Millennial changes in North Atlantic oxygen concentrations

B.A.A. Hoogakker[1*], D.J.R. Thornalley[2], S. Barker[3]

[1]Department of Earth Sciences, University of Oxford, Oxford, OX1 3AN, United Kingom (*correspondence: babetteh@earth.ox.ac.uk)
[2]Department of Geography, University College London, London, WC1E 6BT, United Kingdom (d.thornalley@ucl.ac.uk)
[3]School of Earth and Ocean Sciences, Cardiff University, Cardiff, CF10 3AT, United Kingdom (BarkerS3@cf.ac.uk)

Abstract

Glacial-interglacial changes in bottom water oxygen concentrations [O_2] in the deep northeast Atlantic have been linked to decreased ventilation relating to changes in ocean circulation and the biological pump (Hoogakker et al., 2015). In this paper we discuss seawater [O_2] changes in relation to millennial climate oscillations in the North Atlantic ocean over the last glacial cycle, using bottom water [O_2] reconstructions from 2 cores: 1) MD95-2042 from the deep northeast Atlantic (Hoogakker et al., 2015), and 2) ODP Site 1055 from the intermediate northwest Atlantic. Deep northeast Atlantic core MD95-2042 shows decreased bottom water [O_2] during millennial scale cool events, with lowest bottom water [O_2] of 170, 144, and 166 ±17 µmol/kg during Heinrich ice rafting events H6, H4 and H1. Importantly, at intermediate depth core ODP Site 1055, bottom water [O_2] was lower during parts of Marine Isotope Stage 4 and millennial cool events, with lowest values of 179 and 194 µmol/kg recorded during millennial cool event C21 and a cool event following Dansgaard-Oeschger event 19. Our reconstructions agree with previous model simulations suggesting that glacial cold events may be associated with lower seawater [O_2] across the North Atlantic below ~1 km (Schmittner et al., 2007), although in our reconstructions the changes are less dramatic. The decreases in bottom water [O_2] during North Atlantic Heinrich events and earlier cold events at the two sites can be linked to water mass changes in relation to ocean circulation changes, and possibly productivity changes. At the intermediate depth site a possible strong North Atlantic Intermediate Water cell would preclude water mass changes as a cause for decreased bottom water [O_2]. Instead we propose that the lower bottom [O_2] there can be linked to productivity changes through increased export of organic material from the surface ocean and its subsequent remineralisation in the water column and the sediment.

1. Introduction

Oxygen is vital to all aerobic life. Oxygen solubility in seawater is highly temperature dependent, with salinity playing a secondary role. The [O_2] of a (deep or intermediate) water mass at a particular location is determined by its initial concentration at the region of sinking, the amount of respiration it has undergone, and mixing with other water masses. Both oxygen supply and consumption are ultimately driven by ocean circulation and biology (Schmittner et al., 2007). Climate models predict that oxygen concentrations in the ocean will decrease substantially in response to anthropogenic climate change. Recent expansion of tropical subsurface oxygen miminum zones have been attributed to this effect (Stramma et al., 2010). The warming effect on [O_2] loss is twofold: 1- less oxygen can be dissolved at higher sea water temperatures; 2- warmer surface waters may increase upper ocean stratification, and it is thought that the resulting decreased ventilation effect exceeds that associated with reduced oxygen utilization (Sarmiento et al. 1998; Matear et al. 2000; Plattner et al. 2001; Bopp et al. 2002; Keeling & Garcia 2002; Keeling et al., 2010). A global ocean decline in [O_2] between 1 to 7% has been predicted over the next century (Keeling et al., 2010); over longer timescales (e.g. 100 to 1000's of years) a slowdown in ocean overturning has been predicted to potentially cause an overall decrease in [O_2] of 30%, with declines in the deep ocean projected between 20% to 40% by the year 2800 (Matear and Hirst, 2003; Schmittner et al., 2008; Shaffer et al., 2009). However, there are large uncertainties associated with coarse-resolution ocean models in simulating today's and also future [O_2] distributions (e.g. Jin and Gruber, 2003).

The future reduction in ocean overturning is mainly attributed to changes in surface heat flux and to a lesser extent to surface freshening (Gregory et al., 2005). Beyond the last couple of decades there are no direct observations of deep water [O_2]. However, paleoceanographic proxies of overturning circulation and ocean ventilation as well as redox proxies provide constraints of changes in deep water [O_2] in relation to specific climatic events.

The effects of large-scale changes in Atlantic circulation on deep water [O_2] are probably best studied during the last glacial period, which was punctuated by a series of millennial-scale cold events associated with the advance of large scale iceberg armadas (Bond and Lotti, 1995) and thought to involve systematic changes in the northward heat transport associated with the Atlantic Meridional Ocean Circulation (AMOC) (Stocker and Johnson, 2003; Barker et al., 2011). Nutrient proxies (benthic foraminiferal carbon isotopes ($\delta^{13}C$) & Cd/Ca) and ocean circulation proxies (Pa/Th, ^{14}C ventilation times)(McManus et al., 2004; Hoogakker et al., 2007; Skinner et al., 2010), provide evidence for increased deep water nutrients and reduced ventilation and overturning circulation in the North Atlantic ocean during cold stadial events (Schmittner and Lund, 2015), and point to decreased deep water [O_2]. Redox sensitive proxies are particularly useful to assess qualitative changes in bottom water [O_2] (Nameroff et al., 2002; Pailler et al., 2002; Jaccard et al., 2009). Recently, Hoogakker et al. (2015) refined a novel proxy originally proposed by McCorkle and Emerson (1988), where bottom water [O_2] can be reconstructed from the carbon isotope gradient between bottom water and pore water at the anoxic boundary. Hoogakker et al. (2015) suggest that bottom-water [O_2] in the deep Northeast Atlantic (3.1 km) were 45 and 65 μmol/kg lower during the last and penultimate glacials relative to today. Their reconstructions also showed significantly reduced bottom water [O_2] during extreme cold events associated with large-scale ice rafting and the deposition of ice rafted debris in the North Atlantic (Hoogakker et al., 2015). Here we discuss the underlying causes for millennial scale reductions in bottom water [O_2] in the deep (3.1 km) North Atlantic Ocean. In addition we present new, millennial scale resolved, bottom water [O_2] reconstructions in the North Atlantic from an intermediate depth (1.8 km) core ODP Site 1055, located on the Carolina Slope off North America.

2. Locations

Core MD95-2042 was taken during the 1995 IMAGES cruise from the Iberian Margin (37°48’N, 10°10’W, 3146 m water depth, Figure 1) off southern Portugal in the northeast Atlantic (Bassinot et al., 1996). ODP Site 1055 (32°47 N, 76°17 W, 1798 m water depth, Figure 1) is located in the subtropical northwest Atlantic, slightly upslope of the Blake Outer Ridge on the lower Carolina Slope. Core MD95-2042 is currently bathed in well ventilated ([O_2] of ~245 μmol/kg northward re-circulating Northeast Atlantic Deep Water (NADW), whereas during glacial times bottom waters with a Southern Ocean origin (Southern Source Deep Water, SSDW) became more important (Shackleton et al., 2000; Skinner and Shackleton , 2004). ODP Site 1055 is currently sat within the core of well-oxygenated Labrador Sea Water, with the main flow axis of lower North Atlantic Deep Water being found at greater depths, ~2500-4000m (Stahr and Stanford, 1999). Bottom waters near ODP Site 1055 have slightly higher [O_2] compared with MD95-2042, with values between 250 and 254 μmol/kg (Figure 1). During glacial times and cold stadial periods ODP Site 1055 was largely influenced by Glacial North Atlantic Intermediate Water (GNAIW) (e.g. Evans and Hall, 2008; Thornalley et al 2013).

3. Methods

3.1 Age models

The age models of both cores were constructed by correlating planktonic (surface dwelling) foraminiferal oxygen isotopes ($\delta^{18}O_p$) records with North Greenland Ice Core Project (NGRIP) $\delta^{18}O_{ice}$ (NGRIP Members, 2004). Both marine and ice core records show a series of oscillating cycles of rapid warmings followed by gradual cooling (e.g. Dansgaard-Oeschger cycles), culminating in extreme cold events that are associated with the deposition of massive layers of ice rafted debris (IRD) in the North Atlantic (e.g. Heinrich events) (Heinrich, 1988; Johnsen et al., 1992; NGRIP project Members, 2004; Shackleton et al., 2000; 2004). Typically six Heinrich layers, H1 to H6, have been described for Marine Isotope Stage (MIS) 3 (29 to 60 ka BP), and a further five, H7 to H11, over MIS 4 and 5 (between 60 and 130 ka BP). However outside the Labrador Sea such IRD layers contain conspicuously less detrital carbonate (a defining criterion for a Heinrich layers) and are labelled C19 to C25 (Chapman and Shackleton, 2002). For the interval 0-60 ka the GICC05 age model was applied, whose ages are very similar to that of SFCF 2004 age model as was used previously in Hoogakker et al. (2015). Thornalley et al. (2013) apply a revised chronology prior to 60 ka, based on the speleothem-tuned age model of Barker et al. (2011), and to aid comparison between the two sites the same chronology was applied to MD95-2042 between 60 and 123 ka. Based on these age models, results of core MD95-2042 cover the last 150 kyrs, whilst those of core ODP Site 1055 cover the interval 85 to 59 ka BP (Figure 2).

3.2 Sea-water [O_2]

The biogeochemical cycles of oxygen and carbon are stoichiometrically linked through photosynthesis and respiration. Photosynthesis uses carbon dioxide (CO_2), water, sunlight and nutrients to make organic material and oxygen. The breakdown of organic material, in well oxygenated environments, uses oxygen and produces CO_2. During photosynthesis, organisms preferentially take up light ^{12}C compared with ^{13}C, causing an overall enrichment of the carbon isotopic composition ($\delta^{13}C$) of DIC in surface waters (Kroopnick, 1985, Gruber et al., 1999). When organic material is broken down, the release of light ^{12}C causes a depletion in seawater $\delta^{13}C$-DIC. Globally there is a strong linear relationship between deep water [O_2] and $\delta^{13}C$, where a 50 µmol/kg decrease in [O_2] corresponds to a 0.34‰ decrease in seawater $\delta^{13}C$-DIC (Figure 3), with R^2 between 0.78 and 0.85. However, within the North & South Atlantic and Southern Ocean the data are distributed within a cloud, displaying a much weaker relationship. Some of the increased variability in [O_2] in the Atlantic basins and Southern Ocean is probably related to seawater temperature differences; colder seawater can contain more dissolved oxygen, but also mixing of water masses. Furthermore, $\delta^{13}C$-DIC distributions in the oceans are also affected by temperature dependent fractionation during air-sea gas exchange (Lynch-Stieglitz et al., 1995) and degree of surface water equilibration with the atmosphere (Schmittner et al., 2013) at source waters, biology and also mixing with other water masses (Gruber et al., 1999). During glacial times bottom water $\delta^{13}C$ estimates derived from benthic foraminiferal calcite $\delta^{13}C$ in the deep (> ~2.5 km) Atlantic became more depleted (Curry and Oppo, 2005; Oliver et al., 2010), but uncertainties related to preformed $\delta^{13}C$, air-sea fractionation, terrestrial biomass contributions to deep water $\delta^{13}C$-DIC precludes the use of bottom water $\delta^{13}C$-DIC inferred from benthic foraminifera in the past as a reliable bottom water [O_2] proxy.

Here we apply the refined bottom-water to pore-water (at the anoxic boundary) $\delta^{13}C$ gradient as a quantitative bottom water [O_2] proxy (Hoogakker et al. 2015). This proxy was originally proposed by McCorkle and Emerson (1988) who observed that the carbon isotope gradient between bottom water and pore water at the anoxic boundary ([O_2]=0) in sediments decreases with decreasing bottom-water [O_2]. These changes are attributed to changes in the amount of organic material that can be remineralized; e.g. more organic material can be remineralized under higher bottom water [O_2], releasing more ^{12}C into the pore waters, increasing the bottom water to anoxic pore-water $\delta^{13}C$ gradient ($\Delta\delta^{13}C_{bw\text{-}ab\_pw}$), as supported by pore-water $\delta^{13}C$ and [O_2] models (McCorkle and Emerson, 1988; Gehlen et al., 1999). Hoogakker et al. (2015) furthermore show that additional observations of $\Delta\delta^{13}C_{bw\text{-}ab\_pw}$, inferred from the difference in $\delta^{13}C$ between bottom water and foraminifera living at the anoxic boundary (*Globobulimina* spp.) as well as between bottom water suspension feeding foraminifera (*Cibicioides wuellerstorfi*) and anoxic boundary dwelling foraminifera (*Globobulimina* spp.) all fit the original observations exceptionally well at [O_2] between 55 and 235 μmol/kg. At higher (>235 μmol/kg) [O_2] additional light carbon is added to the pore-water from other remineralization reactions. These observations confirm that $\delta^{13}C_{bw\text{-}ab\_pw}$ can be approximated by the $\delta^{13}C$ difference between test carbonate $\delta^{13}C$ of benthic foraminiferal species that live in bottom water (e.g. *C. wuellerstorfi*) and in the sediment at the dysoxic/anoxic boundary (e.g. *Globobulimina* spp.) at bottom water [O_2] values of 55-235 μmol/kg, where a 0.39‰ increase in $\Delta\delta^{13}C_{bw}$ represents a 50 μmol/kg increase in bottom water [O_2] (Hoogakker et al., 2015). Below we refer to this carbon isotope gradient simply as $\Delta\delta^{13}C$.

4. Results

Both records show relatively well oxygenated water masses for the periods covered, with $\Delta\delta^{13}C$ values of 1.45‰ and higher (Figure 4), amounting to bottom water [O_2] of 144 μmol/kg and higher (Figure 5). Typically seawater is considered hypoxic when [O_2] values of 60 μmol/kg or less are recorded, although median lethal [O_2] varies between different organisms; temperature and CO_2 also influence this threshold (Keeling et al., 2010). At MD95-2042, the LGM, MIS 6, and extreme cold events, are associated with lower [O_2] (Hoogakker et al., 2015), with Heinrich event 4 showing the lowest $\Delta\delta^{13}C$ and thus bottom water [O_2] (Figure 4). At the shallower northwest Atlantic ODP Site 1055, MIS 4 and cold events C19, C20, C21 are associated with a lower $\Delta\delta^{13}C$ and bottom water [O_2]. From ~62 ka BP there is gradual increase in $\Delta\delta^{13}C$, including the latter parts of Heinrich event 6 at ODP Site 1055 (Figure 4), although $\Delta\delta^{13}C$ was lower compared with warm interstadials (Figure 5).

Hoogakker et al. (2015) calculate that the total error associated with bottom-water [O_2] reconstructions using this method at mid- to low latitudes is 17 μmol/kg. This error includes uncertainties associated with variations in the $\delta^{13}C$ of organic carbon of ±1‰ (see Hoogakker et al., 2015 supplementary information for details), which seems a reasonable assumption for the low to mid latitude ocean (Goericke and Fry, 1994). Because of decreased [$CO_{2(aq)}$] during full glacial conditions, $\delta^{13}C_{org}$ was however enriched by 2‰ (Rau et al., 1991) causing an initial overestimation of glacial bottom-water [O_2] and correction of 10 μmol/kg (Hoogakker et al., 2015). The paper of Rau et al. (1991) is of too low resolution to decipher any possible millennial scale oscillations in $\delta^{13}C_{org}$, but generally $\delta^{13}C_{org}$ appears lighter prior to the LGM. It is also important to note that within the North Atlantic Heinrich belt, organic carbon $\delta^{13}C$ values are depleted during glacial times compared to the Holocene, with lightest values (up to -28‰) during Heinrich 4, 2 and 1 (Huon et al., 2002; Schouten et al., 2007). Both Huon et al. (2002) and Schouten et al. (2007) attribute these depletions in organic $\delta^{13}C$ to increased input of terrestrial organic material from either ice rafted debris or wind-blown sources. It is therefore possible that estimates of [O_2] during Heinrich events and cold events C20 and C21 are underestimated. However, as terrestrial plant remains are generally much older in age (Schouten et al., 2007), it is possible that they are largely refractory (insoluble and non-hydrolyzable) and may not have degraded substantially. Because of this unknown we consider estimates of bottom water [O_2] during these Heinrich events and cold events C20 and C21 as *maximum* estimates (Figure 5).

5. Discussion

Millennial scale climate oscillations are a common feature of the last glacial as well as the transition from the previous interglacial (Eemian) to glacial in the North Atlantic (Figure 2). Within the north Atlantic IRD belt, ice-rafting becomes a common feature during millennial scale cooling events when sea-level falls below -45 m (Chapman and Shackleton, 2002). Decreased benthic foraminiferal $\delta^{13}C$ from deep (below 2.5 km) sites in the North Atlantic Ocean provide evidence for widespread changes in bottom water carbonate chemistry during these events (Shackleton et al., 2000; Sarnthein et al., 2001; Chapman and Shackleton, 2002; Thornalley et al., 2013). Reconstruction of $[CO_3^{2-}]$ support the inferred changes in deep bottom water carbonate chemistry (Yu et al., 2008). High resolution intermediate depth North Atlantic records from the northeast Atlantic also generally show lower benthic $\delta^{13}C$ during Heinrich events (Sarnthein et al., 2000; Chapman and Shackleton, 2002; Rasmussen et al., 2003; Peck et al., 2006; Dickson et al., 2008; Thornalley et al., 2010) whereas ODP Site 1055 from the northwest Atlantic, featured here, shows hardly any change (Evans and Hall, 2008; Thornalley et al., 2013). During glacial times reconstructed $[CO_3^{2-}]$ at North Atlantic sites above 2.8 km all show increased concentrations (Yu et al., 2008); to date no inferences have been made with regards to millennial scale climate oscillations.

During most of Marine Isotope Stage 5 (MIS 5), including the transition to glacial conditions, the deep northeast Atlantic was well oxygenated (Figure 5). Between 126 and 109 ka BP *G. affinis* was absent, probably because a reduced organic carbon flux and deep or weakly developed anoxic boundary meant its microhabitat conditions were not met, similar to Holocene conditions (Hoogakker et al., 2015). Following this period $\Delta\delta^{13}C$ is >2.25‰, indicating well oxygenated (>235 µmol/kg) waters. It isn't until after ~ 76 ka BP, coincident with Atlantic cold event C20 that $\Delta\delta^{13}C$ of < 2.25‰ are measured (Figure 4). Applying the $\Delta\delta^{13}C:[O_2]$ calibration equation of Hoogakker et al. (2015), we calculate that during Atlantic cold event C20 bottom water $[O_2]$ at the Iberian Margin was 230±17 µmol/kg (Figure 5, Table 1). Note that if we had used the present-day $\delta^{13}C:[O_2]$ relationship as defined in Figure 3, bottom water $[O_2]$ would be drastically underestimated, with bottom water $[O_2]$ of ~120 µmol/kg during event C20. At the Blake Ridge location (ODP Site 1055), $\Delta\delta^{13}C$ fell below 2.25‰ during North Atlantic cold events C21, and C20, giving bottom water $[O_2]$ of 179 and 230±17 µmol/kg respectively (Table 1). Interestingly, during North Atlantic cold event C20 both the deep northeast Atlantic record and intermediate northwest Atlantic record show the same bottom water $[O_2]$ (Figure 5).

Between 76 and 64 ka BP, roughly coincident with MIS 4, the record of MD95-2042 does not resolve millennial scale oscillations, mainly because *C. wuellerstorfi* was not abundant during this time. In the few instances it did occur $\Delta\delta^{13}C$ was >2.25‰ suggestive of well oxygenated conditions. At the intermediate depth ODP Site 1055 $\Delta\delta^{13}C$ follows *G. ruber* $\delta^{18}O$, where lighter $\delta^{18}O$ values are associated with $\Delta\delta^{13}C$ >2.25‰, and heavier $\delta^{18}O$ values, corresponding to millennial scale cool events, with $\Delta\delta^{13}C$ <2.25‰. During North Atlantic cold event C19 reconstructed bottom water [O_2] at ODP Site 1055 was 213±17 µmol/kg, and the cold period that follows is characterized by bottom water [O_2] of 194±17 µmol/kg (Figure 5, Table 1).

During the later part of MIS 4 and MIS 3, the deep record of MD95-2042 is characterized by bottom water [O_2] variations that follow Greenland climate trends, with high $\Delta\delta^{13}C$ (>2.25‰) values during interstadials, whereas low bottom water [O_2] characterise Heinrich events, with H6, H4 and H1 showing lowest bottom water [O_2] of 170, 144, and 166±17 µmol/kg respectively (Figure 5). Obviously these values still mean well oxygenated bottom water masses, but they are lower compared with warm interstadial intervals (>235 µmol/kg) as well as the LGM (200±17 µmol/kg). At intermediate location ODP Site 1055, early H6 shows slightly lower bottom water [O_2] of 224±17 µmol/kg followed by an increase to >235 µmol/kg (Figure 5, Table 1).

5.1 Causes for millennial scale bottom water [O_2] changes

The glacial decreased bottom water [O_2] values at the Iberian Margin to 200 ±17 µmol/kg (LGM) and 180±17 µmol/kg (MIS 6) (compared with 245 µmol/kg today) have been largely attributed to ocean circulation changes, with a shift in bottom water mass from NADW to SSDW (Hoogakker et al., 2015).

Over the transition from MIS 5 to early MIS 4 a mode change has been suggested in the Atlantic Meridional Overturning Circulation (AMOC) (Bereiter et al., 2012; Thornalley et al., 2013; Barker and Diz, 2014, Böhm et al., 2015). During MIS 5 Bereiter et al. (2012) suggest that AMOC was strong, characterized by southward flow of NADW to the deep South Atlantic. This would imply that NADW and NAIW would have influenced bottom waters at the deep and intermediate site respectively. Several studies have shown that most cold events within MIS 5 are associated with decreased benthic foraminifera $\delta^{13}C$ (Shackleton et al., 2000; Oppo et al., 2001; Evans and Hall, 2008; Hodell et al., 2009), that have often been interpreted to reflect AMOC changes. Guihou et al. (2010), using the kinematic overturning circulation proxy $^{231}Pa/^{230}Th$, show that AMOC export from the North

Atlantic was reduced during the cold events of MIS 5. However Guihou et al. (2011) further show that cold events within MIS 5 and MIS 4 could be associated with stronger AMOC export at shallow depths, which agrees with grain size results of Thornalley et al. (2013) suggesting more vigorous near-bottom flow speeds during millennial cold events at intermediate ODP Site 1055. These results confirm inferences of possible strengthened open ocean convection south of the Greenland-Scotland Ridge driving a strong intermediate depth Atlantic Overturning Circulation cell (Thornalley et al., 2013). It would then be somewhat surprising to find lower bottom water [O_2] during these events as more vigorous North Atlantic Intermediate Water flow is generally associated with better ventilation, although changes in the mode of water mass formation can alter the extent to which newly formed intermediate/deep waters have equilibrated with the atmosphere.

During the glacial, AMOC was considerably different. Rahmstorf (2002) proposed, based on a benthic foraminifera $\delta^{13}C$ synthesis of Sarnthein et al. (1994), that a deep North Atlantic overturning cell with active deep and intermediate water formation in the North Atlantic and Greenland-Iceland-Norwegian (GIN) seas occurred during warm interstadials, active intermediate convection occurred during stadial events, whereas Heinrich events were associated with a significant reduction in overturning strength. Using $^{231}Pa/^{230}Th$ as a kinematic overturning proxy, McManus et al. (2004) suggest that the meridional overturning circulation was significantly reduced during Heinrich Stadial 1. However the picture appears more complicated. Bottom flow speed reconstruction from the deep (3.5 km) northwest Atlantic suggests that flow speed changes at this depth follow an Antarctic temperature signal, showing slow-downs in bottom flow vigour coincident with Antarctic warming events (Hoogakker et al., 2007), which have also been linked with bottom water changes (Gutjahr et al., 2010). Both Hoogakker et al. (2007) and Roberts et al. (2010) suggest that perturbations associated with millennial cool events likely only influenced the shallow overturning cell in the North Atlantic. $^{231}Pa/^{230}Th$ reconstructions covering the intermediate northeast Atlantic over H1 however do not show evidence for a weakened shallow overturning cell (Gherardi et al., 2009). Since then it has emerged that glacial Antarctic Bottom Waters and Glacial Antarctic Intermediate Waters might show a see-saw pattern in the North Atlantic during Heinrich events, where deep waters show an increase in the contribution of high nutrient, low [O_2] glacial Antarctic Bottom Waters, whereas intermediate waters show a decreased contribution of Antarctic Intermediate Water and increased contribution of possibly well ventilated high [O_2], Glacial North Atlantic Intermediate Water (Gutjahr et al., 2008; Gutjahr et al., 2010; Huang et al., 2014; Piotrowski et al., 2005). Whilst changes in bottom water mass may thus have some part to play in the bottom water [O_2] changes at deep sites during Heinrich events, they cannot however explain lower bottom water [O_2] at the intermediate depth site.

In terms of biological mechanisms driving North Atlantic seawater [O_2] changes during Heinrich events, the picture is not clear. Model simulations suggest that export production during Heinrich events was globally reduced (Schmittner et al., 2005; Mariotti et al., 2012, Menviel et al., 2014). Interestingly, while Mariotti et al. (2012) suggest an overall decrease in export production in the North Atlantic, model simulations by Menviel et al. (2014) show increases across large areas in the Atlantic. According to Salguiero et al. (2010) there were no changes in productivity in the northeast Atlantic at MD95-2042. However for the subtropical Northeast Atlantic, McKay et al. (2014) inferred increased primary production in surface waters during H1, causing low oxygen conditions in the underlying (2.5 km) sediments. Furthermore several studies from deep locations in the Atlantic, including Blake Outer Ridge, Bermuda Rise, the Tobago Basin and equatorial region have documented conspicuous increases in opal sediments during Heinrich events and extreme cold events of MIS 5 (Hoogakker et al., 2007; Keigwin and Boyle, 2008; Gil et al., 2009; Griffiths et al., 2013; Meckler et al., 2013). This could imply a change in productivity at oligotrophic gyre locations in the North Atlantic with increased contribution from opal producers, possibly at the expense of carbonate (foraminifera, coccolith, pteropod, aragonite) producers (Brezinski et al., 2002; Griffiths et al., 2013). Recent work by Hoogakker et al. (2013) suggests weaker summer stratification in the northwest Atlantic during H5, which could be associated with a deeper mixed-layer potentially enhancing silicate available to surface waters. In combination with an increased dust flux (Lopez-Martinez et al., 2006), iron fertilization could have supported diatom productivity. More importantly, whilst export of diatoms to the deep ocean is not that efficient, accumulation of diatom deposits in sediments during Heinrich events (Lippold et al., 2009; Griffiths et al., 2013) could provide evidence that more organic rich material was exported to greater water depths during these episodes. Based on this evidence we propose that the lower bottom water [O_2] values at intermediate ODP Site 1055 during extreme millennial scale cool events were driven by increased export production. The model simulation of Marriotti et al. (2012) and Menviel et al. (2014) also suggests an increase in South Atlantic export production, in agreement with an earlier proxy study by Anderson et al. (2009). In their study, Anderson et al. (2009) found highest opal fluxes in the Southern Ocean that are coincident with bottom [O_2] minima at MD95-2042 of H6, H4 and H1. This implies that biological mechanisms also played a role in decreasing bottom water [O_2] at the deep site, either by changing the [O_2] of SSDW in the Southern Ocean, or through increased export across the Atlantic.

Our reconstructed bottom water [O_2] changes across Heinrich events and extreme cool events of MIS 5 agree with a modelling study of Schmittner et al. (2007), who show that intermediate and deep waters of the North Atlantic Ocean were associated with lower bottom [O_2] during such events. Although the UVic model simulations depict the main features of modern oxygen distributions, the North Atlantic results have higher values than observations, whereas large parts of the South Atlantic and Indian/Pacific have lower [O_2] values compared with observations (Schmittner et al., 2007). Furthermore, while compared with modern the model simulations of Schmittner et al. (2007) predict a decrease in bottom water [O_2] of 60 to 90 µmol/kg at the longitude of intermediate site 1055, and 90 to 120 µmol/kg at the longitude of deep site MD95-2042 during meltwater events, our reconstructions suggests more modest decreases in the range of 24 to 76 µmol/kg (9 to 30%) for the intermediate site, and 15 to 101 µmol/kg (5 to 40%) at the deep site (Figure 5). The larger amplitude changes in seawater [O_2] simulated by Schmittner et al. (2007) may be the result of the prescribed pre-industrial boundary conditions with strong AMOC; if they had used a glacial boundary conditions with weaker AMOC the oxygen changes at the deep site might have been smaller. However, it is noted that the model outputs depict a particular (extreme) point in model time, whereas reconstructions from deep sea sediments represent an averaged view where extremes have been smoothed out by bioturbation. Our reconstructions agree with model simulations suggesting an overall decrease in North Atlantic [O_2] during glacial millennial-scale cold events.

6. Conclusions

Reconstructions of deep (MD95-2042) and intermediate (ODP Site 1055) water [O_2] in the North Atlantic during the last glacial portray decreases in bottom water [O_2] during extreme millennial scale cool events associated with ice rafting and meltwater release (H and C events). Whilst our reconstructions support previous model simulations suggesting lower seawater [O_2] during North Atlantic glacial cold events below ~1 km (Schmittner et al., 2007), our reconstructions are much less dramatic. Numerous observations suggest an increased contribution of SSDW (below ~2km) in the North Atlantic during extreme millennial cool events (H1 to 6 and C19 to C25), and so an increase in high-nutrient, low-[O_2] SSDW can explain at least part of the reconstructed bottom water [O_2] change at the deep site. For North Atlantic Intermediate Water, however, there is now evidence suggesting that this overturning cell might have been stronger during millennial cool events. If so, we infer that increased export of organic material from the surface ocean, as observed at numerous locations across the North Atlantic, was responsible for decreased [O_2] at intermediate ODP Site 1055. By extrapolation, such mechanisms would have played a part in the deep Atlantic [O_2] decrease during such events.

Acknowledgements. Comments from A. Schmittner and an anonymous reviewer improved the quality of our paper. This work is supported by UK Natural Environment Research Council (NERC) grants NE/I020563/1 (to B.A.A.H.) and NE/J008133/1 and NE/L006405/1 (to S.B.). This research used samples and/or data provided by the Ocean Drilling Program (ODP). ODP is sponsored by the US National Science Foundation and participating countries (Natural Environment Research Council in the UK) under management of the Joint Oceanographic Institutions (JOI).

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Table 1. Lowest bottom water $[O_2]$ associated with Heinrich and extreme cool events and difference with modern at intermediate North Atlantic ODP Site 1055 (254 µmol kg^{-1} today) and deep North Atlantic site MD95-2042 (245 µmol kg^{-1} today). Note that $[O_2]$ at MD95-2042 during cold event C20 (indicated with *) is not significantly different from modern.

	Bottom water $[O_2]$ in µmol kg^{-1} (± 17 µmol kg^{-1})			
Event	ODP 1055	Diff. with modern	MD95-2042	Diff. with modern
C21	178	76		
C20	230	24	230	15*
C19	213	41		
cool event following C19	194	60		
H6	224	30	170	75
H5a			206	39
H5			209	35
H4			144	101
H3			181	64
H1			166	79

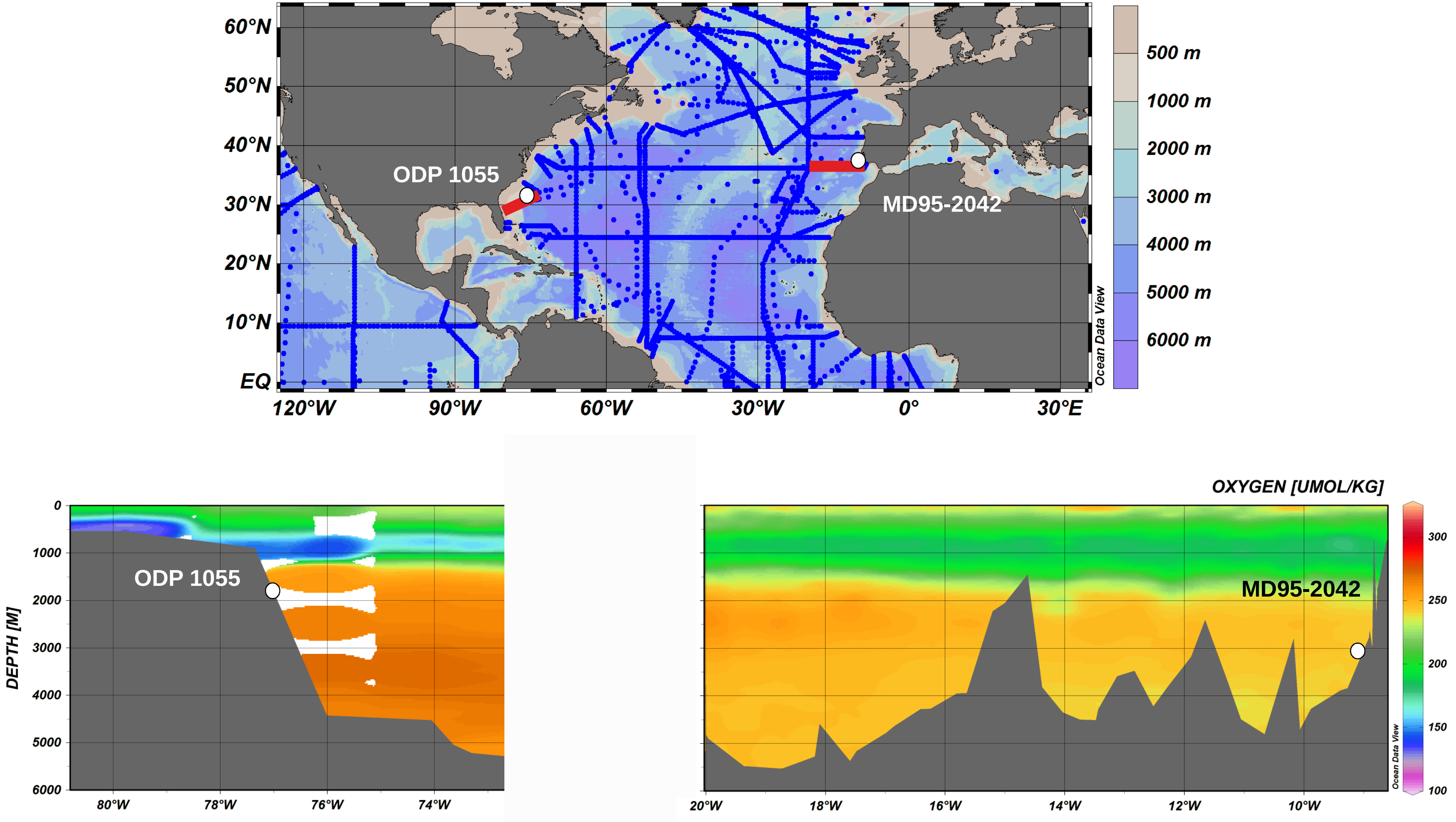
Figure 1. Locations of the two cores (ODP 1055, MD95-2042) used in this study projected on a global bathymetric map (top Figure). The red sections show the locations of the two sea water [O_2] profiles shown in the bottom figure. [O_2] profiles were made using GLODAP version 1.1 bottle data (Key et al., 2004). Cross sections and map were created using Ocean Data View (Schlitzer, R., Ocean Data View, http://odv.awi.de, 2009).

Figure 2. Age models of MD95-2042 and ODP 1055 established by tying planktonic foraminifera oxygen isotopes changes of *Globigerina bulloides* (MD95-2042, Shackleton et al., 2000) and *Globigerinoides ruber* to those of NGRIP. Several Dansgaard-Oeschger interstadial events are numbered in the NGRIP records.

Figure 3. a- Global relationship between seawater [O_2] and $\delta^{13}C$ of DIC. b- Cross-plots of seawater [O_2] and $\delta^{13}C$ for intermediate (1000-1500 m and 1500-2000 m) and deep (2000-3000 m and 3000-4000 m) waters.
Data used to create this figure can be found in the supplementary information and was obtained from http://www.nodc.noaa.gov/OC5/SELECT/dbsearch/dbsearch.html. Only WOD quality controlled data with accepted values (e.g. flag 0) are included.

Figure 4. Benthic foraminifera $\Delta\delta^{13}C$ at deep site MD95-2042 and intermediate ODP Site 1055 and their planktonic foraminifera oxygen isotopes. Original benthic foraminifera $\delta^{13}C$ records (MD95-2042 from Shackleton et al., 2000) of epifaunal *C. wuellerstorfi* (red circles) and deep infaunal *G. affinis* (blue circles) are also shown intercalated between the $\Delta\delta^{13}C$ records. Several Heinrich events and cold events are shown.

Figure 5. Reconstructed bottom water [O_2] at deep site MD95-2042 and intermediate ODP Site 1055 shown with their planktonic foraminifera oxygen isotope records (Shackleton et al., 2000; Thornalley et al., 2013). Heinrich events 1, 3, 4, 5, 5a, 6 and cold events 19, 20 and 21 are shown.



60°N
50°N
40°N
30°N
20°N
10°N
EQ
120°W
90°W
60°W
30°W
0°
30°E
ODP 1055
MD95-2042
Ocean Data View
500 m
1000 m
2000 m
3000 m
4000 m
5000 m
6000 m
OXYGEN [UMOL/KG]
DEPTH [M]
0
1000
2000
3000
4000
5000
6000
80°W
78°W
76°W
74°W
20°W
18°W
16°W
14°W
12°W
10°W
300
250
200
150
100

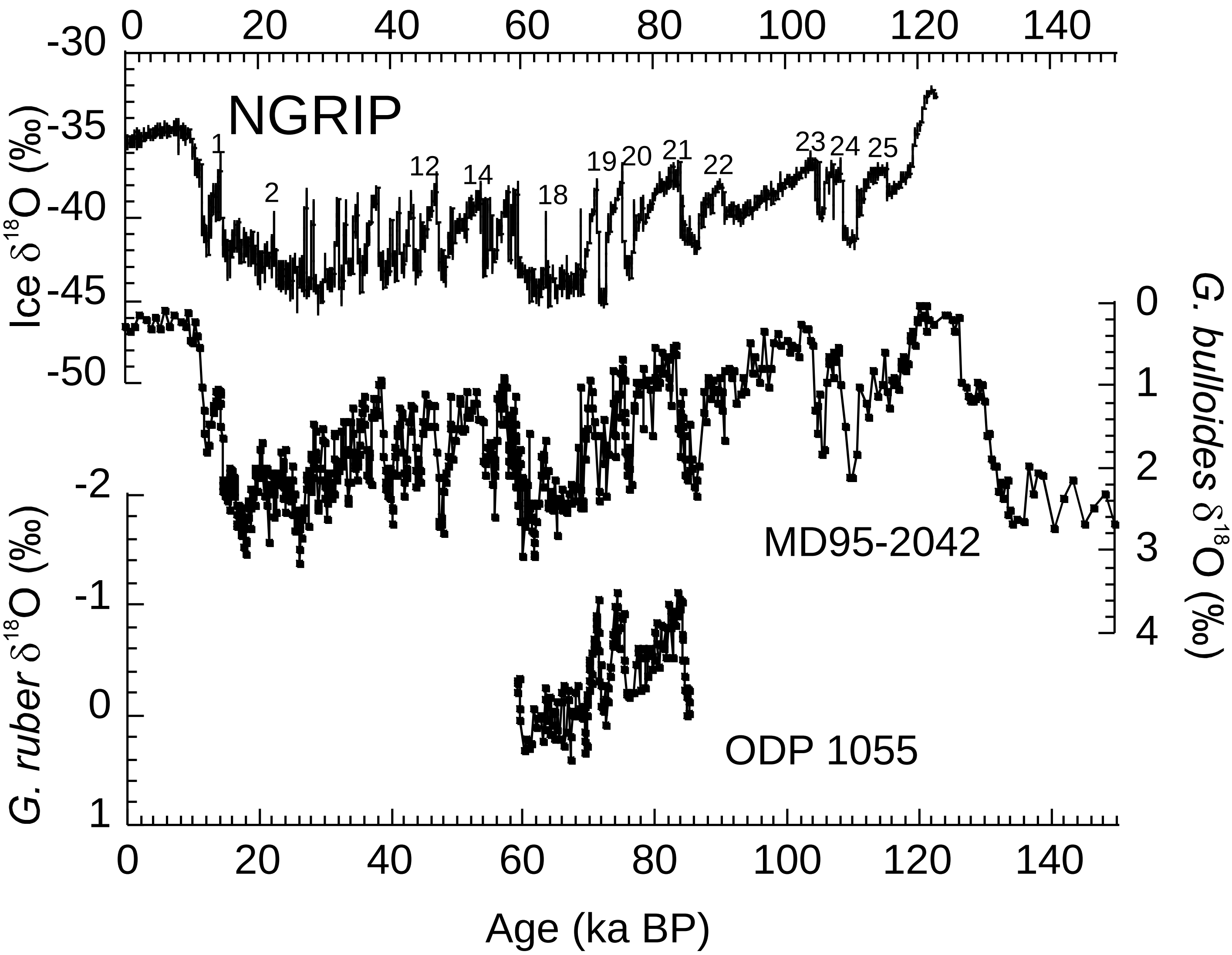
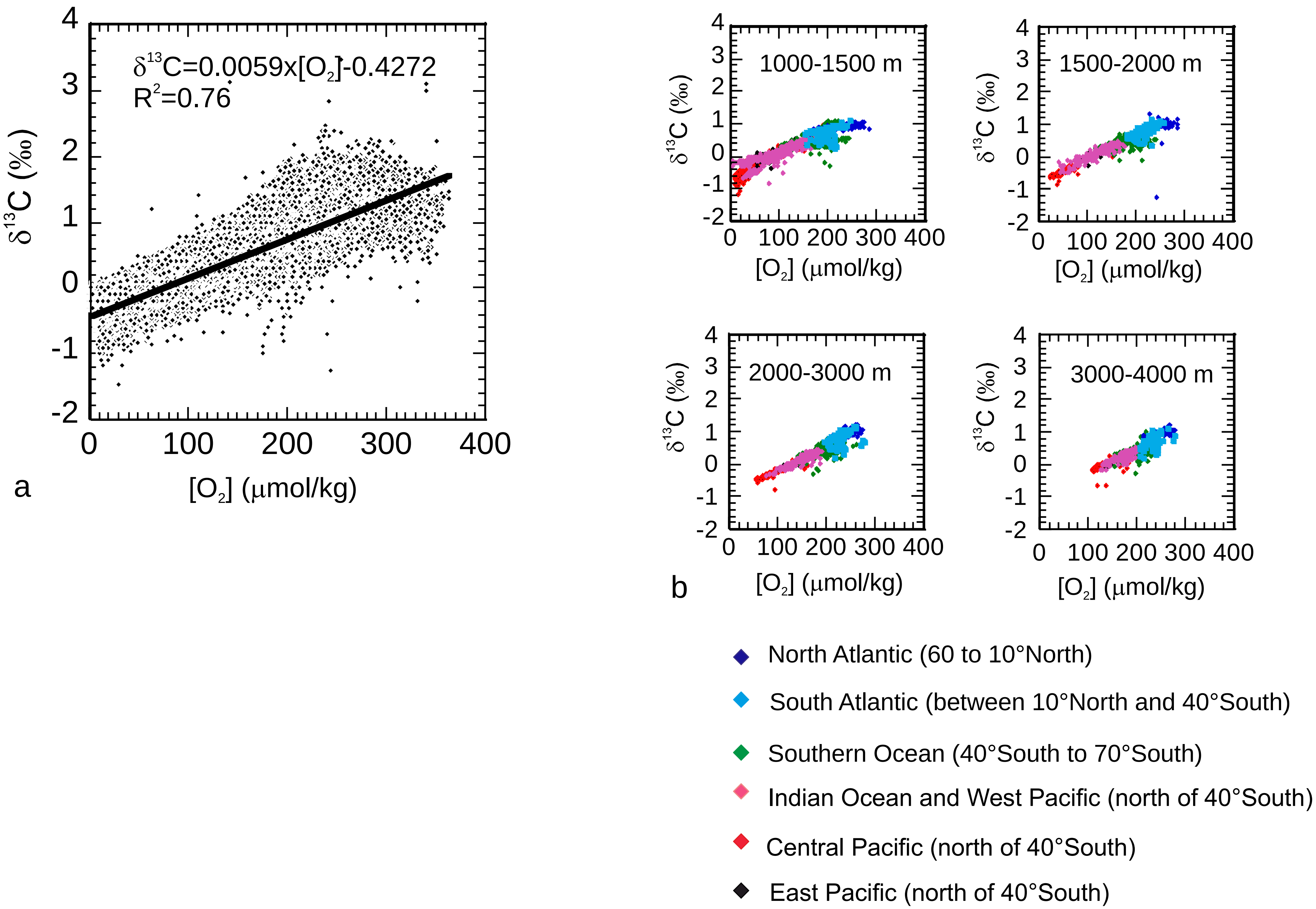
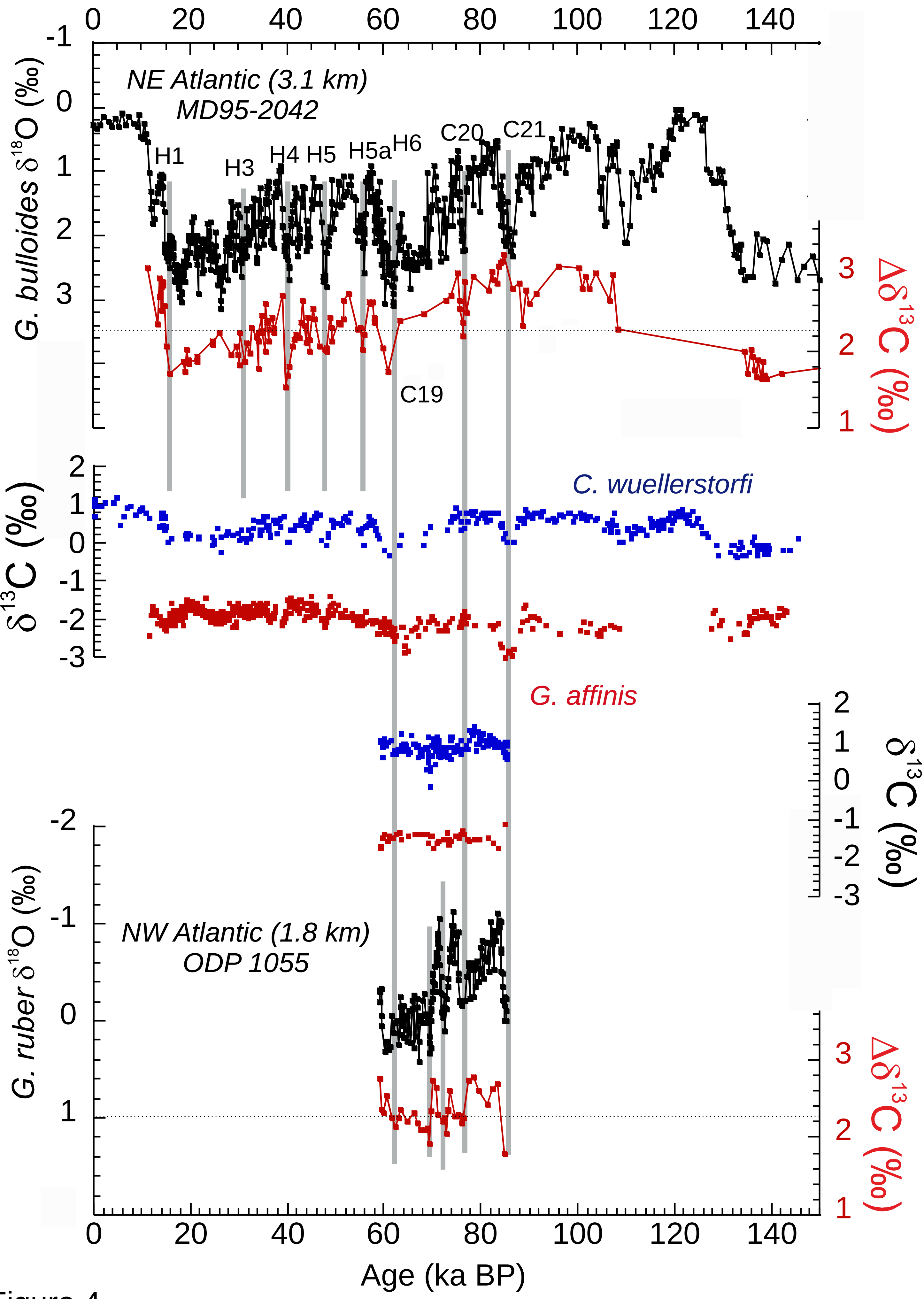

NGRIP
Ice δ18O (‰)
G. bulloides δ18O (‰)
MD95-2042
G. ruber δ18O (‰)
ODP 1055
Age (ka BP)
1
2
12
14
18
19
20
21
22
23
24
25
-30
-35
-40
-45
-50
0
1
2
3
4
-2
-1
0
1
0
20
40
60
80
100
120
140

Figure 2



δ13C=0.0059x[O2]-0.4272
R2=0.76
δ13C (‰)
[O2] (µmol/kg)
a
1000-1500 m
1500-2000 m
2000-3000 m
3000-4000 m
b
North Atlantic (60 to 10°North)
South Atlantic (between 10°North and 40°South)
Southern Ocean (40°South to 70°South)
Indian Ocean and West Pacific (north of 40°South)
Central Pacific (north of 40°South)
East Pacific (north of 40°South)



NE Atlantic (3.1 km)
MD95-2042
H1
H3
H4
H5
H5a
H6
C20
C21
C19
G. bulloides δ18O (‰)
Δδ13C (‰)
δ13C (‰)
C. wuellerstorfi
G. affinis
NW Atlantic (1.8 km)
ODP 1055
G. ruber δ18O (‰)
Age (ka BP)

Figure 4

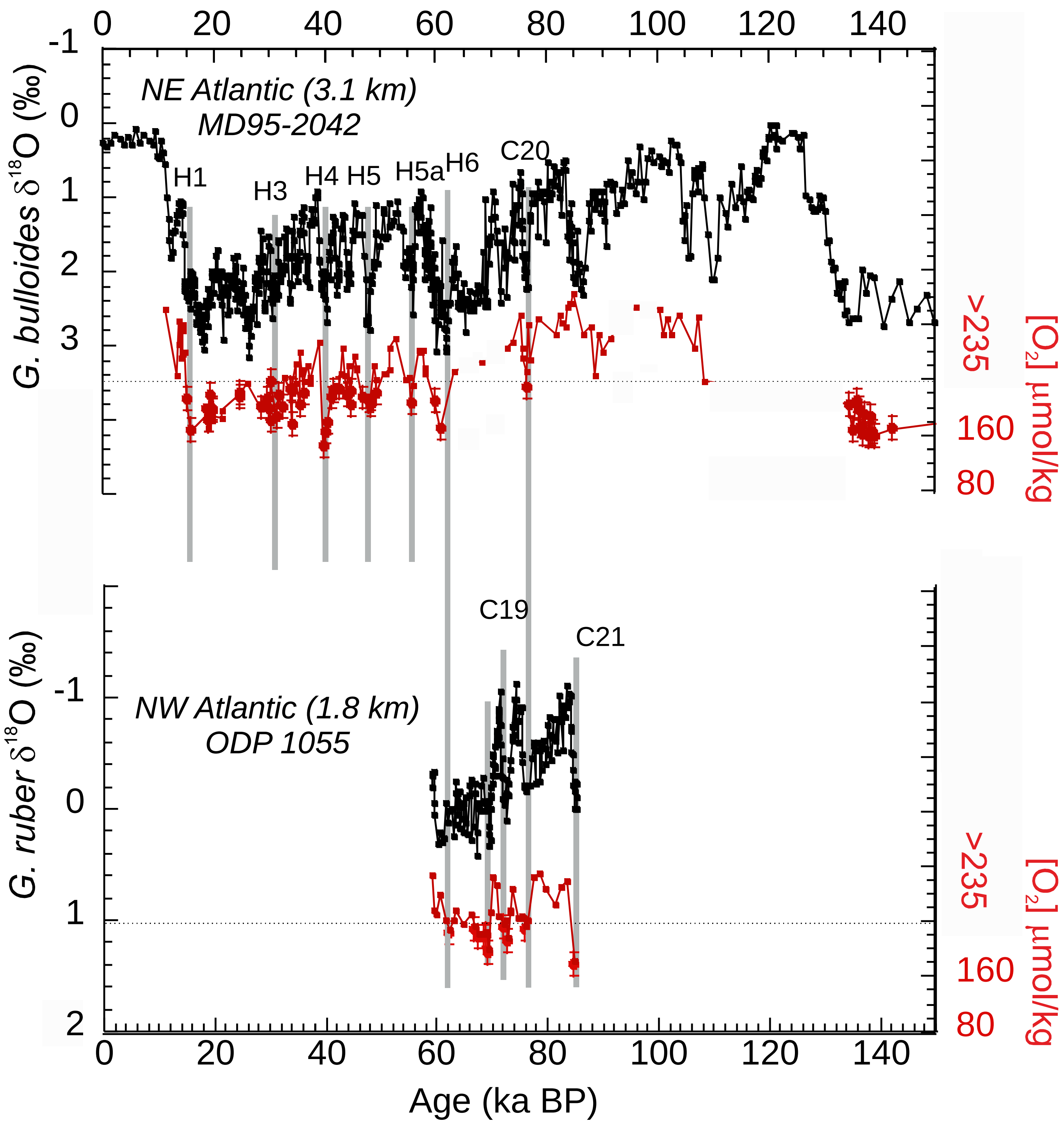

NE Atlantic (3.1 km)
MD95-2042
H1
H3
H4
H5
H5a
H6
C20
G. bulloides δ18O (‰)
>235
160
80
[O2] µmol/kg
NW Atlantic (1.8 km)
ODP 1055
C19
C21
G. ruber δ18O (‰)
Age (ka BP)

Figure 5