense or GNAIW in the

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glacial sense) over the core site may be obtained from a measure of calcium carbonate preservation. Contemporary observations indicate that NADW has a higher alkalinity than CDW. This distribution of alkalinity affects the preservation of calcium carbonate in the deep sea, since the carbonate lysocline will be deeper in regions overlain by NADW (Broecker, 2003). Each millennial increase in benthic $\delta^{13}\text{C}$ corresponds to a small decrease in the abundance and accumulation rate of planktonic foraminifera fragments in ODP-1085 (Fig. 3c), which would be expected if the carbon isotope change were being caused by the mixing of NADW/GNAIW with CDW. This relationship is not straightforward because of a number of factors that can also influence calcium carbonate dissolution, such as changes in the population of foraminifera species (e.g. Berger, 1970) and the release of metabolic CO_2 in sediment porewaters (Broecker, 2003).

The millennial-scale increases in benthic $\delta^{13}\text{C}$ during MIS-10 to 12 were likely caused either by less NADW(GNAIW)/CDW mixing (deepening of the GNAIW/CDW boundary), or by an increase in pre-formed $\delta^{13}\text{C}$ of GNAIW entering the intermediate-depth Cape Basin. Higher flux rates of GNAIW could reduce its residence time in the western Atlantic, thus increasing pre-formed $\delta^{13}\text{C}$ in the South East Atlantic, in agreement with studies showing an enhanced export of this water mass from the North Atlantic during the LGM (Yu et al., 1996; Oppo and Horowitz, 2000). In either case, the data from ODP-1085 point to periodically enhanced transport of GNAIW into the South Atlantic due to higher flux rates or higher mass transport.

5.4 Comparison to North Atlantic and Southern Ocean records

The benthic foraminifera $\delta^{13}\text{C}$ record from ODP-1085 may be compared to other high-resolution datasets covering the period 330–480 ka from the North and South Atlantic Ocean in order to identify basin-wide responses to deep-ocean circulation changes. To maximise the potential for examining sub-orbital variability, only datasets with a temporal resolution of ≤ 500 years have been used in our comparison. Details of these cores are shown in Table 2. Briefly, ODP-980 and ODP-1063 monitor changes in Upper and Lower NADW respectively (Oppo et al., 1998; McManus et al., 1999; Poli et al., 2000;

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Thunell et al., 2002), while ODP-1089 is located within LCDW in the southern Cape Basin, south of ODP-1085 (Hodell et al., 2001). Each record has been placed on a common age-scale by tying benthic $\delta^{18}\text{O}$ to the LR04 stack (Lisiecki and Raymo, 2005) (Fig. 4a and Table 1). This procedure allows an internal comparison to be made within the precision allowed by stratigraphic correlation (~ 2000 years). ODP-1085, ODP-980 and ODP-1089 have been interpolated at 500 year intervals to calculate inter-site gradients. The North Atlantic-South Atlantic gradient has been calculated as $\Delta(980-1085)$ (Fig. 4c), and the vertical Cape Basin gradient has been calculated as $\Delta(1085-1089)$ (Fig. 6). Our selection of records with a high temporal resolution means that changes in water mass end-member values may have affected inter-site the $\delta^{13}\text{C}$ gradients. However, these changes also provide information about the phasing of different modes of deepwater circulation.

5.4.1 $\Delta(980-1085)\delta^{13}\text{C}$ gradient

Assuming that the $\delta^{13}\text{C} \sum\text{CO}_2$ of CDW is primarily controlled by mixing with NADW (Charles et al., 1996; Ninnemann and Charles, 2002), the $\delta^{13}\text{C}$ gradient between NADW source regions and the South Atlantic/Southern Ocean should provide a measure of the southward flux of NADW and thus the relative strength of Northern Hemisphere deepwater production (Oppo et al., 1990; Raymo et al., 1990). From Fig. 4c, $\Delta(980-1085)$ values become lower on several occasions, suggesting an increase in the flux of NADW/GNAIW into the South Atlantic. A strong 41 000 periodicity (Fig. 5) is consistent with the modulation of intermediate-depth ventilation by changes in high-latitude sea-surface temperatures and sea-ice in response to obliquity (Ruddiman and McIntyre, 1984; Raymo et al., 1990).

Negative values of $\Delta 980-1085$ occur at 360 ka, 375 ka, 390 ka, 425 ka and 440 ka, which would suggest a reversal of the modern north-south Atlantic $\delta^{13}\text{C}$ gradient if end-member values remained constant. These reversals are partially due to increases in benthic $\delta^{13}\text{C}$ in ODP-1085 (Fig. 3b) and decreases in benthic $\delta^{13}\text{C}$ in ODP-980 (Fig. 4b), which was sensitive to shoaling of the GNAIW/Southern Component Water

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(SCW) boundary during the last glacial period (Oppo and Lehmann, 1993). Millennial-scale increases in the penetration of SCW into the North Atlantic at the expense of LNADW can also be found in benthic $\delta^{13}\text{C}$ isotope decreases in deep western Atlantic site ODP-1063 (Poli et al., 2000; Fig. 4b), and from increases in sortable silt grain size related to shoaling of the LNADW-derived Deep Western Boundary Current in ODP-1061 (Hall and Becker, 2007). These events correspond particularly well at 360 ka, 375 ka, 390 ka and 470 ka. Consequently, it may be surmised that the flux/mass of GNAIW to the South East Atlantic Ocean increased during periods when several sites suggest less LNADW production and/or more SCW production. This anti-phased relationship was also present during the most recent glacial termination (Marchitto et al., 1998). Since UNADW/GNAIW differs from LNADW by containing a component of Labrador Sea Water (LSW) in addition to the Greenland-Scotland Overflow Waters that are common to both (van Aken, 2000), the contrasting behaviour of these water masses through the MIS-12 to MIS-10 study period points towards a strong variability of deepwater production in the Nordic Seas over millennial timescales during MIS-10 and 12.

Several studies have suggested that MIS-11 was an extremely stable interglacial, with little variability in surface water mass temperature and salinity in the North Atlantic (e.g. Oppo et al., 1998; McManus et al., 2003). However, two decreases in the $\Delta(980\text{--}1085)$ gradient at 410 ka and 400 ka occur alongside increases in benthic $\delta^{13}\text{C}$ in ODP-1085 and show that the Southeast Atlantic NADW/UCDW boundary shoaled at these times. Similar benthic $\delta^{13}\text{C}$ values in ODP-1089 and ODP-1063 (Fig. 4b) suggest that the LCDW/NADW boundary also shoaled during these events, allowing southern-sourced deepwater to spread into the abyssal North Atlantic. There was little IRD deposition in the North Atlantic during 410–390 ka (Oppo et al., 1998; Helmke and Bauch, 2003), which would tend to argue against changes in NADW production. In contrast, there is some evidence of a regional cooling in the Southern Ocean at 410–415 ka (Becquey and Gersonde, 2002; Cortese et al., 2007), which occurs alongside a small (5–10 ppm) increase in atmospheric CO_2 (Siegenthaler et al., 2005). It is

therefore tempting to speculate that these interglacial changes in water mass structure were somehow related to the increased production of deepwaters around Antarctica, although more detailed information from the Southern Ocean would be needed to test this suggestion.

5 5.4.2 $\Delta 1085\text{--}1089 \delta^{13}\text{C}$ gradient

The concentration of atmospheric CO_2 during late Pleistocene glacial periods was ~ 80 ppm lower than during interglacials (e.g. Petit et al., 1999). A number of mechanisms probably combined to produce this change, involving physical changes in ocean temperature, salinity, circulation and mixing, changes in the export of organic carbon to the deep sea, and changes in deep-ocean alkalinity (e.g. Toggweiler, 1999; Stephens and Keeling, 2000; Sigman and Boyle, 2000; Marinov et al., 2005; Broecker, 2003; Sigman and Haug, 2003). To examine the relevance of deepwater ventilation changes on atmospheric CO_2 during MIS-12 to 10, a similar approach to Hodell et al. (2003a) is used, whereby the benthic $\delta^{13}\text{C}$ gradient between high-resolution intermediate water site ODP-1085 and high-resolution deepwater site ODP-1089 is calculated at 500 year intervals between ~ 450 ka and 340 ka. Despite geographical distance, both sites are located within the Cape Basin north of the Subtropical Front, and are characterised by $\sim 70\%$ CaCO_3 concentrations during glacials.

The vertical Cape Basin $\delta^{13}\text{C}$ gradient shown in Fig. 6 closely corresponds to the spliced EPICA Dome C/Vostok atmospheric CO_2 record (Petit et al., 1999; Siegenthaler et al., 2005), in agreement with suggestions that the glacial chemocline that formed at ~ 2 km in the Southern Ocean represents a shift in oceanographic conditions that impacted strongly on atmospheric CO_2 concentrations (Ninnemann and Charles, 2002; Hodell et al., 2003a; Mortyn et al., 2003). From Fig. 6, the first $\sim 0.5\text{‰}$ increase in $\Delta\delta^{13}\text{C}$ took place at 397 ka, accompanying a 30 ppm decrease in CO_2 to fairly stable intermediate levels of ~ 250 ppm. The chemical divide then reached its maximum at 377 ka following a second abrupt rise in $\Delta\delta^{13}\text{C}$, thus leaving other mechanisms to

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explain the remaining 45‰ CO₂ drop. Carbonate deposition continues to increase alongside an increase in carbonate preservation after 375 ka in ODP-1089 (Fig. 6) (Hodell et al., 2001; 2003b). Consequently, the effects of deep-ocean alkalinity change may have become more important than deep-ocean ventilation in forcing CO₂ change later during the transition into MIS-10.

Toggweiler (1999) suggested that an interglacial-glacial shift of –80 ppm in atmospheric CO₂ could be forced by the reduced ventilation of the deep ocean (–21 ppm), along with a decrease in SST and an increase in deep-ocean alkalinity (–59 ppm). The sequence of events suggested by Toggweiler (1999) was that the change in deep-ocean ventilation would impact on CO₂ first, followed by SST and carbonate compensation. A similar sequence of events was proposed by Peacock et al. (2006), who used a box model to suggest that in order to avoid the timing constraints imposed by sea-level change, reduced glacial sea-surface temperatures and reduced high-latitude vertical mixing could explain up to 50 ppm of the initial CO₂ drop leading into MIS-5a to 5d. Alkalinity and nutrient changes could then explain the second part of the CO₂ decline leading into MIS-4. The range of CO₂ found to accompany the initial change in Δ(1085–1089) (~30 ppm) is similar to the 21 ppm modelled by Toggweiler (1999), and therefore supports the role of deep-ocean ventilation as the initial driver of CO₂ decline following the MIS-11 climate optimum.

McManus et al. (1999) suggested that millennial-scale climate variability increases when benthic δ¹⁸O reaches a value of +3.5‰ (or +4.14‰ when corrected for equilibrium effects). The period of “intermediate” δ¹³C stratification in the Cape Basin between 392–378 ka occurs when benthic foraminifera δ¹⁸O in ODP-1085 reaches this threshold, thus suggesting that periods of intermediate ice-volume were also characterised by a unique configuration of water masses in the South Atlantic/Southern Ocean, and a correspondingly unique mode of ocean circulation.

Recent ice-core data has revealed that despite a large amount of deep-ocean carbonate dissolution during MIS-11 (e.g. Ziegler et al., 2003), atmospheric CO₂ concentrations were broadly similar to the Holocene (Siegenthaler et al., 2005). In agree-

ment with this, the vertical $\delta^{13}\text{C}$ gradient between GeoB-1720-2 (near to ODP-1085 at 1995 m depth) and ODP-1089 has an almost identical magnitude of change over termination 1 as during termination 5, and similar interglacial values (Fig. 4d, blue circles). However, the $\delta^{13}\text{C}$ gradient was $\sim 1\text{‰}$ higher during MIS-12 than during MIS-2, yet CO_2 concentrations were, if anything, 5–10 ppm higher during the former glacial period (Siegenthaler et al., 2005). This discrepancy may be due to the slightly deeper depth of GeoB-1720-2 that makes it more sensitive to mixing with CDW during glacials, as seen for ODP-1088 (Fig. 3b). These observations reinforce the proposed role of Southern Ocean stratification in contributing to changes in atmospheric CO_2 (Toggweiler, 1999; Hodell et al., 2003a), and also show that the position of the South Atlantic/Southern Ocean chemocline was located slightly shallower than 2 km during full glacial stages MIS-12, MIS-10 and MIS-2.

6 Conclusions

Intermediate water $\delta^{13}\text{C}$ variability at ODP-1085 was extremely muted between $\sim 480\text{--}330$ ka and can be explained by the continuous influence of northern sourced deepwaters during glacials MIS-10 and MIS-12 (GNAIW) and interglacial MIS-11 (NADW). During glacials, millennial-scale increases in benthic $\delta^{13}\text{C}$ match small decreases in foraminifera fragmentation and imply either an increased flux of GNAIW to the South East Atlantic, or a decrease in the amount of mixing with adjacent CDW due to a temporary deepening of the South Atlantic glacial chemocline. These events correspond to shoaling of the GNAIW/SCW boundary in the north Atlantic, and imply an anti-phased relationship at millennial timescales between the production North Atlantic deepwaters in the Greenland and Labrador Seas respectively. During MIS-11, millennial-scale increases in benthic $\delta^{13}\text{C}$ indicate shoaling of the NADW/UCDW boundary. From comparison to other published core sites, this may reflect the increased penetration of southern-sourced deepwaters into the abyssal North Atlantic Ocean, although the cause of these events remains uncertain.

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Our data also reveals that the detailed vertical Cape Basin $\Delta\delta^{13}\text{C}$ gradient parallels atmospheric CO_2 concentrations derived from the EPICA Dome C and Vostok ice cores. This supports previous suggestions that a strong chemical divide in the glacial Southern Ocean was able to isolate nutrient and CO_2 -rich deepwaters and thus contribute to glacial CO_2 drawdown (Toggweiler, 1999; Hodell et al., 2003a), although this mechanism may have been most important during the initial phases of CO_2 decline following the warmest part of MIS-11. The similarity in the magnitude of the $\delta^{13}\text{C}$ gradient shift over terminations 1 and 5 matches the similar magnitude of CO_2 change observed over each transition (Siegenthaler et al., 2005) and strongly implicates the Southern Ocean as an important store of CO_2 during Middle-Pleistocene glacial periods. Its potential importance for sub-orbital CO_2 changes awaits more detailed gas measurements from the Antarctic ice-core records.

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Table 1. Core sites with benthic $\delta^{13}\text{C}$ data resolution ≤ 500 years used in this study.

Core	Location	Depth	Average $\delta^{13}\text{C}$ data resolution	Reference
ODP-1085	29.2° S, 13.6° E	1713 m	450 years	This study
ODP-980	55.3° N, 14.4° W	2170 m	380 years	Oppo et al. (1998), McManus et al. (1999)
ODP-1089	47.6° S, 9.5° E	4621 m	380 years	Hodell et al. (2003a, 2003b)
ODP-1063	33.4° N, 57.4° W	4583 m	520 years	Poli et al. (2000)

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Table 2. Age control points for each core.

LR04 age/ka	ODP-1085 depth/mbsf	ODP-1089 depth/mcd	ODP-980 depth/mcd	ODP-1063 depth/mcd
341	11.41	—	—	—
344	—	—	—	77.98
345	—	51.8	—	—
347	—	—	45.44	—
348	11.94	—	—	—
354	12.36	53.6	46.74	80.04
363	—	—	47.27	81.73
364	12.84	—	—	—
372	—	—	48.27	—
382	—	58.57	—	—
385	13.71	—	49.94	—
391	—	—	50.84	—
394	—	60.92	—	88.6
397	14.24	61.67	52.16	89.09
423	—	—	56.06	—
424	15.76	64.27	—	—
427	—	64.92	57.48	—
430	15.98	—	—	—
431	—	65.52	—	91.38
438	—	—	58.84	93.13
441	—	66.72	—	—
447	—	—	60.22	—
455	16.61	—	61.07	—
471	17.30	—	62.67	100.75
491	—	—	64.31	107.81

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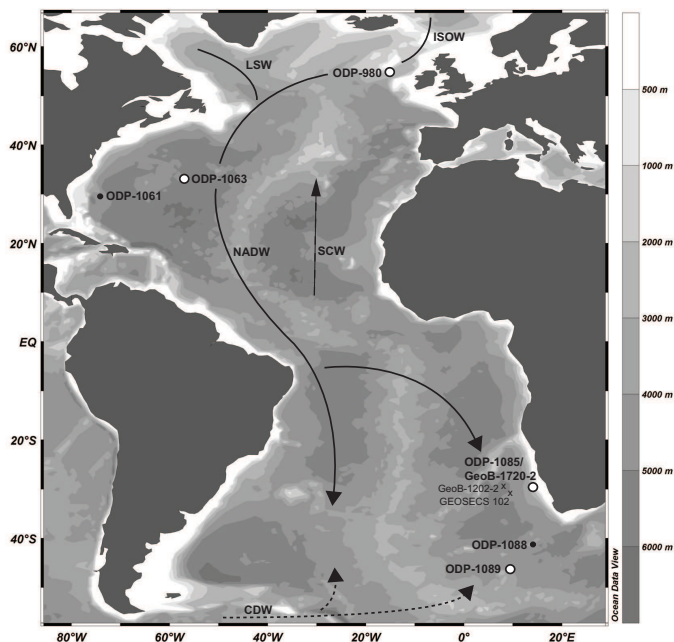


Fig. 1. Locations of tuned benthic $\delta^{13}\text{C}$ records (open circles) and other core sites mentioned in the text (filled circles), created using Ocean Data View (Schlitzer, 2006). The locations of geochemical profiles shown in Fig. 2 are plotted as crosses. Arrows schematically indicate synoptic deep-water flow paths of North Atlantic Deep Water (NADW), Circumpolar Deep Water (CDW, dashed line) and Southern Component Water (SCW, dashed line, comprising CDW and Antarctic Bottom Water) through the North and South Atlantic basins.

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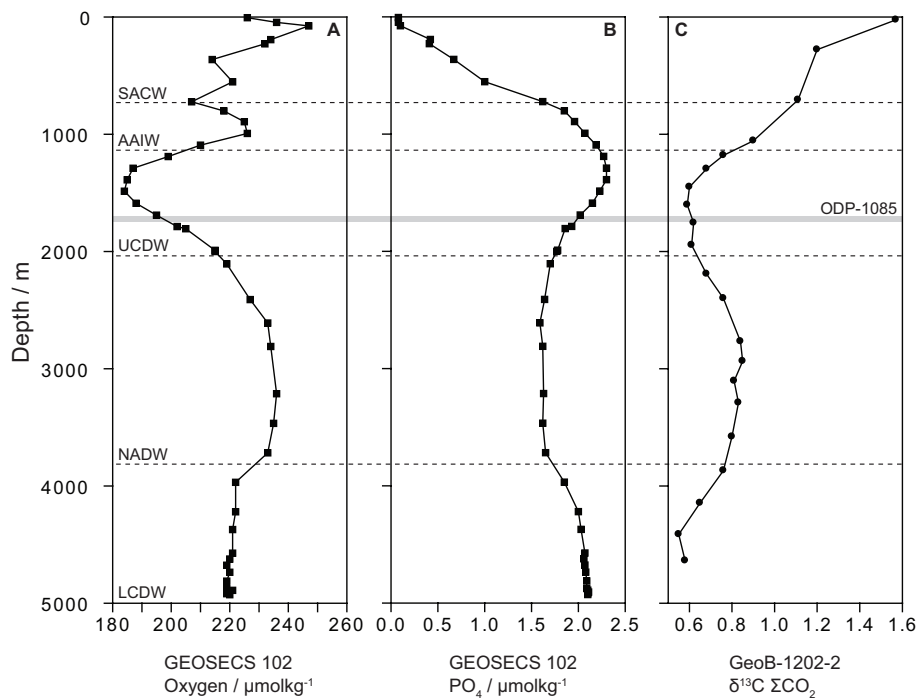


Fig. 2. Dissolved oxygen, phosphate, and $\delta^{13}\text{C} \Sigma\text{CO}_2$ profiles from GEOSECS 102 and GeoB-1202 (Bickert and Wefer, 1999), with delineations of the main deep water masses in the Cape Basin. The depth of studied core ODP-1085 is marked with a shaded horizontal band.

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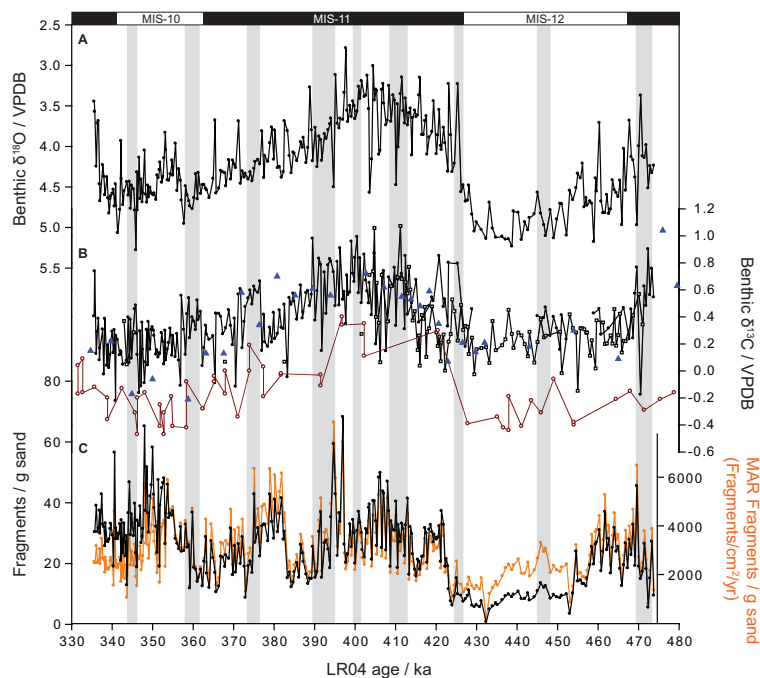


Fig. 3. Benthic isotope and foraminifera fragment data from ODP-1085. **(A)** Benthic $\delta^{18}\text{O}$ data composed of *C. wuellerstorfi* and *Uvigerina* spp. data, the former corrected by +0.64‰. **(B)** $\delta^{13}\text{C}$ data composed of *C. wuellerstorfi* (circles) and *Uvigerina* spp. corrected by +0.9‰ (open squares). Benthic $\delta^{13}\text{C}$ data from ODP-849 and ODP-1088 are plotted on their original timescales and are shown as a thin brown line and blue triangles respectively. **(C)** Abundance (black) and mass accumulation rate (orange) of foraminifera fragments per gram sand >150 μm . Shaded vertical bands represent millennial-scale increases in ODP-1085 benthic $\delta^{13}\text{C}$.

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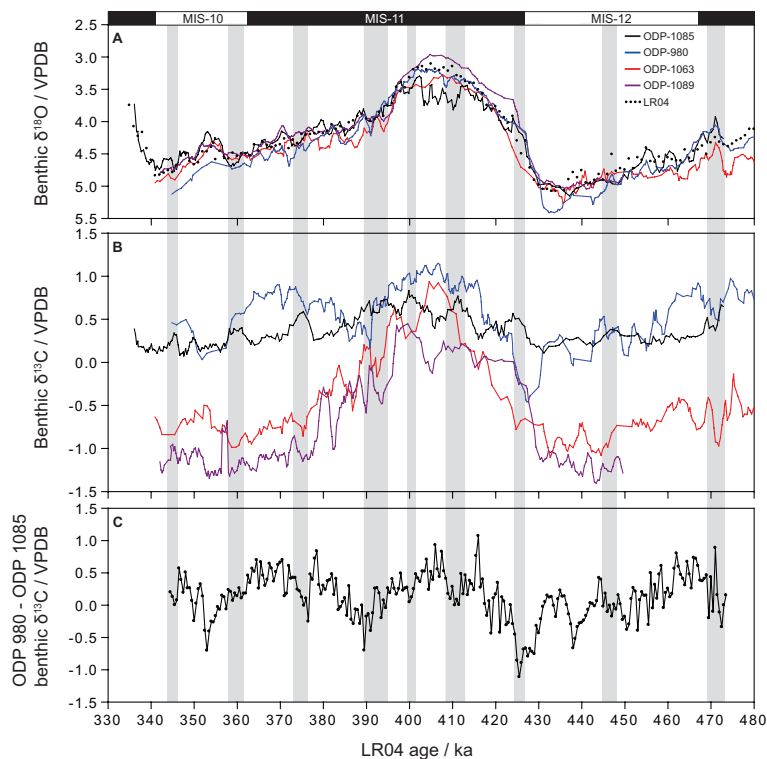


Fig. 4. Sub-millennial resolution benthic carbon isotope data for Atlantic Ocean sites aligned on the LR04 timescale. **(A)** Benthic $\delta^{18}\text{O}$ (5-point running averages). **(B)** Benthic $\delta^{13}\text{C}$ (5-point running averages). **(C)** North-South Atlantic $\delta^{13}\text{C}$ gradient calculated from ODP-980–ODP-1085. Shaded vertical bands as in Fig. 3.

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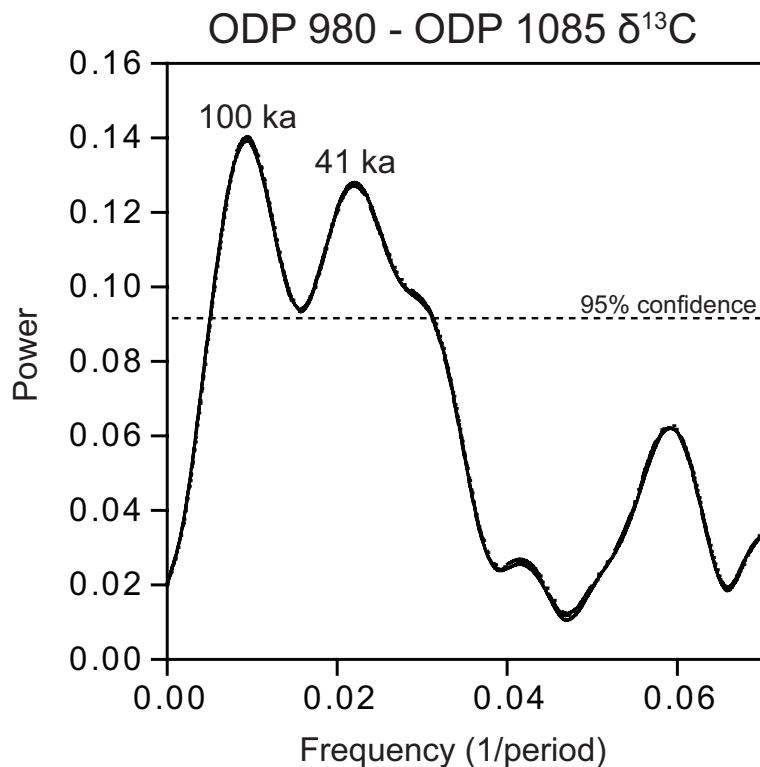


Fig. 5. Spectral response of the $\Delta(980\text{--}1085)\delta^{13}\text{C}$ gradient, calculated using the MC-Clean 2.0 MATLAB algorithm of Heslop and Dekkers (2002). The horizontal line indicates the 95% confidence level across all frequencies estimated from a series of spectra generated from white noise applied to the input time series.

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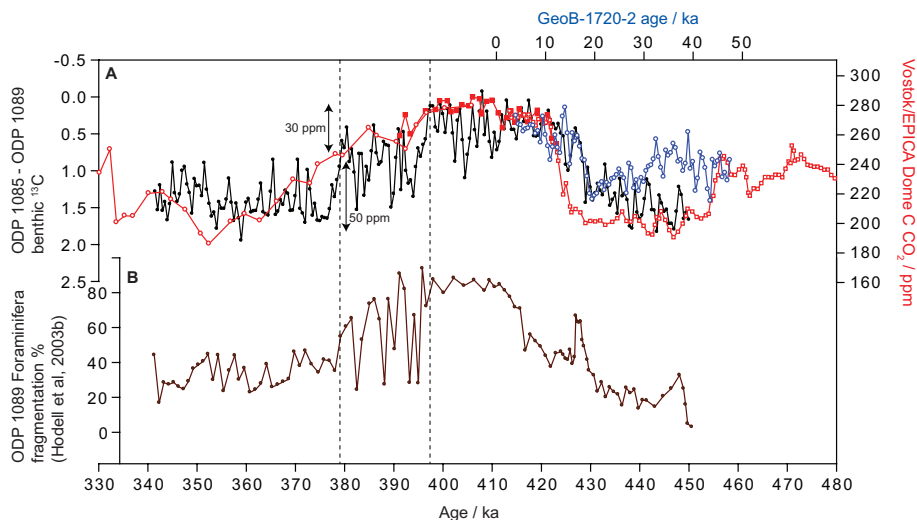


Fig. 6. Cape Basin benthic $\delta^{13}\text{C}$ gradients and atmospheric CO_2 . **(A)** Intermediate-deep Cape Basin $\delta^{13}\text{C}$ gradient calculated from ODP-1085–ODP-1089 (black), plotted alongside the spliced Vostok (open red circles)/EDC (open and closed red squares) CO_2 record on the EDC2 gas age timescale (Petit et al., 1999; Siegenthaler et al., 2005). The intermediate-deep $\delta^{13}\text{C}$ gradient calculated for the last 50,000 years from GeoB-1720-2–ODP-1089 is shown for comparison (open blue circles) on its own ^{14}C age-scale (Dickson et al., in prep., inset horizontal axis). The latter record has been positioned by aligning the steep deglacial decreases in $\delta^{13}\text{C}$, rather than orbital parameters (e.g. Ruddiman, 2005) as the objective is to compare the magnitude of change over the two terminations rather than the timing. **(B)** Foraminifera fragmentation record from ODP-1089 (Hodell et al., 2003b).

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