



Mid-depth respired carbon storage and oxygenation of the eastern equatorial Pacific over the last 25,000 years

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ABSTRACT

A growing body of evidence suggests that respired carbon was stored in mid-depth waters (~1–3 km) during the last glacial maximum (LGM) and released to the atmosphere from upwelling regions during deglaciation. Decreased ventilation, enhanced productivity, and enhanced carbonate dissolution are among the mechanisms that have been cited as possible drivers of glacial CO₂ drawdown. However, the relative importance of each of these mechanisms is poorly understood. New approaches to quantitatively constrain bottom water carbonate chemistry and oxygenation provide methods for estimating historic changes in respired carbon storage. While increased CO₂ drawdown during the LGM should have resulted in decreased oxygenation and a shift in dissolved inorganic carbon (DIC) speciation towards lower carbonate ion concentrations, this is complicated by the interplay of carbonate compensation, export productivity, and circulation. To disentangle these processes, we use a multiproxy approach that includes boron to calcium (B/Ca) ratios of the benthic foraminifera *Cibicides wuellerstorfi* to reconstruct deep-water carbonate ion concentrations ([CO₃²⁻]) and the uranium to calcium (U/Ca) ratio of foraminiferal coatings in combination with benthic foraminiferal carbon isotopes to reconstruct changes in bottom water oxygen concentrations ([O₂]) and organic carbon export. Our records indicate that LGM [CO₃²⁻] and [O₂] was reduced at mid water depths of the eastern equatorial Pacific (EEP), consistent with increased respired carbon storage. Furthermore, our results suggest enhanced mixing of lower Circumpolar Deep Water (LCDW) to EEP mid water depths and provide evidence for the importance of circulation for oceanic-atmospheric CO₂ exchange.

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1. Introduction

The last deglaciation provides important insights into the nature of climate changes during the transition from glacial to interglacial conditions. Specifically, ice core records reveal deglacial periods of increasing boreal winter temperatures that are accompanied by coeval atmospheric CO₂ increases of ~50 ppmv during Heinrich Stadial 1 (HS1; ~17.5–14.7 ka) and ~30 ppmv during the Younger Dryas (YD; ~12.8–11.5 ka) (Hughen et al., 2000; Marcott et al., 2014; Monnin et al., 2001; Petit et al., 1999; Shakun et al., 2012). Over this same period, ice core records of atmospheric radiocarbon content record decreasing Δ¹⁴C values that cannot be accounted for solely by changes in cosmogenic production of ¹⁴C (Hain et al., 2014;

Hughen et al., 2004, 2006; Laj et al., 2002; Muscheler et al., 2004), requiring a transfer of carbon to the atmosphere from a ¹⁴C-depleted carbon reservoir (Sigman and Boyle, 2000). The overall magnitude and duration of the deglacial atmospheric CO₂ increase suggests that the oceans are the likely source of this excess CO₂ to the atmosphere, although the mechanism for this exchange is not fully understood (Broecker, 1982, 2003; Sigman and Boyle, 2000). It has been hypothesized that the oceans stored CO₂ during the last glacial period and released it to the atmosphere in pulses during deglaciation, thus driving the transition to warm interglacial conditions (Broecker, 2003; Chen et al., 2015; François et al., 1997; Marchitto et al., 2007; Sigman and Boyle, 2000; Stephens and Keeling, 2000; Toggweiler, 1999). While cooler ocean temperatures and enhanced oceanic CO₂ solubility likely account for ~15% of the total CO₂ drawdown during the last glacial period (Sigman and Boyle, 2000; Kohfeld and Ridgwell, 2009), other physical and biological mechanisms must be invoked to account for much of the remaining ~85%.

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Specifically, recent evidence suggests that mid depth (1–3 km) waters of the Pacific and Atlantic waters >2 km water depth were poorly ventilated during the last glacial maximum, possibly facilitating the accumulation of a respired carbon pool (LGM; Freeman et al., 2016; de la Fuente et al., 2015; Lund et al., 2011; Ronge et al., 2016; Sikes et al., 2000, 2016; Skinner et al., 2017; Thornalley et al., 2011; Umling and Thunell, 2017). Increased Southern Ocean stratification and/or sea ice extent could have contributed to poorly ventilated waters (Anderson et al., 2009; Keeling and Stephens, 2001; Watson and Naveira Garabato, 2006; Watson et al., 2015), allowing respired carbon to accumulate (Allen et al., 2015; de la Fuente et al., 2017; Yu et al., 2010, 2016) and radiocarbon to decay (Adkins, 2002; Broecker and Barker, 2007; Broecker and Clark, 2010). During deglaciation, a reduction of Southern Ocean sea ice and/or stratification would have allowed ventilation of this ^{14}C -depleted respired carbon reservoir to the atmosphere via upwelling regions, accounting for both the deglacial increase in atmospheric CO_2 and decrease in atmospheric radiocarbon content ($\Delta^{14}\text{C}$). Foraminiferal radiocarbon records document deglacial radiocarbon depletions in shallow subsurface waters (de la Fuente et al., 2015; Ezat et al., 2017; Lindsay et al., 2015; Sikes and Guilderson, 2016; Skinner et al., 2014; Umling and Thunell, 2017), consistent with advection of a respired carbon reservoir to the surface ocean. Furthermore, boron isotopic estimates of surface water pH (Kubota et al., 2015; Martínez-Botí et al., 2015), B/Ca estimates of carbonate ion concentration (Yu et al., 2010), and stable isotopic estimates of upwelling (Bova et al., 2015; Spero and Lea, 2002) suggest that the glacial respired carbon reservoir was released to the atmosphere from upwelling regions such as the eastern equatorial Pacific (EEP) during deglaciation.

However, many questions regarding this marine carbon reservoir still remain unresolved. The validity of radiocarbon-derived ventilation records has been challenged, with mantle sources of radiocarbon-depleted CO_2 suggested as possible contributors to the depleted ^{14}C values recorded in mid-depth cores (Lund et al., 2016; Hasenclever et al., 2017). This necessitates evidence of increased respired carbon storage in the mid-depth water masses to validate the radiocarbon-derived records of reduced glacial ventilation. It has also been suggested that a more efficient biological pump driven by increased nutrient supply (Kumar et al., 1995; Falkowski, 1997), or an alleviation of iron limiting conditions (Martin, 1990) may have worked to export more respired carbon from the surface to deep ocean during the last glacial period (Sarmiento and Toggweiler, 1984). Because the efficiency of the biological pump is modified, in part, by changes in oceanic ventilation, a coupling of these two processes could account for the full deglacial increase in atmospheric CO_2 (Galbraith and Jaccard, 2015; Sigman and Boyle, 2000).

Additionally, permafrost thawing (Crichton et al., 2016; Köhler et al., 2014; Tesi et al., 2016) and carbonate compensation (Broecker, 1982; Broecker and Peng, 1987) have been suggested as complementary mechanisms for driving CO_2 increases. Modeling studies suggest that carbonate compensation could account for up to 40 ppm of the glacial-interglacial atmospheric CO_2 change (Hain et al., 2010; Sigman et al., 2010). Increased oceanic CO_2 storage during the last glacial period would have shifted the equilibrium of dissolved inorganic carbon (DIC) towards CO_2 , resulting in decreased carbonate ion concentrations ($[\text{CO}_3^{2-}]$) and promoting carbonate dissolution. For every unit of CaCO_3 dissolved, seawater $[\text{CO}_3^{2-}]$ and alkalinity are increased in a 1:2 ratio, further increasing the capacity to store CO_2 . When the respired CO_2 reservoir is then ventilated to the surface ocean during deglaciation, the removal of CO_2 promotes CaCO_3 preservation resulting in a deglacial carbonate preservation spike (Berger, 1977; Broecker and Clark, 2001; Hodell

et al., 2001; Jaccard et al., 2009, 2010; Lalicata and Lea, 2011; Marchitto et al., 2005). Previously, carbonate chemistry has most often been constrained qualitatively, by developing records of CaCO_3 accumulation and dissolution (Anderson and Archer, 2002; Berger, 1977; Broecker et al., 1999; Broecker and Clark, 2001; Farrell and Prell, 1989). However, these qualitative methods can be influenced by factors other than changes in $[\text{CO}_3^{2-}]$, such as pore-water dissolution and changes in biological productivity (Broecker, 2008; Emerson and Bender, 1981; Jahnke et al., 1997). To overcome these limitations, several quantitative methods for estimating $[\text{CO}_3^{2-}]$ have been developed, including foraminiferal trace element analyses such as B/Ca (Yu and Elderfield, 2007) and Zn/Ca (Marchitto et al., 2000, 2005).

An increased understanding of the relative importance of ventilation, the biological pump, and carbonate compensation to the atmospheric CO_2 increases during the last glacial-interglacial transition is essential to understanding the role of the oceans in the oceanic-atmospheric transfer of CO_2 on glacial-interglacial cycles. Here, we present multi-proxy records of mid-depth (1.0–3.0 km) and deep-water (>3.0 km) chemistry for the eastern equatorial Pacific over the last 25,000 years to investigate the linkages between respired carbon storage, carbonate dissolution, and ocean ventilation during the last glacial-interglacial transition. Additionally, we evaluate regional trends in respired carbon variability by compiling published records of benthic foraminiferal B/Ca estimates of carbonate chemistry ranging from mid to deep-water depths.

2. Sample material and oceanographic setting

The Panama Basin is an important region for study of the biological pump because it is responsible for ~10% of global ocean primary productivity and is strongly connected to the Southern Ocean (Pennington et al., 2006). Primary productivity in this region is controlled by upwelling strength, thermocline depth, and supply of nutrients to the thermocline (Pennington et al., 2006). In particular, upwelling of the Equatorial Undercurrent (EUC) is an important source of nutrients and CO_2 to surface waters (Fiedler and Talley, 2006). At present, the Panama Basin serves as a major site for the efflux of CO_2 from the surface ocean to the atmosphere (Takahashi et al., 2002). The EEP is composed of primarily Lower Circumpolar Deep Water (LCDW) in deep water depths (>3.0 km) and Pacific Deep Water (PDW) at mid-depths (1.0–3.0 km). LCDW is formed from mixing of Antarctic Bottom Water (AABW) and North Atlantic Deep Water (NADW) in the Southern Ocean (Fiedler and Talley, 2006). The warming and freshening of LCDW forms PDW at mid-depths.

This study utilizes a transect of sediment cores collected from the Panama Basin during R/V Trident cruise TR-163 (Fig. 1, Table 1). For a detailed analysis of the last glacial-interglacial transition we focus on higher accumulation rate cores TR163-23 ($0^\circ 24.6' \text{N}$, $92^\circ 9.6' \text{W}$; 2,730 m) and TR163-20B ($0^\circ 47.4' \text{N}$, $93^\circ 50.4' \text{W}$; 3,200 m) collected from the western flank of the Galapagos margin along with TR163-25 ($1^\circ 39.0' \text{S}$, $88^\circ 27.0' \text{W}$; 2,650 m) collected from the Carnegie Ridge. In addition to the higher accumulation cores, three lower accumulation rate cores were collected from the Cocos Ridge (Fig. 1, Table 1). These six cores span a depth range of 1,620 to 3,200 m and are used here to evaluate and compare mid (~1–3 km) and deep (>3 km) water processes.

3. Methods

3.1. Age model development

The age model for TR163-23 was developed using a combination

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