Quaternary Science Reviews 90 (2014) 80-89

Contents lists available at ScienceDirect

Quaternary Science Reviews

journal homepage: www.elsevier.com/locate/quascirev

Deep South Atlantic carbonate chemistry and increased interocean deep water exchange during last deglaciation

Jimin Yu^{a,b,*}, Robert F. Anderson^{c,**}, Zhangdong Jin^d, Laurie Menviel^{e,f}, Fei Zhang^d, Fredrick J. Ryerson^b, Eelco J. Rohling^{a,g}

^a Research School of Earth Sciences, The Australian National University, Canberra, ACT 0200, Australia

^b Lawrence Livermore National Laboratory, 7000 East Av., Livermore, CA 94550, USA

^c Lamont-Doherty Earth Observatory of Columbia University, 61 Route 9W/PO Box 1000, Palisades, NY 10964-8000, USA

^d State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China

^e Climate Change Research Centre, University of New South Wales, Sydney, Australia

^fARC Centre of Excellence for Climate System, Australia

^g Ocean and Earth Science, University of Southampton, National Oceanography Centre, Southampton SO14 3ZH, UK

ARTICLE INFO

Article history: Received 8 November 2013 Received in revised form 21 February 2014 Accepted 24 February 2014 Available online

Keywords: Deep-sea Carbonate ion Interocean exchange Atmospheric CO₂



Carbon release from the deep ocean at glacial terminations is a critical component of past climate change, but the underlying mechanisms remain poorly understood. We present a 28,000-year high-resolution record of carbonate ion concentration, a key parameter of the global carbon cycle, at 5-km water depth in the South Atlantic. We observe similar carbonate ion concentrations between the Last Glacial Maximum and the late Holocene, despite elevated concentrations in the glacial surface ocean. This strongly supports the importance of respiratory carbon accumulation in a stratified deep ocean for atmospheric CO₂ reduction during the last ice age. After ~9 μ mol/kg decline during Heinrich Stadial 1, deep South Atlantic carbonate ion concentration rose by ~24 μ mol/kg from the onset of Bølling to Preboreal, likely caused by strengthening North Atlantic Deep Water formation (Bølling) or increased ventilation in the Southern Ocean (Younger Drays) or both (Pre-boreal). The ~15 μ mol/kg decline in deep water carbonate ion since ~10 ka is consistent with extraction of alkalinity from seawater by deep-sea CaCO₃ compensation and coral reef growth on continental shelves during the Holocene.

Between 16,600 and 15,000 years ago, deep South Atlantic carbonate ion values converged with those at 3.4-km water depth in the western equatorial Pacific, as did carbon isotope and radiocarbon values. These observations suggest a period of enhanced lateral exchange of carbon between the deep South Atlantic and Pacific Oceans, probably due to an increased transfer of momentum from southern westerlies to the Southern Ocean. By spreading carbon-rich deep Pacific waters around Antarctica for upwelling, invigorated interocean deep water exchange would lead to more efficient CO₂ degassing from the Southern Ocean, and thus to an atmospheric CO₂ rise, during the early deglaciation.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Ice core records reveal stepwise rises in atmospheric CO_2 content since the Last Glacial Maximum (LGM; 22–18 ka) (Monnin et al., 2001), but the reasons for these changes remain elusive. The large carbon reservoir of the deep ocean is thought to have

played an important role in modulating past atmospheric CO_2 changes (Broecker, 1982). A leading hypothesis for the deglacial atmospheric CO_2 rise involves a breakdown of the deep vertical density stratification in the Southern Ocean (Anderson et al., 2009; Sigman et al., 2010a; Burke and Robinson, 2012) that governs the rate of CO_2 exchange between the deep ocean and the atmosphere, a process commonly referred to as "ventilation". The history of deep water carbonate chemistry in the Southern Ocean is critical to inform us about the processes involved in the release of CO_2 to the atmosphere in the past.

Deep water carbonate ion concentration, $[CO_3^{2-}]$ is an important parameter in deciphering the deglacial carbon cycle changes. To a





CrossMark

QUATERNARY

^{*} Corresponding author. Research School of Earth Sciences, The Australian National University, Canberra, ACT 0200, Australia. ** Corresponding author.

E-mail addresses: jimin.yu@anu.edu.au (J. Yu), boba@ldeo.columbia.edu (R. F. Anderson).

first approximation $[CO_3^{2-}] \approx ALK - DIC$, where ALK is alkalinity and DIC is dissolved inorganic carbon, each of which influences the carbon storage in the ocean (Sigman and Boyle, 2000; Sigman et al., 2010a; Yu et al., 2014). Thus, a $[CO_3^{2-}]$ record for a key location such as the deep Southern Ocean would yield critical insights into the processes responsible for past atmospheric CO₂ variations. Until now, a quantitative deep water $[CO_3^{2-}]$ record that can sufficiently resolve millennial timescale variability is lacking in the Southern Ocean. For example, a recently published deep water $[CO_3^{2-}]$ record from the Weddell Sea has only four data points during the last 30,000 years (Rickaby et al., 2010), limiting the use of these results to constrain the processes that have regulated the deglacial rise in atmospheric CO₂. Here, we present the first high-resolution quantitative deep water $[CO_3^{2-}]$ record for the Southern Ocean spanning the last 28,000 years to constrain processes that controlled atmospheric CO₂ variations in the past.

2. Samples and methods

Our reconstruction is based on measurements for sediment core TNO57-21 (41.1°S, 7.8°E, 4981 m) from the southern Cape Basin, South Atlantic Ocean (Fig. 1). The age model of the core is based on 3 new and 20 published radiocarbon dates (Fig. 2; Table S1) (Barker et al., 2009, 2010). It is impossible to use a single planktonic species for radiocarbon dating due to significant shell fragmentation at depths 0–80 cm (corresponding to \sim 4–9 ka) in TNO57-21 and the large sample size requirement for ¹⁴C analysis. We thus used mixed planktonic species for our radiocarbon measurements. Radiocarbon dates are calibrated assuming a constant surface reservoir age of 600 years (Barker et al., 2009) using Calib 6.01 (Stuiver and Reimer, 1993) and the Marine 09 curve (Reimer et al., 2009). Using variable surface reservoir ages (Skinner et al., 2010) has negligible influence on our conclusion (Fig. S1). The average sedimentation rate is 15.6 cm ka⁻¹, which minimizes any influence from bioturbation and facilitates the development of climate records with excellent temporal resolution. The core site is bathed in Lower Circumpolar Deep Water (LCDW), which fills a large volume of the global deep ocean (Fig. 1). Changes in $[CO_3^{2-}]$ of LCDW thus have far-reaching implications for the global carbon cycle.

Our deep water $[CO_3^{2-}]$ reconstruction is based on 67 B/Ca measurements of the epibenthic (a habitat above the sediment– water interface) foraminiferal species *Cibicidoides wuellerstorfi* (Table S2). About 10 cc wet sediments for each sample (1 cm depth interval) from core TNO57-21 were disaggregated in de-ionized water and wet sieved through 63 µm sieves. All *C. wuellerstorfi*, ranging from ~15 to 30 shells in each sample, were picked for all



Fig. 2. Data from core TNO57-21. (A) *C. wuellerstorfi* B/Ca and reconstructed deep water $[CO_3^2^-]$ (red circles) with b-spline smoothing (red curve). The error bar represents the average 2σ $[CO_3^2^-]$ error from analytical uncertainty in B/Ca. (B) %CaCO₃ (green crosses) and ²³⁰Th-normalized CaCO₃ flux (blue squares) (Sachs and Anderson, 2003; this study). (C) Benthic $\delta^{13}C$ (Ninnemann and Charles, 2002). Triangles at the bottom represent new (Table S1) and published (Barker et al., 2010) radiocarbon dates. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

samples from the 250–500 µm size fraction. The shells were then double checked under a microscope before crushing with due attention to use shells of most consistent morphology for B/Ca analyses throughout the core, to minimize any potential influence from changes in shell morphology (Rae et al., 2011). In general, the starting material for each sample has ~12 to 25 shells, equivalent to ~300–600 µg. The shells were cleaned by the "Mg-cleaning" method (Barker et al., 2003; Yu et al., 2007) and B/Ca was measured on ICP-MS using the established procedure (Yu et al., 2005). Foraminiferal B/Ca shows no correlation with Mn/Ca ($R^2 = 0.01$, P = 0.55) or Al/Ca ($R^2 = 0.00$, P = 0.89) or Fe/Ca ($R^2 = 0.00$, P = 0.97)



Fig. 1. Locations of core TNO57-21 and two cores in the Western Equatorial Pacific (WEP) against the pre-industrial seawater $[CO_3^2^-]$. Inset shows the locations of hydrographic sites used for the $[CO_3^2^-]$ section (Key et al., 2004). The map was generated using Ocean Data View (http://odv.awi-bremerhaven.de.). Three key water masses are indicated: NADW = North Atlantic Deep Water, LCDW = Lower Circumpolar Deep Water, and NPDW = North Pacific Deep Water. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(Fig. S2), indicating that B/Ca is not biased by contamination from diagenetic coatings or silicates.

C. wuellerstorfi B/Ca ratios were converted to seawater $[CO_3^{2-}]$ using a sensitivity of 1.14 µmol/mol per µmol/kg specific to this species, as obtained from a global core-top calibration (Yu and Elderfield, 2007) by: $[CO_3^{2-}]_{downcore} = [CO_3^{2-}]_{preindustrial} + \Delta(B/Ca)/$ 1.14, where the preindustrial $[CO_3^{2-}]$, $[CO_3^{2-}]_{preindustrial}$, is estimated using the GLODAP dataset (Key et al., 2004), and $\Delta(B/Ca)$ is the deviation of B/Ca of down-core samples relative to the core-top value. The B/Ca- $[CO_3^{2-}]$ proxy is empirical and the mechanism for the observed relationship remains largely unknown. However, subsequent core-top (Brown et al., 2011; Rae et al., 2011; Raitzsch et al., 2011; Yu et al., 2013a) and down-core (Yu et al., 2010b; Raitzsch et al., 2011; Yu et al., 2013a) studies have strongly corroborated the faithfulness of the B/Ca proxy for deep water $[CO_3^{2-}]$.

Based on core-top samples, Yu and Elderfield (2007) gave an uncertainty of ~ $\pm 9 \ \mu mol/kg \ (2\sigma)$ in deep water [CO₃²⁻] for reconstructions using C. wuellerstorfi B/Ca. This uncertainty should be treated as the worst scenario error because the calculation included errors associated with hydrographic data (at $\sim \pm 5-10 \mu mol/kg$ in seawater Δ [CO₃²⁻]) (Key et al., 2004), bioturbation (associated with sedimentation rates), shell morphology influences, inter- and intrashell variability, and analytical error in B/Ca, all of which have been discussed in Yu et al. (2013a). Reconstruction error in down-core records may be estimated using the variance in B/Ca of duplicate measurements and the sensitivity of B/Ca to $[CO_3^{2-}]$. Down-core reconstruction precision may differ between cores due to different degrees of bioturbation, and could be improved by employing recommendations given in Yu et al. (2013a), which were followed in this study. For example, the reconstruction error is given at ~7 μ mol/kg (2 σ) in core VM28-122 (Yu et al., 2010b). Unfortunately, it is impossible to make duplicates for TNO57-21 due to the limited quantity of sediment available for this study. Here, we assess the error based on the replicates of a consistency standard ($B/Ca = 150 \mu mol/mol$), which was measured during the course of analyzing samples from core TNO57-21 samples. The average uncertainty (2σ) of this consistency standard is ~ $\pm 6 \mu mol/$ mol in B/Ca, corresponding to an error of $\sim \pm 5 \ \mu mol/kg \ (2\sigma)$ in seawater $[CO_3^{2-}]$ assuming a constant sensitivity of 1.14 µmol/mol per µmol/kg. Compared to VM28-122, the slightly better reconstruction error for core TNO57-21 is expected due to faster sedimentation rates at TNO57-21 (~15.7 cm/ka at TNO57-21 vs. ~7 cm/ka at VM28-122), which would minimize bioturbation effects and thus be conducive for improved reconstructions at TNO57-21.

We also measured U-Th isotopes for 36 sediment samples from TNO57-21 to supplement published data (Sachs and Anderson, 2003) and increase the resolution of CaCO₃ and alkenone fluxes and of authigenic uranium during last 28,000 years (Fig. 2: Table S3). Uranium and thorium isotopes were measured in aliquots of the 1-cm thick sediment samples from core TN057-21. Measurements were made by isotope dilution ICP-MS. A 0.5-g aliquot of dried sediment was dissolved using mixed acids in the presence of ²²⁹Th and ²³⁶U spikes. After weighing the final solution, an aliquot ($\sim 1.0\%$ by weight) was removed, spiked with ²³⁰Th and additional 236 U, and diluted with 1% HNO3 + 1% HF. This solution was analyzed without further processing by ICP-MS to measure concentrations of ²³⁸U and ²³²Th. Uranium and Th in the remainder (99%) of the initial solution were purified by anion exchange chromatography, after which ²³⁴U, ²³⁵U and ²³⁰Th were measured by ICP-MS. Details of the method are presented in the work of Fleisher and Anderson (2003). Calculations of CaCO₃ and alkenone fluxes and authigenic uranium are given in Sachs and Anderson (2003).

3. Dissolution effect on benthic B/Ca

In the deep ocean, changes in deep water $[CO_3^{2-}]$ (deep water property) and dissolution of carbonate on the sea floor (including deep and pore water dissolution) are often coupled: when deep water $[CO_3^{2-}]$ is low, dissolution tends to increase and vice versa. This sometimes makes it difficult to distinguish whether a decline in benthic B/Ca is due to a decrease in deep water $[CO_3^{2-}]$ or enhanced dissolution. However, strong evidence exists to argue against dissolution as the driver for changes in benthic B/Ca. First, benthic foraminiferal shells are calcified in corrosive deep waters and, when compared with planktonic shells, are more resistant to dissolution on the sea floor (Howard and Prell, 1994). Second, Rose Bengal stained (recently alive) and non-Rose Bengal stained (already dead and exposed to deep waters for a certain amount time) shells from the same core-top samples yield similar B/Ca ratios, suggesting that dissolution does not significantly affect B/Ca (Yu and Elderfield, 2007). Third, the sensitivity of B/Ca to deep water $\Delta[CO_3^{2-}]$ is sustained at high $[CO_3^{2-}]$ ranges well above the saturation horizon where dissolution of carbonate is minimal (Yu and Elderfield, 2007; Raitzsch et al., 2011; Yu et al., 2013a), supporting that changes in B/Ca are driven by changes in deep water $[CO_3^{2-}]$, not by dissolution.

An insignificant dissolution effect on benthic B/Ca is further supported by comparisons of B/Ca with dissolution proxies at core TNO57-21 (Figs. S3, S4). Overall, benthic B/Ca display weak correlations ($r^2 < 0.10$, P > 0.005; Fig. S4) with the >63 µm size fraction, for a shell fragmentation (>150 um), and the whole shell number (>150 um), with the exception of %CaCO₃ in which case a significant correlation is observed (see below). Careful scrutiny of the data reveals that benthic B/Ca and dissolution proxies have varied differently on millennial timescales. For example, benthic B/ Ca decreased and increased by $\sim 15 \mu mol/mol$ during the transitions into and out of Heinrich Stadial 2 (HS2; 27-24 ka), respectively, which is not observed in any of the dissolution proxies (Fig. S3). During the LGM, benthic B/Ca remained roughly stable, in contrast to obvious trends exhibited by dissolution proxies (steady increases in the >63 μ m fraction, whole shell number and %CaCO₃ and a steady decline in fragmentation) (Fig. S3). At the transition from Bølling/Allerød (B/A; 14.5–12.9 ka) to Younger Dryas (YD; 12.9–11.8 ka), benthic B/Ca increased by \sim 10 μ mol/mol, compared to substantial decreases in the $>63 \ \mu m$ fraction and whole shell number, an increase in foraminifera shell fragmentation, and roughly stable %CaCO₃ (Fig. S3).

4. Reliability of $\delta^{13}\text{C}$ and B/Ca in C. wuellerstorfi for deep water signals

The fidelity of using epifaunal benthic foraminifera (e.g., Cibici*doides* spp.) in reconstructions of deep water chemistry in the Southern Ocean is a matter of debate. It has been speculated that the extremely low $\delta^{13}C$ in C. wuellerstorfi from the glacial deep Southern Ocean might be caused by their habitat preference in a fluff layer where fluid δ^{13} C is decreased by degradation of organic matter (the "Mackensen effect") (Mackensen et al., 1993). If true, then respiration of biogenic matter should also increase DIC and decrease $[CO_3^{2-}]$ of the microenvironment, resulting in concomitant decreases in δ^{13} C and $[CO_3^{2-}]$ (this is also true for increased organic matter respiration in deep water). However $[CO_3^{2-}]$ (this study) and δ^{13} C (Ninnemann and Charles, 2002) at TNO57-21 display no correlation over the last 28,000 years and show opposite trends during Heinrich Stadial 1 (HS1; 17.5-14.5 ka) (Fig. 2A, C). Furthermore, a recent core-top survey shows that Cibicidoides reliably records deep water δ^{13} C in a wide region (~40–80°S) of the South Atlantic (Mackensen, 2012), and the low glacial benthic δ^{13} C is highly reproducible at various locations from the Southern Ocean (Ninnemann and Charles, 2002). Based on the above, we interpret $\delta^{13}C$ and B/Ca of benthic foraminifera at site TNO57-21 as a reliable recorders of the $\delta^{13}C$ of DIC and $[CO_3^2-]$ of bottom waters, respectively.

5. Deep water $[CO_3^{2-}]$, %CaCO₃, and ²³⁰Th-normalized CaCO₃ flux

Over the past 28 ka, B/Ca-derived deep water $[CO_3^{2-}]$ shows similar large-scale variations to sediment carbonate content (% CaCO₃) and ²³⁰Th-normalized CaCO₃ flux (Sachs and Anderson, 2003) (Fig. 2). Changes in deep water $[CO_3^{2-}]$ explain 43% of the variance in %CaCO₃ in TNO57-21 (Fig. S4). Although $[CO_3^{2-}]$ differs in detail from %CaCO₃ and CaCO₃ flux due to secondary factors (see below), the overall agreement corroborates the notion (Farrell and Prell, 1989; Hodell et al., 2001; Anderson et al., 2008) that CaCO₃ dissolution, regulated by deep water $[CO_3^{2-}]$, is a significant driver for CaCO₃ abundance in sediments of the deep Cape Basin (Hodell et al., 2001), as well as in the deep Indian and Pacific Oceans (Farrell and Prell, 1989; Anderson et al., 2008; Yu et al., 2013a).

Although they are broadly similar over the last 28,000 years (Fig. 2, S4d), sediment %CaCO₃ and deep water $[CO_3^{2-}]$ derived from B/Ca in C. wuellerstorfi differ in detail. The differences include: (i) from 27 to 28 ka to HS2, deep water $[CO_3^{2-}]$ declined, but %CaCO₃ remained low; (ii) %CaCO₃ displays a clear rising trend by $\sim 30\%$ during the LGM, in contrast to roughly stable deep water $[CO_3^{2-}]$; (iii) the increase in %CaCO₃ halted, but showed no decline as observed in deep water $[CO_3^{2-}]$, during HS1; and (iv) sediment % CaCO₃ remained roughly constant from the B/A to the Pre-Boreal (PB; 11.8–10 ka), when deep water $[CO_3^{2-}]$ rose by ~12 μ mol/kg (Fig. 2A). These differences cannot be attributed to dilution of CaCO₃ by detrital sediments because %CaCO₃ and ²³⁰Th-normalized CaCO₃ flux show very similar patterns over the course of the past 28,000 years ($R^2 = 0.95$, n = 60, P < 0.0001) (Fig. 2B) (Sachs and Anderson, 2003). Dissimilar patterns of alkenone flux and %CaCO₃ indicate an insignificant role of pore water dissolution in CaCO₃ preservation in core TNO57-21 during the last 28 ka (Sachs and Anderson, 2003) (see Fig. 2B, S9c; SI text). We attributed observed differences between $(CaCO_3 and [CO_3^{2-}])$ to secondary processes affecting carbonate abundance in sediments, in addition to deep water $[CO_3^{2-}]$ changes. We speculate that sediment CaCO₃ content and flux at the site of TNO57-21 are further influenced by factors including winnowing and focusing of fine carbonate particles by deep currents (Sachs and Anderson, 2003) and changes in surface productivity (Karlin et al., 1992; Lyle et al., 2000; Sachs and Anderson, 2003). These secondary factors complicate the interpretation of CaCO₃ accumulation quantitatively in terms of deepwater $[CO_3^{2-}]$. By contrast, C. wuellerstorfi is an epibenthic species that lives above the deep water-sediment boundary and hence records deep water chemistry (Corliss, 1985; Lutze and Thiel, 1989). Benthic B/Ca methodology is based on extensive core-top calibrations (Yu and Elderfield, 2007; Rae et al., 2011; Raitzsch et al., 2011; Yu et al., 2013a) and its validity is strongly supported by down core studies (Yu et al., 2008, 2010b, 2013a; Raitzsch et al., 2011). In the text, we focus on B/Ca-derived deep water $[CO_3^{2-}]$ for paleoceanographic interpretations.

6. LGM

Deep water $[CO_3^2^-]$ at TNO57-21 displays similar values during the LGM (86.9 ± 3.4 µmol/kg, n = 18, 1 standard deviation) and the late Holocene (~83.0 µmol/kg, n = 2, 0–5 ka) (Fig. 2A). Small changes in $[CO_3^2^-]$ of < ~5 µmol/kg between the Holocene and the LGM are also observed in the deep Indian and Pacific Oceans (Fig. 3;

SI text) (Anderson and Archer, 2002; Yu et al., 2010a, 2013a). Assuming equilibrium between the surface ocean and the atmosphere, surface water $[CO_3^{2-}]$ would have been ~60 µmol/kg higher than today (preindustrial) during the LGM (Lea et al., 1999; Foster, 2008; Yu et al., 2013b), when atmospheric CO₂ was ~90 part per million by volume (ppmv) lower (Fig. 4H) (Monnin et al., 2001). Although the spatial distribution of surface water $[CO_3^{2-}]$ in the world ocean during the LGM remains undetermined, it is reasonable to expect that the surface waters which contributed to newly formed deep water would have had a substantially higher preformed $[CO_3^{2-}]$ than today. The observation that LGM deep water $[CO_3^{2-}]$ was similar to the present therefore reveals an increased surface-to-deep $[CO_3^{2-}]$ gradient in the LGM ocean (Fig. 3).

In seawater, remineralization of biogenic matter increases DIC but has little influence on ALK, resulting in a net decrease in $[CO_3^{2-}]$ (Yu et al., 2008; Yu et al., 2014). Therefore, the difference between LGM and modern levels of respiratory CO₂ in the deep sea must have been sufficiently large to titrate the greater preformed $[CO_3^{2-}]$ of LGM surface waters down to levels close to those existing in the modern deep ocean. This inferred increase in respiratory CO₂ in the glacial-age deep water is consistent with lower dissolved O₂ concentrations in the deep Pacific Ocean during the LGM (Galbraith et al., 2007; Bradtmiller et al., 2010; Jaccard and Galbraith, 2012). It is also consistent with inferences of increased stratification in the glacial ocean (Lund et al., 2011; Burke and Robinson, 2012), which, by limiting the ventilation of high-DIC deep waters, would have facilitated the buildup of CO₂ in the deep ocean and contributed to the low atmospheric CO₂ levels of the LGM (Sigman and Boyle, 2000: Sigman et al., 2010a).



Fig. 3. Vertical seawater $[CO_3^{2-}]$ distributions during the LGM and today. LGM data are for the North Atlantic (Yu et al., 2010a), equatorial (EQ) Atlantic (Raitzsch et al., 2011), South Atlantic (this study), and Indo-Pacific Oceans (Yu et al., 2010a; Yu et al., 2013a). Error bars represent 1 standard deviation of values from the LGM. Modern global seawater $[CO_3^{2-}]$ is from the eWOCE dataset (http://www.ewoce.org/). Squares along the top x-axis represent surface water $[CO_3^{2-}]$ reconstructions for the tropical Atlantic during the Holocene and the LGM (Foster, 2008). Little change in deep Indo-Pacific $[CO_3^{2-}]$ is also supported by foraminiferal assemblage analyses (Anderson and Archer, 2002). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. Marine and atmospheric records over the past 28 ka. (A) North Atlantic Deep Water formation strength from Pa/Th (McManus et al., 2004). (B) $[CO_3^{-7}]$ at TNO57-21 (this study) and GGC48 (Yu et al., 2010a). (C) Benthic δ^{13} C at TNO57-21 (Ninnemann and Charles, 2002) and GGC48 (Yu et al., 2010a). (D) $\Delta\Delta^{14}$ C, the benthic–atmospheric Δ^{14} C offset, for TNO57-21 (Barker et al., 2010) and MD01-2386 (Broecker et al., 2007). In (B–D), red solid circles are for TNO57-21, while green empty symbols are for WEP cores. (E) Opal flux in the Antarctic Zone (Anderson et al., 2009). (F) Atmospheric Δ^{14} C (Reimer et al., 2009). (G) Atmospheric δ^{13} CO₂ (Schmitt et al., 2012). (H) Atmospheric CO₂ (Monnin et al., 2001). (I) EDML ice core δ^{18} O (Barbante et al., 2006). Ice core data are on the age model of (Lemieux-Dudon et al., 2010). Error bars in (B, C, F, G) are 1 σ uncertainties, the ellipse in (D) represents approximate average 2σ error, and curves in (B, G) are b-spline smoothing. Triangles at base represent radiocarbon dates for TNO57-21 (SI Text) (Barker et al., 2010). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

7. Deep South Atlantic $[CO_3^{2-}]$ evolution since the Last Glacial

After a ~2 μ mol/kg drop at the very end of the LGM [CO₃²⁻] decreased by ~7 μ mol/kg at ~16.6 ka during HS1 to a minimum of ~77 μ mol/kg at 15.6 ka (Figs. 2A and 4B). This decline in [CO₃²⁻] is independently supported by an increase in shell fragmentation in the same core (Fig. S3) (Barker et al., 2010). A decrease of similar magnitude in deep water [CO₃²⁻] at the location of TNO57-21 also occurred during HS 2 (Fig. 2). This may imply a systematic link

between Heinrich Stadials and changes in deep South Atlantic $[CO_3^2^-]$ chemistry, although $[CO_3^2^-]$ changes during previous Heinrich events are to be reconstructed.

Starting at ~14.6 ka, deep water $[CO_3^{2-}]$ at TNO57-21 increased by ~12 μ mol/kg over ~500 years and stayed at about 91 μ mol/kg over the remainder of the B/A (Fig. 4B). This increase in deep water $[CO_3^{2-}]$, together with the concurrent $>0.3_{\infty}^{\circ}$ increase in benthic δ^{13} C (Fig. 4C) (Ninnemann and Charles, 2002) and ~160% rise in $\Delta \Delta^{14}$ C [the offset between benthic and contemporary atmospheric Δ^{14} C (Reimer et al., 2009)] (Fig. 4D) (Barker et al., 2010), can be explained by rapid ventilation of the deep South Atlantic by high- $[CO_3^{2-}]$ and ¹⁴C-enriched North Atlantic Deep Water (NADW) (Figs. 1 and 4A) (McManus et al., 2004; Barker et al., 2010). NADW reinvigoration is also thought to have been responsible for improved carbonate preservation and for increases in both benthic δ^{13} C and $\Delta\Delta^{14}$ C at 3.3–3.6 km water depth in the North Pacific at around 14.6 ka (Fig. S5) (Galbraith et al., 2007). This suggests widespread ventilation of the global abyss by low-DIC NADW, and a sizable carbon loss from the deep ocean. Paradoxically, owing to an efficient offsetting effect from an increase in the biological pump that enhanced respired DIC at intermediate depths in the Indian and Pacific Oceans (Galbraith et al., 2007; Jaccard and Galbraith, 2012), only a small net quantity of CO₂ was released to the atmosphere (~10 ppmv rise in atmospheric CO_2) at the onset of B/A (Fig. 4H) (Monnin et al., 2001).

During the YD and PB, deep water $[CO_3^{2-}]$ at TNO57-21 increased by a further $\sim 12 \ \mu mol/kg$ to a peak value of $\sim 104 \ \mu mol/kg$ at ~ 10 ka (Fig. 4B). Given the weakened export of NADW during the YD (Fig. 4A) (McManus et al., 2004), we attribute the rise in deep water $[CO_3^{2-}]$ at TNO57-21 to enhanced ventilation from the Southern Ocean. The formation of Antarctic Bottom Water could be enhanced associated with warming in Antarctica during the YD (Fig. 4I) (Barbante et al., 2006) as simulated by (Menviel et al., 2011), and with intensified upwelling in the Southern Ocean during the YD and PB as inferred from opal accumulation records (Fig. 4E) (Anderson et al., 2009). Whatever combination of ventilation processes occurred in the Southern Ocean, the associated release of CO₂ from the deep ocean to the atmosphere (SI Text) likely contributed to the initial $\sim 0.2\%$ drop in $\delta^{13}CO_2$ and 25 ppmv rise in atmospheric CO₂ during the YD (Fig. 4G, H) (Monnin et al., 2001; Schmitt et al., 2012).

Together with the concurrent >0.2% increase in benthic δ^{13} C, the peak deep water $[CO_3^{2-}]$ of ~ 104 μ mol/kg at 10 ka in TNO57-21 (Fig. 4B, C) suggests that ventilation of the deep Cape Basin was further improved during the PB. At this time, besides sustained ventilation from the Southern Ocean (Fig. 4E) (Anderson et al., 2009), the deep Cape Basin ventilation was also affected by low-DIC and high- $[CO_3^{2-}]$ NADW (Fig. 1) as inferred from sediment Pa/ Th (Fig. 4A) (McManus et al., 2004). During the PB, atmospheric CO₂ reached a plateau while atmospheric δ^{13} CO₂ rose (Fig. 4G, H) (Monnin et al., 2001; Schmitt et al., 2012). This suggests that the net release of CO₂ from the deep ocean was in balance with net uptake by the terrestrial biosphere (Elsig et al., 2009). Insufficient data exist to assess how and where carbon transfer between the deepsea and the atmosphere occurred during this period. Based on the coeval deep water $[CO_3^{2-}]$ increase at TNO57-21 and sustained high opal fluxes south of the Antarctic Polar Front (Fig. 4E) (Anderson et al., 2009), we suggest that degassing of CO_2 via intensified upwelling in the Southern Ocean (SI Text) may have played a significant role in supplying the carbon required for forest regrowth during the PB.

Since 10 ka, deep water $[CO_3^2^-]$ at TNO57-21 has plunged by ~15 µmol/kg, while benthic δ^{13} C in the same core has remained relatively stable (Fig. 4B, C). The stable benthic δ^{13} C, which is sensitive to the accumulation of respiratory CO₂, indicates that the

 $[CO_3^{2-}]$ decline must have resulted from a greater decrease in oceanic ALK than in oceanic DIC. This inferred ALK decrease is consistent with two contributing factors inferred from modeling studies (Broecker and Peng, 1987; Opdyke and Walker, 1992; Ridgwell et al., 2003; Menviel and Joos, 2012): (i) CaCO₃ compensation and (ii) burial of CaCO₃ on continental shelves (SI Text). Owing to its high sedimentation rate, our record reveals for the first time a clear acceleration of the $[CO_3^{2-}]$ decline at ~8 ka (Fig. 4B), when the substantial regrowth of corals on continental shelves occurred (Vecsei and Berger, 2004). Detailed reconstruction of deep water $[CO_3^{2-}]$ changes is critical for evaluating the influence of different factors on Holocene atmospheric CO₂ (Ridgwell et al., 2003; Elsig et al., 2009; Menviel and Joos, 2012). Due to its detailed features and minimal influence from bioturbation at a key location in the Southern Ocean, our record provides exceptional constraints for models to better quantify the relative contributions of various processes to the 20 ppmv rise in atmospheric CO₂ since ~8 ka (Fig. 4H) (Monnin et al., 2001).

8. Increased interocean deep water exchange during HS1

An intriguing feature of our record is the \sim 7 µmol/kg decline in $[CO_3^{2-}]$ during HS1 (Fig. 4B), which contrasts with contemporary $[CO_3^{2-}]$ increases previously observed in the deep Indian and Pacific Oceans (Yu et al., 2010a). It appears that the $[CO_3^{2-}]$ decline mainly occurred during the late HS1 (14.5–16.6 ka) (Fig. 4B). Two-phase changes during HS1 have been observed in many, but not all (such as Pa/Th: Fig. 4A), high-resolution marine and ice core records (Broecker and Putnam, 2012). Since our $[CO_3^{2-}]$ record is the first to resolve millennial timescale changes in the deep South Atlantic, it would be premature at this stage to discuss two-phase $[CO_3^{2-}]$ changes within HS1 without more records of equal resolution. We thus treat the $[CO_3^{2-}]$ decline as occurring broadly during HS1, making no attempt to interpret features within HS1. We acknowledge that if the two-phase $[CO_3^{2-}]$ change is confirmed by additional records in the future, then our interpretation may need to be revised.

The $[CO_3^{2-}]$ decline during HS1 is surprising and counterintuitive, given the intensified upwelling in the Southern Ocean suggested by increased opal fluxes (Fig. 4E) (Anderson et al., 2009). Everything else being equal, transfer of CO₂ from the deep ocean to the surface ocean and the atmosphere by upwelling should deplete DIC and hence increase $[CO_3^{2-}]$ in the deep Southern Ocean during HS1, opposite to our reconstruction (Fig. 4B). The decrease in $[CO_3^{2-}]$ at TNO57-21 coincides with $\sim 0.2\%$ increase in benthic $\delta^{13}C$ (Fig. 4B, C) (Ninnemann and Charles, 2002), and this combination rules out the possibility that the observed decline in $[CO_3^{2-}]$ during HS1 reflects reduced penetration of high-[CO₃²⁻] and high- δ^{13} C NADW relative to low- $[CO_3^{2-}]$ and low- $\delta^{13}C$ LCDW (Fig. 1) (Key et al., 2004: Yu et al., 2010a). We can also dismiss a phytodetritus effect (Mackensen et al., 1993) on benthic δ^{13} C based on the high reproducibility of δ^{13} C (Ninnemann and Charles, 2002) and the absence of any correlation between δ^{13} C and $[CO_3^{2-}]$ at TNO57-21 (Section 4). Any increased organic matter respiration in deep water at the site would decrease both δ^{13} C and $[CO_3^{2-}]$, which is not observed during HS1. Instead, we propose in the following a new explanation that is consistent with all observations, which invokes increased admixture of a deep Pacific water mass as the cause of the concurrent δ^{13} C rise and $[CO_3^{2-}]$ drop in the deep Cape Basin.

Today, deep water $[CO_3^2^-]$ is lower in the Pacific Ocean than in the deep Cape Basin (Fig. 1). This $[CO_3^2^-]$ gradient was even greater during the LGM, as illustrated by comparing reconstructed $[CO_3^2^-]$ records from TNO57-21 and core MW91-9 GGC48 (0°, 161°E, 3400 m) (GGC48 hereafter) from the Western Equatorial Pacific (WEP; Figs. 1 and 4B) (Yu et al., 2010a). The two cores also display large contrasts in benthic δ^{13} C during the LGM, with Pacific values up to $\sim 0.5\%$ higher, despite similar Holocene values (Fig. 4C) (Ninnemann and Charles, 2002; Yu et al., 2010a). The lower glacial benthic δ^{13} C at TNO57-21 does not necessarily imply a greater burden of respired CO₂ at the site, because deep water δ^{13} C is further influenced by factors such as preformed values and air-sea exchange (Broecker and Maier-Reimer, 1992; McCave et al., 2008). But benthic δ^{13} C may be used to assess past deep water mixing (Curry and Oppo, 2005), and we find the deep water δ^{13} C in different sectors of the Southern Ocean and in the equatorial Pacific Ocean displayed much larger contrasts during the LGM, indicating reduced interocean exchange of deep water than today (Fig. 5). In addition, a larger $\Delta\Delta^{14}$ C gradient is observed between core TNO57-21 and WEP core MD01-2386 (1.1°N, 130°E, 2820 m) during the LGM (Fig. 4D) (Key et al., 2004; Broecker et al., 2007; Barker et al., 2010), further supporting the inferred glacial reduction in the interocean exchange of deep water.

Overall, therefore, we infer that the LGM ocean was characterized not only by reduced vertical mixing associated with enhanced stratification (Lund et al., 2011; Burke and Robinson, 2012), but also by an increased chemical dissimilarity between deep waters in the Atlantic and Pacific Oceans (Figs. 4B–D and 5). This combination supports the view (McCave et al., 2008) that deep water masses in the world's ocean basins were physically more isolated from each other during the LGM due to reduced lateral exchange via the Southern Ocean.

During the early deglaciation, the deep water $[CO_3^{2-}]$ gradient between TNO57-21 and GGC48 started to diminish, as $[CO_3^{2-}]$ at TNO57-21 fell and $[CO_3^{2-}]$ at GGC48 rose (Fig. 4B) (Yu et al., 2010a). The deep water $[CO_3^{2-}]$ at both sites reached comparable values during late HS1 (~15.8–14.6 ka), the only time when complete convergence in $[CO_3^{2-}]$ occurred over the last 28,000 years (Fig. 4B). During HS1, benthic δ^{13} C and $\Delta\Delta^{14}$ C at site TNO57-21 also converged with those at 3.4 and 2.8 km water depths in the WEP, respectively (Fig. 4C, D), as well as with those at 3.8 km water depth in the South Atlantic (Skinner et al., 2010) and 2.7–3.6 km water depth in the North Pacific (Galbraith et al., 2007) (Figs. S5, S6).

A change in each of our examined proxies by itself may be caused by multiple processes. For example, benthic δ^{13} C is further influenced by factors in addition to interocean exchange of deep water, including gas exchange and preformed water chemistry. Benthic $\Delta \Delta^{14}$ C may be complicated by changes in surface reservoir ages, but this has negligible influence on the HS1 $\Delta\Delta^{14}C$ convergence between deep South Atlantic and Pacific records (Fig. S7). However, an extraordinary coincidence would be required to explain the convergence observed in all three proxies by invoking simultaneous changes in the preformed chemistry of the different water masses. Instead, it is most straightforward to attribute the concurrent convergence of all three proxies to better mixing of deep waters between the South Atlantic and Pacific Oceans during HS1 than during the LGM. Our interpretation is also consistent with a wider suite of geochemical proxies including neodymium isotopes and authigenic uranium from TNO57-21 (Figs. S8, S9; SI text) (Sachs and Anderson, 2003; Piotrowski et al., 2005, 2012). It is worth noting that increased interocean deep water exchange during HS1 differs from ventilation of global abyssal ocean at the onset of B/A (see above), when the formation of low-DIC NADW was much strengthened compared to HS1 (Fig. 4A) (McManus et al., 2004).

9. Mechanism and implication for deglacial atmospheric CO₂ rise

Our inferred erosion of the spatial isolation of deep water masses during HS1 is roughly coeval with the intensified upwelling



Fig. 5. Bathymetric distributions of δ^{13} C during the LGM (A) and today (B). The large δ^{13} C dissimilarity shown in (A) suggests a poorly mixed deep ocean during the LGM. This is in stark contrast to much reduced δ^{13} C variability in the modern ocean (B), where deep waters are well mixed. There must have been an increase in lateral exchange of deep water from the LGM to today. Our data (Fig. 4) explain when (HS1) and how (increased lateral mixing) this increase occurred, and provide new insights into the global carbon cycle during the last deglaciation. Data source: LGM benthic δ^{13} C (curves in A) are from (McCave et al., 2008) and references therein; modern hydrographic data are compiled in the eWOCE dataset (http://www.ewoce.org/) and are for sites (curves in B) close to the locations of cores used for the LGM profile reconstructions in (A): S Atlantic – sites 7320/16288 (11.5° E, 49.6° S), S Indian – sites 7516/7522 (57.9° E, 47.7° S), S. Pacific – sites 11724/11727/7426 (175.9° E, 30.9° S), EQ Pacific – site 11690 (165° E, 0° N). LGM and Holocene averages for cores GGC48 and TN057-21 are shown by blue circles and red squares with error bars representing 1 standard deviation of values from the designated age intervals, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and breakdown of deep vertical stratification in the Southern Ocean during the rapid warming in Antarctica (Fig. 4E, I) (Barbante et al., 2006; Anderson et al., 2009). The synchronicity of these events suggests that they may be linked to one another by a common mechanism. Northern Hemisphere insolation-induced fresh water input into the North Atlantic at Last Glacial termination led to a reduction of NADW formation during HS1 (Fig. 4A) (McManus et al., 2004; Liu et al., 2009; He et al., 2013). Through atmospheric teleconnections, a NADW shutdown may also cause poleward displacement or strengthening of the Southern Hemisphere westerlies (McGlone et al., 2010; Putnam et al., 2010), as invoked previously to account for increased opal fluxes in the Southern Ocean (Fig. 4E) (Anderson et al., 2009). Changes in the southern westerlies may have increased lateral (zonal) exchange of deep waters around Antarctica (Ho et al., 2012) through more efficient transfer of momentum from the winds to the ocean at the critical latitudes of the Drake Passage (Toggweiler et al., 2006), while also enhancing the meridional overturning in the Southern Ocean via Ekman pumping (Toggweiler et al., 2006; Anderson et al., 2009; Morrison and Hogg, 2013) (Fig. 6).

The deep Pacific Ocean stores the largest amount of carbon in the ocean-land biosphere-atmosphere system today (Broecker, 1982; Key et al., 2004), and proxies suggest an even larger carbon stock in the deep Pacific during the LGM (Bradtmiller et al., 2010; Jaccard and Galbraith, 2012). Reduced glacial interocean mixing would have facilitated storage of low- $[CO_3^{2-}]$, old-¹⁴C, low-O₂ (Galbraith et al., 2007; Bradtmiller et al., 2010; Jaccard and Galbraith, 2012) and, presumably, high-DIC waters in the deep Pacific Ocean (Figs. 1 and 4B–D), contributing to low atmospheric CO₂ during the LGM (Fig. 4H) (Monnin et al., 2001). Whatever the nature of the physical processes responsible for increased lateral mixing during HS1, they must have contributed to the ventilation of CO₂ from the deep Pacific. Interocean exchange of deep waters is constrained to occur via the Southern Ocean, where enhanced vertical mixing during HS1 was recorded by the burial flux of biogenic opal (Fig. 4E) (Anderson et al., 2009). Consequently, it is reasonable to infer that a portion, although not necessarily all, of the deep water exchanging between the South Atlantic and Pacific Oceans was subject to entrainment by the processes driving vertical mixing, thereby enhancing the ventilation of DIC previously stored in deep Pacific waters.

Geochemical tracers cannot be used to quantify the relative contributions by vertical and lateral deep water exchange to the deglacial increase in deep ocean ventilation, but they inform us that both occurred. Recent modeling suggests that transport by the Antarctic Circumpolar Current (ACC; linked to lateral deep water exchange) is much less sensitive to changes in the southern westerlies than is meridional overturning circulation (Morrison and Hogg, 2013). However, the westerlies in their model runs are in a modern poleward-shifted position, under which condition ACC is possibly in an eddy-saturated state. By contrast, the transition from the LGM to HS1 might involve a much larger poleward shift in the position of the westerlies (possibly beginning from a position during the LGM equatorward of their modern location), which could impose a stronger impact on Southern Ocean hydrography. In light of the compelling evidence for homogenization of deep waters during HS1, and the implications for understanding climate-related changes in atmospheric CO2, we hope that our findings will encourage investigators to dig deeper into the processes involved and help reconcile the physical oceanographic models with paleoceanographic observations.

10. Conclusion

Using a high-resolution reconstruction of $[CO_3^2^-]$ in the deep South Atlantic, we describe the sequence of events that shaped the ocean carbon cycle and atmospheric CO₂ since the last ice age. During the initial phase of deglaciation, increased lateral exchange of deep water between the Pacific and Atlantic Oceans enhanced the ventilation of CO₂ from the deep sea by the contemporary intensification of vertical mixing. The initial chemical signature of North Atlantic Deep Water occurred during the Bølling (~ 14.5 ka),



Fig. 6. Schematic illustration of processes affecting deglacial interocean deep water exchange and CO_2 degassing. (A) LGM. (B) HS1. Compared to the LGM, deep South Atlantic–Pacific carbon exchange during HS1 was enhanced by increased meridional (isopycnal) mixing (Morrison and Hogg, 2013) and by increased Antarctic Circumpolar Current flow (Ho et al., 2012), probably due to a poleward shift and/or intensification of Southern Westerlies (Toggweiler et al., 2006; Anderson et al., 2009). By distributing CO_2 -rich deep Pacific waters around Antarctica, increased interocean mixing would have augmented CO_2 degassing in the Southern Ocean during the breakdown of vertical stratification (Anderson et al., 2009; Sigman et al., 2010); Burke and Robinson, 2012) and sea ice retreat (Bianchi and Gersonde, 2004; Divine et al., 2010) during HS1. Thicker lines indicate increased fluxes or wind stress. Figure is modified from Charles and Fairbanks (1992). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

while the principal Holocene feature of the record indicates extraction of alkalinity from seawater by $CaCO_3$ deposition on continental shelves. Our study provides an unprecedented high-resolution deep water $[CO_3^{2-}]$ record in the South Atlantic to improve our understanding of the global carbon cycle in the past.

Author contributions

J.Y. designed and managed the project and measured B/Ca. R.F.A. measured Th–U. J.Y. and R.F.A. developed interpretation and wrote the manuscript with assistance from all authors. Z.J. and F.Z. picked and prepared benthic foraminifera for B/Ca and ¹⁴C dating. All authors commented on the manuscript.

Acknowledgments

Core material used in this study was provided by the Lamont-Doherty Earth Observatory Deep-sea Sample Repository. We thank W.S. Broecker, X. Wang, P. De Deckker, S. Eggins, and B. Opdyke for discussions, P. Tomascak, B. Yan, and P. Wang for laboratory assistance, and Robbie Toggweiler and two anonymous reviewers for comments. This work is supported by ARC DP140101393, the Lawrence Livermore National Laboratory's Lawrence Fellowship Program, a Lamont-Doherty Postdoctoral Fellowship, and a Comer Science and Education Foundation Fellowship (JY), the CAS/SAFEA International Partnership Program for Creative Research Teams (JY/ZJ), the US NSF (RFA; OCE 0823507), and a contribution from Laureate Fellowship FL120100050 (EJR).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.quascirev.2014.02.018.

References

- Anderson, D.M., Archer, D., 2002. Glacial-interglacial stability of ocean pH inferred from foraminifer dissolution rates. Nature 416, 70–73.
- Anderson, R.F., Ali, S., Bradtmiller, L., Nielsen, S.H.H., Fleisher, M.Q., Anderson, B.E., Burckle, L.H., 2009. Wind-driven upwelling in the Southern Ocean and the deglacial rise in atmospheric CO₂. Science 323, 1443–1448.
- Anderson, R.F., Fleisher, M.Q., Lao, Y., Winckler, G., 2008. Modern CaCO₃ preservation in equatorial Pacific sediments in the context of late-Pleistocene glacial cycles. Mar. Chem. 111 (1-2), 30–46. http://dx.doi.org/10.1016/j.marchem.2007. 1011.1011.
- Barbante, C., Barnola, J.M., Becagli, S., Beer, J., Bigler, M., Boutron, C., Blunier, T., Castellano, E., Cattani, O., Chappellaz, J., Dahl-Jensen, D., Debret, M., Delmonte, B., Dick, D., Falourd, S., Faria, S., Federer, U., Fischer, H., Freitag, J., Frenzel, A., Fritzsche, D., Fundel, F., Gabrielli, P., Gaspari, V., Gersonde, R., Graf, W., Grigoriev, D., Hamann, I., Hansson, M., Hoffmann, G., Hutterli, M.A., Huybrechts, P., Isaksson, E., Johnsen, S., Jouzel, J., Kaczmarska, M., Karlin, T., Kaufmann, P., Kipfstuhl, S., Kohno, M., Lambert, F., Lambrecht, A., Lambrecht, A., Landais, A., Lawer, G., Leuenberger, M., Littot, G., Loulergue, L., Luthi, D., Maggi, V., Marino, F., Masson-Delmotte, V., Meyer, H., Miller, H., Mulvaney, R., Narcisi, B., Oerlemans, J., Oerter, H., Parrenin, F., Petit, J.R., Raisbeck, G., Raynaud, D., Rothlisberger, R., Ruth, U., Rybak, O., Severi, M., Schmitt, J., Schwander, J., Siegenthaler, U., Siggaard-Andersen, M.L., Spahni, R., Steffensen, J.P., Stenni, B., Stocker, T.F., Tison, J.L., Traversi, R., Udisti, R., Valero-Delgado, F., van den Broeke, M.R., van de Wal, R.S.W., Wagenbach, D., Wegner, A., Weiler, K., Wilhelms, F., Winther, J.G., Wolff, E., Members, E.C., 2006. One-to-one coupling of glacial climate variability in Greenland and Antarctica. Nature 444, 195–198. http://dx.doi.org/10.1038/Nature05301.
- Barker, S., Diz, P., vautravers, M., Pike, J., Knorr, G., Hall, I.R., Broecker, W., 2009. Interhemispheric Atlantic seesaw response during the last deglaciation. Nature 457, 1097–1102.
- Barker, S., Greaves, M., Elderfield, H., 2003. A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry. Geochem. Geophys. Geosyst. 4, 8407. http://dx.doi.org/10.1029/2003GC000559.
- Barker, S., Knorr, G., Vautravers, M., Diz, P., Skinner, L., 2010. Extreme deepening of the Atlantic overturning circulation during deglaciation. Nat. Geosci. 3, 567– 571.
- Bianchi, C., Gersonde, R., 2004. Climate evolution at the last deglaciation: the role of the Southern Ocean. Earth Planet. Sci. Lett. 228, 407–424. http://dx.doi.org/ 10.1016/j.epsl.2004.10.003.
- Bradtmiller, L., Anderson, R.F., Sachs, J., Fleisher, M.Q., 2010. A deeper respired carbon pool in the glacial equatorial Pacific Ocean. Earth Planet. Sci. Lett. 299 (3-4), 417–425. http://dx.doi.org/10.1016/j.epsl.2010.1009.1022.
- Broecker, W., 1982. Glacial to interglacial changes in ocean chemistry. Progr. Oceanogr. 2, 151–197.
- Broecker, W., Clark, E., Barker, S., Hajdas, I., Bonani, G., Moreno, E., 2007. Radiocarbon age of late glacial deep water from the equatorial Pacific. Paleoceanography 22, PA2206. http://dx.doi.org/10.1029/2006PA001359.
- Broecker, W., Maier-Reimer, E., 1992. The influence of air and sea exchange on the carbon isotope distribution in the sea. Glob. Biogeochem. Cycle 6, 315–320.
- Broecker, W., Putnam, A.E., 2012. How did the hydrologic cycle respond to the twophase mystery interval? Quat. Sci. Rev. 57, 17–25 http://dx.doi.org/10.1016/ j.quascirey.2012.09.024.
- Broecker, W.S., Peng, T.H., 1987. The role of CaCO₃ compensation in the glacial to interglacial atmospheric CO₂ change. Glob. Biogeochem. Cycle 1, 15–29.
- Brown, R.E., Anderson, L.D., Thomas, E., Zachos, J.C., 2011. A core-top calibration of B/Ca in the benthic foraminifers Nuttallides umbonifera and Oridorsalis umbonatus: a proxy for Cenozoic bottom water carbonate saturation. Earth Planet. Sci. Lett. 310, 360–368. http://dx.doi.org/10.1016/j.epsl.2011.08.023.
- Burke, A., Robinson, L.F., 2012. The Southern Ocean's role in carbon exchange during the last deglaciation. Science 335, 557–561. http://dx.doi.org/10.1126/ science.1208163.

- Charles, C.D., Fairbanks, R.G., 1992. Evidence from southern-ocean sediments for the effect of North-Atlantic deep-water flux on climate. Nature 355, 416–419. http://dx.doi.org/10.1038/355416a0.
- Corliss, B.H., 1985. Microhabitats of benthic foraminifera within deep-sea sediments. Nature 314, 435–438.
- Curry, W.B., Oppo, D., 2005. Glacial water mass geometry and the distribution of δ¹³C of ΣCO₂ in the western Altantic Ocean. Paleoceanography 20, PA1017. http://dx.doi.org/10.1029/2004PA001021.
- Divine, D.V., Koc, N., Isaksson, E., Nielsen, S., Crosta, X., Godtliebsen, F., 2010. Holocene Antarctic climate variability from ice and marine sediment cores: insights on ocean-atmosphere interaction. Quat. Sci. Rev. 29, 303–312. http:// dx.doi.org/10.1016/j.quascirev.2009.11.012.
- Elsig, J., Schmitt, J., Leuenberger, D., Schneider, R.R., Eyer, M., Leuenberger, M., Joos, F., Fischer, H., Stocker, T.F., 2009. Stable isotope constraints on Holocene carbon cycle changes from an Antarctic ice core. Nature 461, 507–510.
- Farrell, J.W., Prell, W.L., 1989. Climatic change and CaCO₃ preservation: an 800,000 year bathymetric reconstruction from the central equatorial Pacific Ocean. Paleoceanography 4, 447–466.
- Fleisher, M.Q., Anderson, R.F., 2003. Assessing the collection efficiency of Ross Sea sediment traps using Th-230 and Pa-231. Deep-Sea Res. II Topical Stud. Oceanogr. 50, 693–712. http://dx.doi.org/10.1016/S0967-0645(02)00591-X. PII: S0967-0645(02)00591-X.
- Foster, G.L., 2008. Seawater pH, pCO₂ and [CO₃²⁻] variations in the Caribbean Sea over the last 130 kyr; a boron isotope and B/Ca study of planktic foraminifera. Earth Planet. Sci. Lett. 271, 254–266. http://dx.doi.org/10.1016/j.epsl.2008.1004.1015.
- Galbraith, E.D., Jaccard, S.L., Pedersen, T.F., Sigman, D.M., Haug, G.H., Cook, M., Southon, J.R., Francois, R., 2007. Carbon dioxide release from the North Pacific abyss during the last deglaciation. Nature 449, 890–893.
- He, F., Shakun, J.D., Clark, P.U., Carlson, A.E., Liu, Z.Y., Otto-Bliesner, B.L., Kutzbach, J.E., 2013. Northern hemisphere forcing of southern hemisphere climate during the last deglaciation. Nature 494, 81–85. http://dx.doi.org/ 10.1038/Nature11822.
- Ho, S.L., Mollenhauer, G., Lamy, F., Martinez-Garcia, A., Mohtadi, M., Gersonde, R., Hebbeln, D., Nunez-Ricardo, S., Rosell-Mele, A., Tiedemann, R., 2012. Sea surface temperature variability in the Pacific sector of the Southern Ocean over the past 700 kyr. Paleoceanography 27. http://dx.doi.org/10.1029/2012pa002317. Artn Pa4202.
- Hodell, D.A., Charles, C.D., Sierro, F.J., 2001. Late Pleistocene evolution of the ocean's carbonate system. Earth Planet. Sci. Lett. 192, 109–124.
- Howard, W.R., Prell, W.L., 1994. Late Quaternary CaCO₃ production and preservation in the Southern Ocean – implications for oceanic and atmospheric carbon cycling. Paleoceanography 9, 453–482.
- Jaccard, S.L., Galbraith, E.D., 2012. Large climate-driven changes of oceanic oxygen concentrations during the last deglaciation. Nat. Geosci. 5, 151–156. http:// dx.doi.org/10.1038/Ngeo1352.
- Karlin, R., Lyle, M., Zahn, R., 1992. Carbonate variations in the Northeast Pacific during the Late Quaternary. Paleoceanography 7, 43–61. http://dx.doi.org/ 10.1029/91pa03077.
- Key, R.M., Kozyr, A., Sabine, C.L., Lee, K., Wanninkhof, R., Bullister, J.L., Feely, R.A., Millero, F.J., Mordy, C., Peng, T.H., 2004. A global ocean carbon climatology: results from Global Data Analysis Project (GLODAP). Glob. Biogeochem. Cycle 18. http://dx.doi.org/10.1029/2004GB002247.
- Lea, D., Bijam, J., Spero, H., Archer, D., 1999. Implications of a carbonate ion effect on shell carbon and oxygen isotopes for glacial ocean conditions. In: Fischer, G., Wefer, G. (Eds.), Use of Proxies in Paleoceanography: Examples from the South Atlantic. Springer-Verlag, Berlin Heidelberg, pp. 513–522.
- Lemieux-Dudon, B., Blayo, E., Petit, J.R., Waelbroeck, C., Svensson, A., Ritz, C., Barnola, J.M., Narcisi, B.M., Parrenin, F., 2010. Consistent dating for Antarctic and Greenland ice cores. Quat. Sci. Rev. 29, 8–20.
- Liu, Z., Otto-Bliesner, B.L., He, F., Brady, E.C., Tomas, R., Clark, P.U., Carlson, A.E., Lynch-Stieglitz, J., Curry, W., Brook, E., Erickson, D., Jacob, R., Kutzbach, J., Cheng, J., 2009. Transient simulation of Last Deglaciation with a new mechanism for Bolling-Allerod warming. Science 325, 310–314. http://dx.doi.org/ 10.1126/science.1171041.
- Lund, D.C., Adkins, J.F., Ferrari, R., 2011. Abyssal Atlantic circulation during the Last Glacial Maximum: constraining the ratio between transport and vertical mixing. Paleoceanography 26. http://dx.doi.org/10.1029/2010pa001938.
- Lutze, G.F., Thiel, H., 1989. Epibenthic foraminifera from elevated microhabitats: Cibicidoides wuellerstorfi and Planulina ariminensis. J. Foraminifer. Res. 19, 153–158.
- Lyle, M., Mix, A.C., Ravelo, A.C., Andreasen, D., Heuser, L., Olivarez, A., 2000. Millennial-scale CaCO₃ and C_{org} events along the Northern and central California margins: stratigraphy and origins. In: Lyle, M., Koizumi, I., Richter, C., Moore, T.C. (Eds.), Proceedings of the Ocean Drilling Program, Scientific Results, pp. 163–182.
- Mackensen, A., 2012. Strong thermodynamic imprint on recent bottom-water and epibenthic delta C-13 in the Weddell Sea revealed: implications for glacial Southern Ocean ventilation. Earth Planet. Sci. Lett. 317, 20–26. http:// dx.doi.org/10.1016/j.epsl.2011.11.030.
- Mackensen, A., Hubberten, H.-W., Bickert, T., Fischer, G., Fütterer, D.K., 1993. The δ^{13} C in benthic foraminiferal tests of *Fontbotia wuellerstorfi* (schwager) relative to the δ^{13} C of dissolved inorganic carbon in Souther Ocean deep water: implications for glacial ocean circulation models. Paleoceanography 8, 587–610.
- McCave, I.N., Carter, L., Hall, I.R., 2008. Glacial–interglacial changes in water mass structure and flow in the SW Pacific Ocean. Quat. Sci. Rev. 27, 1886–1908. http://dx.doi.org/10.1016/j.quascirev.2008.07.010.

- McGlone, M.S., Turney, C.S.M., Wilmshurst, J.M., Renwick, J., Pahnke, K., 2010. Divergent trends in land and ocean temperature in the Southern Ocean over the past 18,000 years. Nat. Geosci. 3, 622–626. http://dx.doi.org/10.1038/Ngeo931.
- McManus, J., Francois, R., Gherardi, J.-M., Keigwin, L., Brown-Leger, S., 2004. Collapse and rapid resumption of Atlantic meridional circulation linked to deglacial climate changes. Nature 428, 834–837.
- Menviel, L., Joos, F., 2012. Toward explaining the Holocene carbon dioxide and carbon isotope records: results from transient ocean carbon cycle—climate simulations. Paleoceanography 27. http://dx.doi.org/10.1029/2011pa002224.
- Menviel, L., Timmermann, A., Timm, O.E., Mouchet, A., 2011. Deconstructing the Last Glacial termination: the role of millennial and orbital-scale forcings. Quat. Sci. Rev. 30, 1155–1172. http://dx.doi.org/10.1016/j.quascirev.2011.02.005.
- Monnin, E., Indermuhle, A., Dällenbach, A., Fluckiger, J., Stauffer, B., Stocker, T.F., Raynaud, D., Barnola, J.M., 2001. Atmospheric CO₂ concentrations over the Last Glacial Termination. Science 291, 112–114.
- Morrison, A.K., Hogg, A.M., 2013. On the relationship between Southern Ocean Overturning and ACC transport. J. Phys. Oceanogr. 43, 140–148. http:// dx.doi.org/10.1175/Jpo-D-12-057.1.
- Ninnemann, U.S., Charles, C.D., 2002. Changes in the mode of Southern Ocean circulation over the last glacial cycle revealed by foraminiferal stable isotopic variability. Earth Planet. Sci. Lett. 201, 383–396.
- Opdyke, B.N., Walker, J.C.G., 1992. Return of the coral-reef hypothesis basin to shelf partitioning of CaCO₃ and its effect on atmospheric CO₂. Geology 20, 733–736.
- Piotrowski, A., Galy, A., Nicholl, J.A.L., Roberts, N., Wilson, D.J., Clegg, J.A., Yu, J., 2012. Reconstructing deglacial North and South Atlantic deep water sourcing using foraminiferal Nd isotopes. Earth Planet. Sci. Lett. 357–358, 289–297.
- Piotrowski, A., Goldstein, S.J., Hemming, S.R., Fairbanks, R.G., 2005. Temporal relationships of carbon cycling and ocean circulation at glacial boundaries. Science 307, 1933–1938.
- Putnam, A.E., Denton, G.H., Schaefer, J.M., Barrell, D.J.A., Andersen, B.G., Finkel, R.C., Schwartz, R., Doughty, A.M., Kaplan, M.R., Schluchter, C., 2010. Glacier advance in southern middle-latitudes during the Antarctic Cold Reversal. Nat. Geosci. 3, 700–704. http://dx.doi.org/10.1038/Ngeo962.
- Rae, J.W.B., Foster, G.L., Schmidt, D.N., Elliott, T., 2011. Boron isotopes and B/Ca in benthic foraminifera: proxies for the deep ocean carbonate system. Earth Planet. Sci. Lett. 302, 403–413. http://dx.doi.org/10.1016/ j.epsl.2010.12.034.
- Raitzsch, M., Hathorne, E.C., Kuhnert, H., Groeneveld, J., Bickert, T., 2011. Modern and late Pleistocene B/Ca ratios of the benthic foraminifer Planulina wuellerstorfi determined with laser ablation ICP-MS. Geology 39, 1039–1042. http:// dx.doi.org/10.1130/G32009.1.
- Reimer, P.J., Baillie, M.G.L., Bard, E., Bayliss, A., Beck, J.W., Blackwell, P.G., Ramsey, C.B., Buck, C.E., Burr, G.S., Edwards, R.L., Friedrich, M., Grootes, P.M., Guilderson, T.P., Hajdas, I., Heaton, T.J., Hogg, A.G., Hughen, K.A., Kaiser, K.F., Kromer, B., McCormac, F.G., Manning, S.W., Reimer, R.W., Richards, D.A., Southon, J.R., Talamo, S., Turney, C.S.M., van der Plicht, J., Weyhenmeyer, C.E., 2009. Intcal09 and Marine09 radiocarbon age calibration curves, 0–50,000 years cal BP. Radiocarbon 51, 1111–1150.
- Rickaby, R.E.M., Elderfield, H., Roberts, N., Hillenbrand, C.-D., Mackensen, A., 2010. Evidence for elevated alkalinity in the glacial Southern Ocean. Paleoceanography 25, PA1209. http://dx.doi.org/10.1029/2009PA001762.
- Ridgwell, A.J., Watson, A.J., Maslin, M.A., Kaplan, J.O., 2003. Implications of coral reef buildup for the controls on atmospheric CO₂ since the Last Glacial Maximum. Paleoceanography 18. http://dx.doi.org/10.1029/2003PA000893.
- Sachs, J.P., Anderson, R.F., 2003. Fidelity of alkenone paleotemperatures in southern Cape Basin sediment drifts. Paleoceanography 18. http://dx.doi.org/10.1029/ 2002pa000862. Artn 1082.
- Schmitt, J., Schneider, R., Elsig, J., Leuenberger, D., Lourantou, A., Chappellaz, J., Kohler, P., Joos, F., Stocker, T.F., Leuenberger, M., Fischer, H., 2012. Carbon isotope constraints on the deglacial CO₂ rise from ice cores. Science 336, 711–714. http://dx.doi.org/10.1126/science.1217161.
- Sigman, D.M., Boyle, E.A., 2000. Glacial/interglacial variations in atmospheric carbon dioxide. Nature 407, 859–869.
- Sigman, D.M., Hain, M.P., Haug, G.H., 2010a. The polar ocean and glacial cycles in atmospheric CO₂ concentration. Nature 466, 47–55.
- Sigman, D.M., Hain, M.P., Haug, G.H., 2010b. The polar ocean and glacial cycles in atmospheric CO₂ concentration. Nature 466, 47–55. http://dx.doi.org/10.1038/ Nature09149.
- Skinner, L., Fallon, S.J., Waelbroeck, C., Michel, E., Barker, S., 2010. Ventilation of the Deep southern ocean and deglacial CO₂ rise. Science 328, 1147–1151.
 Stuiver, M., Reimer, P.J., 1993. Extended ¹⁴C data-base and revised Calib 3.0 ¹⁴C age
- Stuiver, M., Reimer, P.J., 1993. Extended ¹⁴C data-base and revised Calib 3.0 ¹⁴C age calibration program. Radiocarbon 35, 215–230.
- Toggweiler, J.R., Russell, J.L., Carson, S.R., 2006. Midlatitude westerlies, atmospheric CO₂, and climate change during the ice ages. Paleoceanography 21, PA2005. http://dx.doi.org/10.1029/2005PA001154, 002006.
- Vecsei, A., Berger, W.H., 2004. Increase of atmospheric CO₂ during deglaciation: constraints on the coral reef hypothesis from patterns of deposition. Glob. Biogeochem. Cycle 18. http://dx.doi.org/10.1029/2003gb002147.
- Yu, J.M., Day, J., Greaves, M., Elderfield, H., 2005. Determination of multiple element/calcium ratios in foraminiferal calcite by quadrupole ICP-MS. Geochem. Geophys. Geosyst. 6, Q08P01. http://dx.doi.org/10.1029/2005GC000964.
- Yu, J.M., Elderfield, H., 2007. Benthic foraminiferal B/Ca ratios reflect deep water carbonate saturation state. Earth Planet. Sci. Lett. 258, 73–86. http://dx.doi.org/ 10.1016/j.epsl.2007.1003.1025.

- Yu, J.M., Elderfield, H., Greaves, M., Day, J., 2007. Preferential dissolution of benthic foraminiferal calcite during laboratory reductive cleaning. Geochem. Geophys. Geosyst. 8, Q06016. http://dx.doi.org/10.1029/02006GC001571.
 Yu, J.M., Elderfield, H., Piotrowski, A., 2008. Seawater carbonate ion-δ¹³C sys-
- Yu, J.M., Elderfield, H., Piotrowski, A., 2008. Seawater carbonate ion-δ¹³C systematics and application to glacial–interglacial North Atlantic ocean circulation. Earth Planet. Sci. Lett. 271, 209–220. http://dx.doi.org/10.1016/ j.epsl.2008.1004.1010.
- Yu, J., Broecker, W., Elderfield, H., Jin, Z.D., McManus, J., Zhang, F., 2010a. Loss of carbon from the deep sea since the Last Glacial Maximum. Science 330, 1084– 1087. http://dx.doi.org/10.1126/science.1193221.
- Yu, J., Foster, C.L., Elderfield, H., Broecker, W.S., Clark, E., 2010b. An evaluation of benthic foraminiferal B/Ca and 8¹¹B for deep ocean carbonate ion and pH reconstructions. Earth Planet. Sci. Lett. 293, 114–120. http://dx.doi.org/10.1016/j.epsl.2010.02.029.
- Yu, J., Anderson, R.F., Jin, Z.D., Rae, J., Opdyke, B.N., Eggins, S., 2013a. Responses of the deep ocean carbonate system to carbon reorganization during the Last Glacial–interglacial cycle. Quat. Sci. Rev. 76, 39–52. http://dx.doi.org/10.1016/ j.quascirev.2013.06.020.
- Yu, J., Thornalley, D.J.R., Rae, J., McCave, I.N., 2013b. Calibration and application of B/ Ca, Cd/Ca, and 8¹¹B in *Neogloboquadrina pachyderma* (sinistral) to constrain CO₂ uptake in the subpolar North Atlantic during the last deglaciation. Paleoceanography 28, 1–16. http://dx.doi.org/10.1002/palo.20024.
- Yu, J., Anderson, R.F., Rohling, E.J., 2014. Deep ocean carbonate chemistry and glacial-interglacial atmospheric CO₂ changes. Oceanography 27 (1), 16–25. http://dx.doi.org/10.5670/oceanog.2014.04.