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
[f] ARC 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 19 March 2014

Keywords:
Deep-sea
Carbonate ion
Interocean exchange
Atmospheric CO_2

ABSTRACT

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 CO_2 reduction during the last ice age. After ~9 μmol/kg decline during Heinrich Stadial 1, deep South Atlantic carbonate ion concentration rose by ~24 μmol/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 μmol/kg decline in deep water carbonate ion since ~10 ka is consistent with extraction of alkalinity from seawater by deep-sea $CaCO_3$ 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 CO_2 degassing from the Southern Ocean, and thus to an atmospheric CO_2 rise, during the early deglaciation.

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

---

* 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).

http://dx.doi.org/10.1016/j.quascirev.2014.02.018

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 CO_2 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 CO_2. 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 CO_2 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 ~4–9 ka) in TNO57-21 and the large sample size requirement for ^{14}C 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 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 ($R^2 = 0.00$, $P = 0.97$)

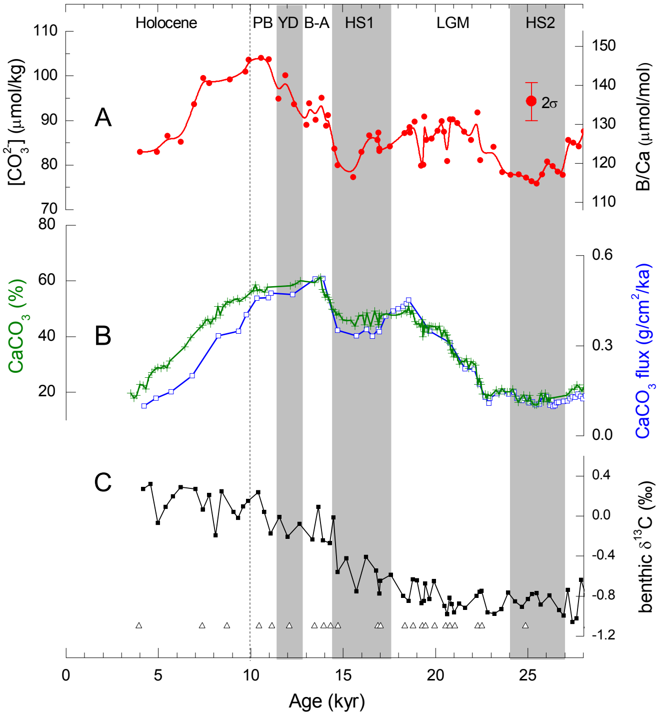

Fig. 2. Data from core TNO57-21. (A) *C. wuellerstorfi* B/Ca and reconstructed deep water $[CO_3^{2-}]$ (red circles) with b-spline smoothing (red curve). The error bar represents the average 2σ $[CO_3^{2-}]$ error from analytical uncertainty in B/Ca. (B) %$CaCO_3$ (green crosses) and ^{230}Th-normalized $CaCO_3$ 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.)

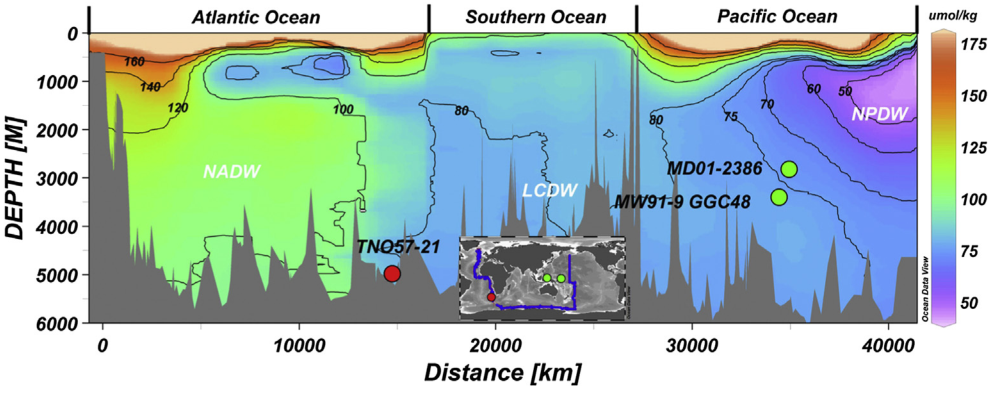

Fig. 1. Locations of core TNO57-21 and two cores in the Western Equatorial Pacific (WEP) against the pre-industrial seawater $[CO_3^{2-}]$. Inset shows the locations of hydrographic sites used for the $[CO_3^{2-}]$ section (Key et al., 2004). The map was generated using Ocean Data View (http://odv.awi-bremerhaven.de.). 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.)