1 **Southwest Pacific deep water carbonate chemistry linked to high southern latitude**
2 **climate and atmospheric CO₂ during the last glacial termination**

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13
14 **Abstract**

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16 A greater amount of CO₂ was stored in the deep sea during glacial periods, likely via
17 greater efficiency of the biologic pump and increased uptake by a more alkaline ocean.
18 Reconstructing past variations in seawater carbonate ion concentration (a major
19 component of alkalinity) enables quantification of the relative roles of different oceanic
20 CO₂ storage mechanisms and also places constraints on the timing, magnitude, and
21 location of subsequent deep ocean ventilation. Here, we present a record of deep-water
22 inorganic carbon chemistry since the Last Glacial Maximum (LGM; ~19-23 ka BP),
23 derived from sediment core RR0503-83 raised from 1,627 meters in New Zealand's Bay
24 of Plenty. The core site lies within the upper limit of southern-sourced Circumpolar Deep

Water (CDW), just below the lower boundary of Antarctic Intermediate Water (AAIW). We reconstruct past changes in bottom water inorganic carbon chemistry from the trace element and stable isotopic composition of calcite shells of the epibenthic foraminifer *Cibicidoides wuellerstorfi*. A record of ΔCO_3^{2-} ($\Delta\text{CO}_3^{2-} = [\text{CO}_3^{2-}]_{in situ} - [\text{CO}_3^{2-}]_{saturation}$) derived from the foraminiferal boron to calcium ratio (B/Ca) provides evidence for greater ice-age storage of respired CO_2 and reveals abrupt deglacial shifts in $[\text{CO}_3^{2-}]_{in situ}$ of up to $30 \mu\text{mol/kg}$ (5 times larger than the difference between average LGM and Holocene values). The rapidity of these changes suggests the influence of changing water mass structure and atmospheric circulation in addition to a decrease in CO_2 content of interior waters.

1. Introduction

Marine paleoceanographic records indicate that lower atmospheric CO_2 during ice ages, including the Last Glacial Maximum (LGM; ~19-23 ka BP), can primarily be attributed to greater carbon storage in the ocean (e.g., Burke and Robinson, 2012; Jaccard et al., 2009; Sikes et al., 2000; Yu et al., 2010). These deep sea records have independently confirmed earlier predictions for glacial carbon storage that were based on mass-balance calculations (e.g., Broecker, 1982). Between ~ 18 and 11 ka, ice core records of atmospheric gas composition reveal two periods of relatively steady pCO_2 rise, which are associated with warming Antarctic surface temperatures. These periods are separated by the Antarctic Cold Reversal (ACR), during which Antarctic temperatures briefly decreased (Monnin et al., 2001). Three episodes of more rapid CO_2 rise punctuate this

broader deglacial pattern (Marcott et al., 2014). During the two periods of Antarctic warming, upwelling intensified in the Southern Ocean, likely accompanied by CO₂-degassing from upwelled deep waters (Anderson et al., 2009). Sites of ocean CO₂ degassing have been inferred from surface-ocean records in the equatorial Pacific and Southern Ocean (Martinez-Boti et al., 2015). Additional constraints are needed to link these sites with interior water masses, which will improve estimates of changing ocean CO₂ storage during the deglaciation. Such constraints may be gleaned from records of past seawater inorganic carbon chemistry from key locations.

In this study, we determine the ratio of boron to calcium (B/Ca) in benthic foraminifer shells, a proxy for the calcite saturation state of ocean bottom waters as quantified by the parameter ΔCO_3^{2-} (Brown et al., 2011; Rae et al., 2011; Raitzsch et al., 2011; Yu and Elderfield, 2007). This parameter, representing the difference between the *in situ* carbonate ion concentration and the concentration that would be required for calcite saturation ($\Delta\text{CO}_3^{2-} = [\text{CO}_3^{2-}]_{in\ situ} - [\text{CO}_3^{2-}]_{saturation}$) is often used in lieu of the full calcite saturation parameter ($\Omega = [\text{Ca}^{2+}][\text{CO}_3^{2-}]_{in\ situ} / [\text{Ca}^{2+}][\text{CO}_3^{2-}]_{saturation}$) because the concentration of calcium ion in seawater is roughly constant on short (<1 Million year) timescales (Millero, 2006). Boron incorporation varies among benthic foraminifer species, with epifaunal species, particularly *Cibicidoides wuellerstorfi* (also called *Planulina wuellerstorfi*) exhibiting the highest B/Ca values and also the highest sensitivity to bottom water ΔCO_3^{2-} . No mechanism for the observed relationship between B/Ca and ΔCO_3^{2-} has yet been identified, but consistent results for benthic foraminiferal samples derived from different ocean basins and measured in different laboratories

provide strong empirical evidence for a reproducible and global pattern (Figure S1) (Rae et al., 2011; Yu and Elderfield, 2007). If temperature, salinity, and pressure are known, then the concentration of carbonate ion in seawater ($[\text{CO}_3^{2-}]_{in situ}$) may be calculated from ΔCO_3^{2-} .

When combined, the effects of lower glacial sea surface temperature, higher glacial seawater salinity, and lower carbon content of the terrestrial biosphere account for <10 ppmv of the observed 80 – 100 ppmv glacial-interglacial change (Sigman and Boyle, 2000). Seawater inorganic carbon chemistry (including $[\text{CO}_3^{2-}]$) is therefore thought to play a dominant role in driving atmospheric CO_2 fluctuations (Boyle, 1988; Archer et al., 2000; Sigman and Boyle, 2000). To draw down CO_2 to glacial levels, surface-ocean dissolved inorganic carbon (DIC) and/or total alkalinity (TA) must have changed. Specifically, it has been suggested that glacial CO_2 draw-down can be attributed to the combined effect of two processes: 1) greater efficiency of the biologic pump (a pathway that exports organic material to deeper ocean waters and to the sea floor), perhaps due to enhanced iron fertilization and/or ocean stratification (Martin, 1990), and 2) greater alkalinity of the glacial ocean due to dissolution of seafloor carbonates (Broecker and Peng, 1987; Sigman and Boyle, 2000; Anderson et al., 2014; Yu et al., 2014). These processes are thought to be linked: greater biologic pump efficiency leads to greater export of organic matter to the deep sea, and the resulting respired CO_2 has the potential to lower seawater pH and drive CaCO_3 dissolution, thereby increasing alkalinity (Sigman and Boyle, 2000; Archer et al., 2000). Carbonate dissolution and organic matter respiration have very different effects on deep water composition: dissolution raises

[CO₃²⁻] without exerting a strong impact on $\delta^{13}\text{C}$ of DIC, while respiration tends to drive both $\delta^{13}\text{C}$ and [CO₃²⁻] to lower values (Yu et al., 2008). If constraints can be placed on [CO₃²⁻] and $\delta^{13}\text{C}$ across glacial cycles, then new insight may be gained into the processes controlling atmospheric CO₂.

2. Core Site and Regional Oceanography

The sediment core RR0503-83 (36.7375°S, 176.6398°E, 1627 m) consists of overlapping, spliced trigger and piston cores collected by the RV Roger Revelle in New Zealand's Bay of Plenty (Figure 1). Core RR0503-83 is part of a multi-core transect spanning ~ 600 to 4000 m water depth, which was designed to enable geochemical reconstruction of water column properties in this region across ice age cycles (Sikes et al., submitted). The Bay of Plenty was targeted for its location relative to subsurface water formation areas and for the presence of volcanic tephras that provide age constraints independent of changes in marine ¹⁴C reservoir age. RR0503-83 was chosen for the present study based on its sedimentation rate (~ 9 cm/1,000 yr) and depth position near 1,600 m, making it likely to record changes in upper deep water inorganic carbon chemistry while also containing an adequate number of benthic foraminifera to enable trace element analysis at high resolution throughout the core.

Marine sedimentary drifts and basins in the southwest Pacific are well-situated to record changes in seawater inorganic carbon chemistry of waters exchanged between the Pacific Ocean, which contains CO₂-rich deep water, and the Southern Ocean, a region of major

117 air-sea CO₂ exchange (Takahashi et al., 2002; Takahashi et al., 2009). Circulation here is
 118 dynamic, with seasonally migrating fronts that are also thought to have shifted
 119 dramatically during past climate events (Nelson and Cooke, 2001; Sikes et al., 2009; De
 120 Deckker et al., 2012; Putnam et al., 2013a). At the southern end of New Zealand's South
 121 Island lies the Subtropical Front (STF), a sharp atmospheric and oceanic boundary with
 122 warm air and warm, salty Subtropical Water (STW) to the north and cooler air and cold,
 123 fresher Antarctic Surface Water (AASW) to the south (Orsi et al., 1995). The Bay of
 124 Plenty is located north of the North Island and just west of the Tonga-Kermadec Ridge,
 125 which runs roughly NNE-SSW near 180°W longitude. At the sea surface, flow is
 126 primarily west-to-east via the East Auckland Current (Brodie, 1960; Heath, 1985), but in
 127 the interior (~1000-2000 m), water masses exchange across the porous Tonga-Kermadec
 128 Ridge system (Bostock et al., 2013; Davis, 2005).
 129
 130 South of the STF, the Antarctic Circumpolar Current (ACC) transports waters eastward,
 131 and some of this deep circumpolar flow is diverted northward and eastward around the
 132 Campbell Plateau and Chatham Rise as the Deep Western Boundary Current (DWBC),
 133 while some intermediate and deep water is swept into the South Pacific anticyclonic gyre
 134 (Macdonald et al., 2009; Orsi et al., 1999; Reid, 1997). The northward flow of the
 135 DWBC is partly balanced by southward flow of Pacific Deep Water (PDW) (Sloyan and
 136 Rintoul, 2001; Talley, 2013). Thus, in the southwest Pacific region, the interior flow can
 137 be grouped into three main layers: abyssal flow (DWBC, with neutral density $\Upsilon_n > 28.16$
 138 kg/m³, northward), deep flow consisting of PDW and Circumpolar Deep Water (CDW,
 139 $\Upsilon_n \approx 27.8$ kg/m³, south/north, with southward PDW dominating), and Antarctic

Intermediate Water flow (AAIW, $\Upsilon_n \approx 27.15 - 27.7 \text{ kg/m}^3$, northward, with some east/west flow in the Bay of Plenty) (Ganachaud and Wunsch, 2000; Reid, 1997; Stanton, 2002; Talley, 2013).

As PDW flows southward out of the North Pacific, it gradually loses density by mixing with warmer overlying waters in the tropics (Talley, 2013) and accumulates nutrients and metabolic CO_2 along its path (Key et al., 2004). In the south Pacific, CDW is transported northwards out of the Southern Ocean into the same isopycnal ranges as PDW (Macdonald et al., 2009; Talley, 2013).

Today, site RR0503-83 is located within this depth range just above the low-oxygen core of PDW that was identified by Talley (2013) at $\sim 1700 \text{ m}$ at 35°S (neutral density of $\Upsilon = 27.8 \text{ kg m}^{-3}$, Figure S2). Nearby modern bottom water properties (oxygen concentration and $\delta^{13}\text{C}_{\text{DIC}}$ of $\sim 155 \mu\text{mol/kg}$ and $\sim 0.4 \text{ ‰}$, respectively) lie in between typical PDW and CDW values, consistent with the idea that the core site is currently influenced by a mixture of PDW and CDW, specifically, upper CDW (uCDW; McCave et al., 2008) (Figure S2a). The fact that the modern oxygen concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ near site 83 are lower than the ranges identified for Antarctic Intermediate Water (AAIW), and that the core site lies below the local salinity minimum (Figures 1B, S2b), confirm that this site does not currently lie within but rather below AAIW, which is generally identified as a high-oxygen, low-salinity tongue centered at $1,000 \text{ m}$ depth, ranging $\sim 500 - 1500 \text{ m}$ depending on location (Bostock et al., 2013) (Figure S2).

Thus, site 83 in the Bay of Plenty is expected to feel the effects of any changes in the chemical composition and/or latitudinal extent of deep waters (PDW/CDW), and it may also be influenced by significant changes in the thickness or vertical extent of AAIW.

3. Methods

3.1 Age control

Visible tephra layers within core RR0503-83 have been previously identified by their unique geochemical compositions and tied to a regional tephra-stratigraphic framework (Shane et al., 2006), the chronology of which is based on radiocarbon dating of volcanic deposits on land (Lowe et al., 2013). In addition, 9 radiocarbon dates were determined from analyses of foraminiferal calcite from the planktonic species *Globorotalia inflata* (Table 1). Radiocarbon concentrations were determined at Lawrence Livermore National Laboratories by accelerator mass spectrometry (AMS) on cracked, weak acid leached, foraminiferal tests. Using Calib v7, conventional ^{14}C ages were converted to calendar years according to the MARINE13 calibration curve (Reimer et al., 2013), assuming a constant reservoir age of 400 ± 100 years. In this region, previous work established that during the last 10,000 years (^{14}C age), surface ocean reservoir ages were ~ 400 years (Sikes et al., 2000), thus we assume a surface reservoir age of 400 years for the shallowest *G. inflata* sample in the JPC (16-17 cm, 2.99 – 3.22 cal ky BP, 95% confidence interval). Close agreement (≤ 600 year difference) between the age of the Mamaku tephra (7.9 – 8.1 cal ky BP) and the ages of stratigraphically adjacent *G. inflata*

samples, both above and below the tephra, provide additional evidence for small surface reservoir ages during the Holocene (Table 1, Figure 2). Together, the age constraints provided by the Holocene radiocarbon sample from JPC and several volcanic tephtras were used to construct age models for RR0503-83 JPC and TC (Figure 2). Throughout the manuscript, calibrated radiocarbon ages are reported in thousands of years before 1950 (hereafter, “ka”).

Radiocarbon results derived from early deglacial *G. inflata* samples (~ 20 to 15 ka) were not used in construction of the age models due to large uncertainty regarding surface reservoir age during this time interval (e.g., Sikes et al., 2000). Samples of *G. inflata* stratigraphically adjacent to terrestrially-dated tephtras confirm this. The marine reservoir ages for these intervals inferred from the difference between the *G. inflata* age and the known tephra age (e.g., Sikes et al., 2000) yield surprisingly old results (>2,000 yrs). These results are enigmatic, have been excluded from the age model, and are being investigated in a separate study. Results are shown in Table 1.

3.2 Core sampling and trace element analysis

From RR0503-83TC, 10 samples were derived from the 10 to 140 cm depth interval (~ 1 to 14 ka), and from RR0503-83 JPC, 59 samples were derived from the 17 to 180 cm depth interval (~ 2 to 27 ka) (Table 1). These records, overlapping between 2 and 14 ka, contain chronozones for the LGM (~19 to 23 ka; Chronozone Level 1 in Mix et al. (2001)), late LGM (18 to 20 ka), Heinrich Stadial 1 (HS1, ~18 to 14.5 ka, Barker et al.

(2009); Cheng et al., 2009), Antarctic Cold Reversal (14.5 to 12.9 ka, Blunier et al., (1997)), Younger Dryas Stadial (12.9 to 11.7 ka, Rasmussen et al., 2006), and Holocene (~11.7 to present, *ibid*).

Single-species samples were selected for trace element analysis from the LGM through the Holocene (~ past 10 kyr, sampling every ~ 1,000 years), with high-resolution (1 cm, ~ 200 yr) sampling between 19 and 12 ka. Sediment samples were washed with deionized water through a 63 μm sieve, and benthic foraminifers were hand-picked from the >250 μm size fraction under a light microscope. If there were not enough *C. wuellerstorfi* specimens within a single sample to yield 250 μg calcite, adjacent samples were combined to achieve an adequate sample weight, provided that the stable isotopes in the two samples were similar. Of the final 70 mono-specific samples analyzed for trace elements, 49 span 1 cm depth intervals (~100 years) and 21 are comprised of combined depth intervals (average age span for a combined sample = 300 years). Foraminiferal samples were partially crushed between two clean glass slides, transferred to acid-cleaned vials, and subjected to standard oxidative and reductive cleaning protocols to remove clay particles, organic matter, oxides, and adsorbed contaminants (Boyle & Keigwin, 1985, as outlined in Rosenthal et al., 1997).

Cleaned samples were dissolved in ultrapure 0.065 N HNO_3 and analyzed on a sector-field inductively coupled mass spectrometer (Thermo Scientific Element XR) at Rutgers University. To improve washout efficiency and reduce boron memory effect between samples, anhydrous ammonia gas was injected into a high purity quartz cyclonic spray

chamber, which raised the pH of the injected sample (> 9.14 , NBS scale; assessed by monitoring spray-chamber waste). This addition converts boric acid into soluble ammonium borate, which is more easily removed during wash out (Al-Ammar et al., 2000). Typical B blank levels are ~ 0.15 ppb ($< 2\%$ of [B] of foraminifera samples) and remain stable ($\pm 1\%$) throughout an analytical run (Babila et al., 2014). Any samples with Al/Ca, Ti/Ca, Mn/Ca and/or Fe/Ca values greater than 10 times the mean were assumed to be contaminated, and were excluded from further interpretation (5 total). Analyses were performed in December 2011 and August 2012, and repeated analysis of two consistency standards with B/Ca of 33.4 and 238.5 $\mu\text{mol/mol}$ yielded standard deviations of 2 and 4 $\mu\text{mol/mol}$, respectively. If the calcium concentration ([Ca]) of sample solutions is not constant, matrix corrections are sometimes necessary to account for any systematic influence of solution [Ca] on trace element ratios. To assess this potential effect, six matrix standards spanning 1.5 to 8 mM Ca were analyzed at the beginning and end of each ICP-MS run (sample [Ca] fell within this range). Matrix correction was not necessary for 66% of the total samples ($n = 42$), because B/Ca of matrix standards did not covary with solution [Ca] within those analytical runs. For the one analytical run in which B/Ca did decrease slightly with solution [Ca], corrections were minor: average matrix adjustment for B/Ca was 0.5 $\mu\text{mol/mol}$ (typically $< 1\%$ of measured values), and did not exceed 2.5 $\mu\text{mol/mol}$ ($n = 22$).

3.3 Estimation of seawater inorganic carbon chemistry

Paleo-seawater carbonate ion concentrations ($[\text{CO}_3^{2-}]$) were calculated in two steps. First, ΔCO_3^{2-} was derived from B/Ca according to the modern core-top calibration of Yu et al. (2013) shown in Figure S1 (including data from Brown et al., 2011; Rae et al., 2011; Raitzsch et al., 2011; Yu and Elderfield, 2007; Yu et al., 2013):

$$\text{B/Ca } (\mu\text{mol/mol}) = 1.14 (\pm 0.04) \times \Delta\text{CO}_3^{2-} (\mu\text{mol/kg}) + 176.6 (\pm 1.0)$$

Next, ΔCO_3^{2-} values were converted to $[\text{CO}_3^{2-}]_{in situ}$ according to the equation:

$$\Delta\text{CO}_3^{2-} (\mu\text{mol/kg}) = [\text{CO}_3^{2-}]_{in situ} - [\text{CO}_3^{2-}]_{sat}$$

where $[\text{CO}_3^{2-}]_{sat}$ is the $[\text{CO}_3^{2-}]$ required for calcite saturation ($\Omega = 1.0$), which depends on pressure, temperature, and salinity.

3.4 Isotope analysis

Between 1 and 5 tests of the epibenthic foraminifer *Cibicidoides wuellerstorfi* were handpicked from the $>150 \mu\text{m}$ sediment fraction for stable isotope analyses. These monospecific benthic foraminiferal samples were analyzed using a Micromass Optima Mass Spectrometer equipped with an automated Multiprep system at the Rutgers University Stable Isotope Laboratory. Samples were reacted in concentrated phosphoric acid for 15 minutes at 90°C . Measured values are reported using standard δ -notation as compared to

Vienna PeeDee Belemnite using an internal laboratory standard that is routinely calibrated with NBS-19 (1.95 ‰ $\delta^{13}\text{C}$, -2.20 ‰ $\delta^{18}\text{O}$) (Coplen et al., 1983).

4. Results

Average glacial B/Ca values at site 83 are $194 \pm 2 \mu\text{mol/mol}$ (± 2 standard errors of the mean, se) between 26 and 20 ka (Figure 3). Starting at ~ 20 ka, B/Ca decreases to $\sim 180 \mu\text{mol/mol}$, then rises through Heinrich Stadial 1 (HS1, $\sim 18 - 14.6$ ka) to the start of the Antarctic Cold Reversal (ACR, $14.5 - 12.8$ ka), to a maximum value of $\sim 212 \mu\text{mol/mol}$. Following the ACR, B/Ca remains slightly variable, but settles to average Holocene values higher than the LGM, $198 \pm 2 \mu\text{mol/mol}$ (± 2 se).

We constrain the influence of pressure, temperature, and salinity (p, T, S) on glacial-interglacial changes in $[\text{CO}_3^{2-}]_{\text{sat}}$ by calculating Holocene and LGM $[\text{CO}_3^{2-}]_{\text{sat}}$ from independent p, T, and S estimates. These parameters have the potential to influence $[\text{CO}_3^{2-}]_{\text{sat}}$ through their influence on carbonate equilibrium constants. Assuming eustatic sea-level rise from the coral records of Peltier and Fairbanks (2013) and a corresponding salinity decrease in a well-mixed ocean, we estimate the influence of deglacial sea level rise on bottom water p and S to be 135 dbar and 1.2 salinity units, respectively. In addition, bottom waters in the Pacific and Southern Oceans are estimated to have warmed $\sim 2^\circ\text{C}$ between the LGM and Holocene (Adkins et al., 2002; Elderfield et al., 2012; Gradstein et al., 2004; McCave et al., 2008). Although Mg/Ca was determined for these samples, T was not estimated because Mg/Ca in *C. wuellerstorfi* may be influenced by

additional factors (Yu and Elderfield, 2008). Using these constraints, the Holocene-LGM effects of p, T and S on $[\text{CO}_3^{2-}]_{\text{sat}}$ are estimated at -1.54, +0.45, and +0.38 $\mu\text{mol/kg}$, respectively, with a net effect ($\sim 0.8 \mu\text{mol/kg}$) that is smaller than the uncertainty in ΔCO_3^{2-} reconstructed from B/Ca. Consequently, the influence of p, T, and S can be considered negligible across the LGM-Holocene transition. Accordingly, we apply a constant $[\text{CO}_3^{2-}]_{\text{sat}}$ value of 58.5 $\mu\text{mol/kg}$ for the full record (calculated using modern GLODAP values of 2.74°C, 34.57 S, and 1,627 dbar, respectively; (Key et al., 2004)). Combining this constant value with B/Ca-derived ΔCO_3^{2-} estimates (Table 1, Figure 3) yields a $[\text{CO}_3^{2-}]$ record ranging from 50 to 80 $\mu\text{mol/kg}$ (Figures 3, 4, and 5).

The benthic foraminiferal $\delta^{13}\text{C}$ record for site 83 is described in detail in Sikes et al. (in preparation). During the LGM, $\delta^{13}\text{C}$ values of foraminifera from the benthic genus *Cibicidoides* ($\delta^{13}\text{C}_{\text{Cib}}$) hover near 0 ‰, rising over the course of the termination to ~ 0.7 ‰ by the late Holocene (Figure 3).

5. Discussion

5.1 Comparison of LGM and Late Holocene

Throughout much of the modern deep sea, patterns of $[\text{CO}_3^{2-}]$ and $\delta^{13}\text{C}$ of total dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) are dominated by the degradation of organic matter (Broecker and Peng, 1982; Yu et al., 2008). The generation of CO_2 with an isotope signature typical of marine organic matter has the effect of increasing DIC, decreasing $[\text{CO}_3^{2-}]$, and driving

average $\delta^{13}\text{C}_{\text{DIC}}$ to more depleted values (Figure 4, green line). Consequently, in modern deep waters, $[\text{CO}_3^{2-}]$ and $\delta^{13}\text{C}_{\text{DIC}}$ decrease in proportion as organic matter is respired, on average, by a „Redfield’ slope of 1/43 ‰ per $\mu\text{mol/kg}$ (Yu et al., 2008). This process is largely responsible for the very low $[\text{CO}_3^{2-}]$ and $\delta^{13}\text{C}_{\text{DIC}}$ in the modern deep Pacific (Yu et al., 2008). Superimposed upon this primary control are the effects of air-sea CO_2 exchange, which tend to deplete $\delta^{13}\text{C}_{\text{DIC}}$ of North Atlantic surface waters and enrich $\delta^{13}\text{C}_{\text{DIC}}$ of Southern Ocean surface waters relative to Redfield-based expectations in the modern ocean (Lynch-Stieglitz et al., 1995).

Our results imply changes in ocean storage of respired CO_2 during the deglaciation, with low- ΔCO_3^{2-} , low- $\delta^{13}\text{C}$ waters dominating during the LGM and higher- ΔCO_3^{2-} , higher- $\delta^{13}\text{C}$ waters prevailing in the Holocene. This deglacial transition is shown in a $\delta^{13}\text{C}$ - $[\text{CO}_3^{2-}]$ cross-plot (Figure 4), with LGM (blue) values ultimately rising to Holocene (red) values. In the background, modern-ocean seawater data (gray-scale points) illustrate how respiration tends to raise seawater DIC through the liberation of CO_2 from isotopically-depleted organic carbon, so that data in the lower left (dark circles) represent seawater characterized by low $[\text{CO}_3^{2-}]$, low $\delta^{13}\text{C}_{\text{DIC}}$, and higher DIC (typically corresponding to higher CO_2 , not shown), while data in the upper right (lighter circles) represent seawater characterized by higher $[\text{CO}_3^{2-}]$, higher $\delta^{13}\text{C}_{\text{DIC}}$, and lower DIC (Key et al., 2004). Considered in the context of the modern data, the paleo record suggests either 1) degassing of CO_2 from deep waters, or 2) a circulation change in this region leading to replacement of a relatively isolated, low- ΔCO_3^{2-} , CO_2 -rich LGM water mass by a better-ventilated water mass in the Holocene (e.g., a change in water mass boundary position).

These possibilities are not mutually exclusive, and both would result in a net loss of CO₂ from the ocean. For example, in the case of a water mass boundary shift, an increase in the volume of better ventilated AAIW and a decrease in the volume of poorly ventilated UCDW would drive a decrease in mean ocean CO₂ storage. This transition from low- ΔCO_3^{2-} , low- $\delta^{13}\text{C}$ to higher- ΔCO_3^{2-} , higher- $\delta^{13}\text{C}$ values at deep sites (between ~2000 – 4000 m) has also been observed in the Equatorial Pacific and Indian Oceans, though not uniformly across all sites (Yu et al., 2010). Possible driving mechanisms for this transition are discussed in sections 5.2 – 5.5.

The most robust and universal feature of the combined Indo-Pacific records is that the vertical [CO₃²⁻] profiles for Holocene and LGM are quite similar (Figure 5). At the same time, Pacific records of authigenic uranium and opal flux indicate that LGM DIC was higher than that of the Holocene (Bradtiller et al., 2010; Jaccard et al., 2009, 2012, 2014). Because the Indo-Pacific constitutes ~ 75% of the global ocean, these two observations – that LGM and Holocene deep [CO₃²⁻] values were similar while LGM DIC was higher – means that mean ocean alkalinity must also have been higher during the LGM (TA – DIC $\approx$ [CO₃²⁻]). This points to an important role for dissolution of seafloor CaCO₃ in lowering CO₂ during glacial periods (Bradtiller et al., 2010; Broecker, 1982; Yu et al., 2014b).

Our benthic B/Ca results, when combined with paleo-records and model estimates for [CO₃²⁻] of the surface ocean also imply changes in vertical chemical gradients, possibly although not necessarily linked to physical stratification, since the LGM. Low glacial

atmospheric $p\text{CO}_2$ values likely reflect a lower whole-ocean surface ocean $p\text{CO}_2$, corresponding to higher surface-ocean $[\text{CO}_3^{2-}]$, considering the rapid exchange of CO_2 between the surface ocean and atmosphere (Takahashi et al., 2002) and the minor net impact of reconstructed salinity, temperature, and terrestrial biosphere changes on glacial $p\text{CO}_2$ levels (Broecker and Peng, 1982; Sigman and Boyle, 2000; Hönisch and Hemming, 2005). Models and records of surface $[\text{CO}_3^{2-}]$ indicate glacial values at least 40-50 $\mu\text{mol/kg}$ greater than today (Barker and Elderfield, 2002; Lea et al., 1999). In contrast, our B/Ca reconstruction yields mid-depth LGM ΔCO_3^{2-} values $\sim 4 \mu\text{mol/kg}$ lower than Holocene values (Figure 3). In light of the observed surface ocean increase of $\sim 40\text{-}50 \mu\text{mol/kg}$, this benthic record requires that the surface-to-deep carbonate ion gradient in the Bay of Plenty was at least $45 \mu\text{mol/kg}$ greater during the LGM than it is today.

The enhanced vertical chemical gradient suggested by our data in turn suggests greater ocean stratification and/or a more efficient biologic pump operating in the southwest Pacific during the LGM, consistent with other sedimentary records of stratification and deep-water isolation in the Pacific and Southern Oceans from $\delta^{13}\text{C}$ and ^{14}C (Anderson et al., 2009; Burke and Robinson, 2012; Ninnemann and Charles, 2002; Sikes et al., 2000; Yu et al., 2014b). These results from Bay of Plenty core 83 are also consistent with a B/Ca record in the South Atlantic, interpreted to reflect greater stratification of the Southern Ocean during the LGM (Yu et al., 2014a). Enhanced biological productivity during glacial periods, perhaps the result of greater dust and nutrient input (Anderson et al., 2014; Lamy et al., 2014; Martinez-Garcia et al., 2014), may also have contributed to the larger glacial difference between surface and deep $[\text{CO}_3^{2-}]$ in the Southern

Hemisphere. Our observations in the Southwest Pacific indicate that the position of this large surface-to-deep $[\text{CO}_3^{2-}]$ gradient must have been located at some depth above site 83, which today sits at 1,627 meters water depth.

What drove the transition from the LGM state, characterized by a strong, relatively shallow chemical gradient, to the Holocene state, characterized by relatively well-ventilated interior waters and decreased carbon storage? Considering that the existing B/Ca records from the Pacific Ocean are either stable or rise only slightly across the transition from the LGM to the Holocene (Yu et al., 2010), the rapid and large shifts in B/Ca observed at site 83 during deglaciation are unexpected (Figure 3A). The two most prominent features of our deglacial record are (Figure 6C): 1) the decrease in $[\text{CO}_3^{2-}]$ between 20 and 18 ka, and 2) the overall increase in $[\text{CO}_3^{2-}]$ between ~ 17.5 and 14 ka. Below, we discuss these features in a greater regional context and propose a scenario for the last deglaciation.

5.2 Late glacial period, between 20 and 18 ka

Between ~ 20 and 18 ka, prior to the onset of HS1, B/Ca drops about $12 \mu\text{mol/kg}$, while $\delta^{13}\text{C}$ drops by about -0.14 ‰ from LGM values (Figure 3). In the following paragraphs, we discuss scenarios that could account for these observations, including an upward displacement of the AAIW-CDW boundary and/or a temporary injection of atmospherically derived carbon into the ocean.

The sharp decline in $[\text{CO}_3^{2-}]$ inferred from our B/Ca data is accompanied by a small but significant decline in atmospheric CO_2 (Figure 6B) (Marcott et al., 2014), as well as by an enrichment in the carbon isotopic composition of atmospheric CO_2 (Figure 6A; $\delta^{13}\text{C}_{\text{atm}}$) (Schmitt et al., 2012). All else being equal, an injection of CO_2 into seawater over a relatively short period of time ($< 2,000$ years, before significant carbonate compensation occurs; Archer et al., 2000) is expected to drive down $[\text{CO}_3^{2-}]$ (Zeebe and Wolf-Gladrow, 2001). Thus, collectively, these atmosphere and ocean records imply a brief increase in storage of ^{13}C -depleted CO_2 in upper circumpolar deep waters, perhaps by increased export efficiency of the biologic pump. An injection of ~ 12 Petagrams of carbon (12 PgC; the amount implied by a 6 ppm atmospheric CO_2 decline, assuming initial values of 198 ppm, 400 PgC) into $\sim 4\%$ of the total ocean volume (a rough estimate for upper CDW), would induce 1) a $[\text{CO}_3^{2-}]$ decrease of $\sim 12 \mu\text{mol/kg}$, similar to what we observe, and 2) a $\delta^{13}\text{C}$ decrease of $\sim 0.14 \text{‰}$ (assuming $\delta^{13}\text{C}$ of $\text{CO}_2 = -18\text{‰}$), which equals the observed decline between 21 and 18 ka.

An equally plausible explanation for these observations is an upward displacement of the boundary between relatively well-ventilated, CO_2 -poor intermediate waters (higher $[\text{CO}_3^{2-}]$ and $\delta^{13}\text{C}_{\text{DIC}}$) and relatively poorly-ventilated, CO_2 -rich circumpolar deep waters (lower $[\text{CO}_3^{2-}]$ and $\delta^{13}\text{C}_{\text{DIC}}$). Such a displacement might have been caused by a northward shift of the STF, which has the power to drive a shoaling of the ocean thermocline (Toggweiler, 2006; Hain et al., 2014). There is evidence for a northward STF shift at this time, including a sharp increase in % polar species of planktonic foraminifera in the South Atlantic at 19 ka (Barker et al., 2009), and changes in planktonic foraminiferal

stable isotopic records from the Bay of Plenty, which suggest changing hydrography near New Zealand at this time, likely tied to frontal movement (Schiraldi et al., 2014). Glacier re-advances in New Zealand culminating $18,220 \pm 500$ years ago (Putnam et al., 2013b) strongly suggest a northward displacement of the atmospheric STF during at least the latter part of this period, since such a shift would lead to temporary northward expansion of cold, Antarctic air masses, lowering snowlines in New Zealand and creating favorable conditions for glacier expansion.

Radiocarbon evidence provides additional support for this scenario, though the connection is less straightforward. Hain et al. (2014) demonstrated that negative discrepancies between observations of atmospheric $\Delta^{14}\text{C}$ and a carbon cycle box model could be reconciled by imposing a deepening of the thermocline during HS1 and Younger Dryas Stadial (YDS) in the model. Hain et al. (2014) also note a positive data-model discrepancy between 20 and 18 ka, which is not fully explained. Considering the evidence for a northward-shifted STF between 20 and 18 ka, we suggest that part of the model-data discrepancy might be reconciled by invoking a northward shift of the STF and a corresponding shoaling (thinning) of the thermocline. In other words, during HS1 and YDS, the thermocline may have deepened, increasing ventilation of interior waters and releasing old (depleted) $\Delta^{14}\text{C}$ to the atmosphere, while between 20 and 18 ka, the thermocline likely shoaled, reducing the volume of the ocean containing relatively young ($\Delta^{14}\text{C}$ - enriched) DIC in the ocean.

An alternative scenario to explain the observed decrease in B/Ca between 20 and 18 ka could involve a shift in ocean circulation that brought low- $[\text{CO}_3^{2-}]$ water into the Bay of Plenty from the North Pacific or Southern Oceans. However, there is currently no clear evidence for an influx from the North Pacific. To date, equatorial Pacific records have not yet demonstrated $[\text{CO}_3^{2-}]$ values lower than $\sim 70 \mu\text{mol/kg}$ (Yu et al., 2013), while the Bay of Plenty record approaches extremely low values of $\sim 55 \mu\text{mol/kg}$, suggesting that sites to the north are not likely sources of the low- $[\text{CO}_3^{2-}]$ water observed in the Bay of Plenty. A record of benthic $\delta^{11}\text{B}$ from the North Pacific has been interpreted as a pulse of local deep-water formation during the deglaciation (Rae et al., 2014), and although this water is expected to be characterized by low pH, and perhaps also low $[\text{CO}_3^{2-}]$, this deep-water formation pulse occurred almost 2 kyr too late to explain the $[\text{CO}_3^{2-}]$ decrease between 20 and 18 ka at site 83.

An influx of water from the south is plausible, though constraints on $[\text{CO}_3^{2-}]$ in Southern Ocean source waters are extremely scarce. One B/Ca record from a core in the Weddell Sea indicates that ΔCO_3^{2-} was quite low during the LGM, and then increased across the deglaciation (Rickaby et al., 2010). This record suggests that, immediately following the LGM, the Southern Ocean may have been a source of relatively low $[\text{CO}_3^{2-}]$ water to the southwest Pacific. Due to paucity of foraminifera, this record only contains 3 data points during the last 25 ky, and deep water temperatures at this site are poorly characterized, so reported ΔCO_3^{2-} can not yet be translated into $[\text{CO}_3^{2-}]$ for direct comparison with our record. More data from the Southern Ocean, accompanied by temperature and salinity

constraints, are needed to augment the existing data and firmly establish $[\text{CO}_3^{2-}]$ of deep waters in this region during the LGM and subsequent deglaciation.

In the absence of clear evidence for another driver, we suggest that a northward shift of the STF and accompanying changes in 1) biologic pump efficiency, and/or 2) changes in the depth of the boundary between better-ventilated AAIW and poorly ventilated UCDW constitute the most likely explanations for the available marine and terrestrial observations from this period. Further work is needed to confirm the combination of physical and biological factors that could have caused this somewhat unexpected apparent increase in CO_2 ocean storage during the 20 to 18 ka interval.

5.3 Heinrich Stadial 1 (~18 – 14.6 ka)

During HS1, $[\text{CO}_3^{2-}]$ at site 83 increased from $\sim 60 \mu\text{mol/kg}$ to almost $90 \mu\text{mol/kg}$ (Figure 6C). As discussed in section 5.1, on relatively short timescales, $[\text{CO}_3^{2-}]$ and pCO_2 in seawater are inversely related, such that an influx of CO_2 tends to drive a decrease in $[\text{CO}_3^{2-}]$, while a degassing of CO_2 tends to drive an increase in $[\text{CO}_3^{2-}]$ (e.g., Zeebe and Wolf-Gladrow, 2001). Thus, our observations are consistent with the idea that enhanced ventilation of the interior Southern Ocean occurred during this time (Anderson et al., 2009; Burke and Robinson, 2012). Degassing of metabolic CO_2 across this interval in our record is also supported by the concurrent increase in benthic $\delta^{13}\text{C}$, consistent with the reduced inventory of isotopically depleted, metabolic CO_2 . Further, when $\delta^{13}\text{C}$ and $[\text{CO}_3^{2-}]$ are combined (Figure 4), the transition from early HS1 (light blue dots) to late

HS1 (white dots) proceeds roughly along the Redfield slope, as defined by modern ocean data (gray dots), which is driven primarily by influx and efflux of metabolic CO₂ (Yu et al., 2008).

What drove this loss of CO₂ to the atmosphere? One way to enhance CO₂ loss from the ocean is to increase the upwelling of deep CO₂-rich waters to the sea surface. Such upwelling of interior waters may be induced by wind forcing or by buoyancy fluxes (Gordon, 1971; Lumpkin and Speer, 2007; Talley, 2013). These mechanisms are not mutually exclusive (Anderson and Carr, 2010), and both have been discussed as potential drivers of enhanced mixing and CO₂ outgassing during HS1 (Anderson et al., 2009; Barker et al., 2009; Denton et al., 2010; Hain et al., 2014), with buoyancy discussed primarily in the context of variable heat flux into the Southern Ocean. Another way to alter air-sea CO₂ fluxes is to change the efficiency of the biologic pump (e.g., by changing Fe fertilization). Although there is strong evidence that Fe fertilization likely played a role in CO₂ regulation on glacial-interglacial timescales, major differences in the structure of dust records and ocean upwelling records (Anderson et al., 2009; Martínez-Boti et al., 2015) point to a greater role for changing ocean physics than for declining Fe flux during HS1, although the latter certainly contributed. Below, we consider both terrestrial and marine records to assess the possible role of the westerly winds in degassing of interior waters during HS1.

The timing of HS1 has been defined from Northern Hemispheric paleoclimate records (e.g., Bard et al., 2000; Barker et al., 2009; Cheng et al., 2009). The start of HS1 at ~ 18

ka has also been identified as a key environmental turning point in many paleoclimate studies in the Southern Hemisphere, with evidence for a regime shift apparent in pollen, loess, glacial landforms, marine sediment, and ice core records (e.g., McGlone et al., 1984; Newnham et al., 1989; Barker et al., 2009; Parrenin et al., 2013; Putnam et al., 2013a; DeDeckker et al., 2012). Fortuitously, the widely distributed Rerewhakaaitu tephra (17.6 – 18.2 ka, 2σ range calculated with Intcal13, Table 1) provides a well-dated age marker in the greater Bay of Plenty region, allowing accurate alignment of marine and terrestrial records and providing confidence in the synchronous nature of these changes (Lowe et al., 2013; Newnham et al., 2003). Collectively, the geologic, chemical, and biological evidence points to a strong warming trend beginning shortly before deposition of the tephra and continuing through HS1. The rapidity and widespread nature of this warming has been interpreted as the result of a southward shift of the westerly winds, extending warm subtropical air masses poleward (Newnham et al., 2003; Putnam et al., 2013a).

Today, CDW and AAIW both experience adiabatic (wind-driven) upwelling in the Southern Ocean (Talley, 2013). Positioned at the upper limit of CDW today, site 83 is expected to be bathed by waters subject to wind-driven upwelling in the past as well. The timing of the $[\text{CO}_3^{2-}]$ rise coincides with increased upwelling indicated by opal accumulation near the Antarctic Polar Front (Anderson et al., 2009), expansion of warm-temperate podocarp forest in New Zealand (Newnham et al., 1989), a sharp decrease in marine mass accumulation rates (Carter et al., 2000), and rapid warming and glacier recession in both New Zealand and Patagonia (Denton et al., 1999; Putnam et al., 2013b).

The sharpness of some of these changes (e.g., $\sim 4^{\circ}\text{C}$ warming in New Zealand in ~ 800 years, Putnam et al., 2013b) seems more consistent with the idea of a hemisphere-wide shift in STF/westerly wind position, which can occur very rapidly, as opposed to the more gradual trapping of heat in the Southern Hemisphere ocean/atmosphere system of the thermal bipolar seesaw mechanism (Crowley, 1992; Stocker and Johnsen, 2003). This seesaw mechanism invokes the thermal inertia of the southern ocean-atmosphere system to explain links between rapid events in the North Atlantic region to more gradual changes observed in the South across deglaciations (Barker et al., 2011). Shifts in the balance of heat between the hemispheres are likely to play a role during this period, especially since this balance is intimately linked with wind strength and position (Toggweiler and Russell, 2008). However, to explain the rise in $[\text{CO}_3^{2-}]$ beginning at $\sim 17.5\text{-}18$ ka, coincident with several dramatic shifts convincingly linked by the Rerewhakaaitu ash, it appears that some nimble mechanism must be involved, and we suggest that shifting westerly wind position is the most likely candidate. Regardless of mechanism, the close coincidence in timing of the sharp rise in $[\text{CO}_3^{2-}]$ during late HS1 and the rapid rise in atmospheric CO_2 at 16.3 ka suggests a close link; it is possible that the $[\text{CO}_3^{2-}]$ rise reflects rapid ocean degassing at this time (Marcott et al., 2014).

In summary, our $[\text{CO}_3^{2-}]$ and $\delta^{13}\text{C}$ results are consistent with ventilation of CO_2 from mid-depth waters during HS1. The mechanism for this release is not definitively constrained by the data; however, when combined with other records from around the Southern Hemisphere these results are consistent with a southward shift of the southern

westerlies and deepening of the boundary between AAIW and uCDW/PDW, resulting in ventilation of CO₂ from a large volume of deep water.

5.4 The Antarctic Cold Reversal (14.5 – 12.8 ka)

During the ACR, [CO₃²⁻] at site 83 reached its maximum value in the 30 kyr record, and the average [CO₃²⁻] value was higher than that of the LGM or HS1 (Figure 6C). In the Southern Hemisphere, the ACR is a time of temporary atmospheric cooling and restratification of Southern Ocean surface waters (Anderson et al., 2009; Carter et al., 2008), and a plateau in the atmospheric CO₂ record (Marcott et al., 2014; Monnin et al., 2001). The interruption of the [CO₃²⁻] rise during this same period may be linked to this restratification and pause in CO₂ ventilation, events which have been attributed to a temporary northward shift of the westerly winds (Anderson et al., 2009).

Ocean records from water depths > 1000 m suggest that the ACR was also a time of increased vigor of North Atlantic Deep Water (NADW) formation (McManus et al., 2004), ultimately leading to a fundamental shift in global thermohaline circulation (Hodell et al., 2003; Ninnemann and Charles, 2002). The elevated [CO₃²⁻] in the Bay of Plenty at this time may also reflect a rapid influx of well-ventilated NADW into the Southern Ocean, which then exported a mixture of better-ventilated, warmer waters to the South Pacific. Local records of bottom water temperature, benthic foraminiferal δ¹³C, and ε_{Nd} support this scenario, with warming temperatures, enriched δ¹³C, and a more negative, Atlantic-like ε_{Nd} signature during the ACR (Elderfield et al., 2012; Noble et al.,

2013). However, the lower temporal resolution of these records makes it difficult to determine whether these changes occurred as rapidly as our observed increase in B/Ca of *C. wuellerstorfi* in the Bay of Plenty. Considering the relatively long pathway from the North Atlantic to the Southwest Pacific, it is difficult to envision how changes in NADW formation rate could cause such rapid changes in bottom water chemistry at the site of Core 83. The abrupt change in Core 83 makes a local forcing seem more likely.

5.5 Ventilation puzzles

Immediately preceding and following the ACR, CO₂ rises rapidly in two distinct pulses at 14.8 and 11.7 ka, respectively (Marcott et al., 2014). At the same time, B/Ca at site 83 rose rapidly, though the second B/Ca rise is not well resolved (Figure 6). Although we can not provide a full explanation based on the available data, the fact that rising B/Ca tends to coincide with atmospheric CO₂ pulses is intriguing.

Finally, it is puzzling that while [CO₃²⁻] in the Southwest Pacific rises in concert with CO_{2atm} during HS1, and even appears to rise rapidly during deglacial atmospheric CO₂ pulses described above, it does not rise consistently (even decreases slightly) during the second broad CO_{2atm} increase following the ACR (Figure 6). It is possible that, by the late deglaciation, excess CO₂ had been effectively stripped from this water mass, and ventilation proceeded from progressively deeper ocean layers. As Atlantic Meridional Circulation reinvigorated during the mid-termination (McManus et al., 2004), ocean ventilation may not have been driven by the same mechanism(s), sourced from the same

region(s), or escaped from the same region(s) (Martínez-Boti et al., 2015), thus rendering our site less sensitively linked to changes in $\text{CO}_{2\text{atm}}$. As increased input of NADW shifted the density structure of the Southern Ocean and surrounding basins during the deglaciation (Adkins, 2013), injecting heat to greater depths, this may have led to ventilation of progressively deeper water masses.

5.5 Conclusions

The surface-to-deep carbonate ion gradient in the Bay of Plenty was at least $45 \mu\text{mol/kg}$ greater during the LGM than it is today. These results indicate that a strong vertical chemical gradient must have been located at some depth above the core site (1,627 m), constraining this boundary to shallower depths than previous studies (Yu et al., 2014a). The shoaling and strengthening of this gradient during the LGM could have been caused by 1) a stronger biological pump with export production enhanced by dust fertilization, or 2) greater physical stratification during the LGM, which would have made the biological pump more efficient, even without stimulation of productivity. These two possibilities are not mutually exclusive. If the greater chemical gradient during the LGM reflects greater stratification of the water column, then the stratification must have occurred above the depth of the core site. Additional records that provide a more direct measure of water column density structure (e.g., $\delta^{18}\text{O}$ gradients) will help resolve changes in stratification in this region.

Between 20 and 18 ka, $[\text{CO}_3^{2-}]$ decreased rapidly at site 83, accompanied by a small decline in atmospheric CO_2 (Marcott et al., 2014) and an enrichment in $\delta^{13}\text{C}_{\text{atm}}$ (Schmitt et al., 2012) (Figure 6). Collectively, these atmosphere and ocean records imply a brief increase in storage of ^{13}C -depleted CO_2 in mid-depth waters. In light of the evidence for cooling at this time in parts of the Southern Hemisphere, we suggest that these changes were driven by a northward shift of the STF between 20 and 18 ka, which drew cold air masses northward and could have shifted the boundary between AAIW and CDW upward, and/or increased the efficiency of the biologic pump by modifying dust delivery to the ocean surface.

Throughout HS1 ($\sim 18 - 14.6$ ka), average $[\text{CO}_3^{2-}]$ increased as $\text{CO}_{2\text{atm}}$ rose (Marcott et al., 2014; Monnin et al., 2001), implying rapid ventilation of uCDW. The mechanism by which CO_2 may be ventilated is not constrained by our data; however, it appears that the drop in $[\text{CO}_3^{2-}]$ between 20 and 18 ka, as well as the dramatic rise in $[\text{CO}_3^{2-}]$ between 17 and 14 ka, are consistent with the expected response of water mass structure to meridional displacement of the westerly winds. An interesting feature of our record is that the relative rate of $[\text{CO}_3^{2-}]$ change and atmospheric CO_2 change ($\Delta[\text{CO}_3^{2-}]/\Delta\text{CO}_2$) is not constant across the termination; $[\text{CO}_3^{2-}]$ drops sharply between 20 and 18 ka during a relatively small $\text{CO}_{2\text{atm}}$ decline, and rises more slowly during HS1 during a more dramatic $\text{CO}_{2\text{atm}}$ rise. We speculate that the first large $[\text{CO}_3^{2-}]$ change was limited to a smaller, more constricted volume of water during the early termination, before glacial stratification broke down, and the later $[\text{CO}_3^{2-}]$ change during HS1 constituted a slightly muted $\Delta[\text{CO}_3^{2-}]/\Delta\text{CO}_2$ response due to the involvement of a much larger ocean volume.

This idea is supported by the early divergent behavior of $[\text{CO}_3^{2-}]$ records from the South Atlantic (Yu et al., 2014a), East Equatorial Pacific (Yu et al., 2013), and southwest Pacific (this study), which later converge during HS1 (Figure 6C), suggesting a common influence and increased communication between these regions later in the deglaciation. Comparison of our relatively shallow benthic $[\text{CO}_3^{2-}]$ record from the southwest Pacific with one from the deeper South Atlantic reveals that $[\text{CO}_3^{2-}]$ began to rise at the shallower site first (~ 17 ka), with $[\text{CO}_3^{2-}]$ at the deeper site rising later (~ 16 ka; Figure 6C). Assuming that rising $[\text{CO}_3^{2-}]$ indicates loss of CO_2 gas from seawater, these results suggest that CO_2 was ventilated to the atmosphere from progressively deeper layers during the deglaciation.

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Core	Depth		Age	95% confidence bounds			Notes
	cm	cm		ka	ka	ka	
83 JPC	16	17	3.1	3.0	3.2		Calculated from ¹⁴C age BP (<i>G. inflata</i>), MARINE13
83 JPC	23	24	13.1	13.0	13.3		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 JPC	24	25	13.6	13.5	13.8		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 JPC	24	25	13.7	13.6	13.9		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 JPC	26	27	14.0	13.8	14.2		Waiohau tephra (recalculated with SHCAL13), position inferred from coarse fraction peak
83 JPC	35	36	17.8	17.7	18.0		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 JPC	35	36	17.9	17.7	18.0		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 JPC	36	37	18.2	18.0	18.3		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 JPC	36	37	18.1	17.9	18.3		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 JPC	64	68	17.9	17.6	18.2		Rerewhakaaitu tephra (recalculated with SHCAL13)
83 JPC	65	66	19.8	19.6	20.0		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 JPC	66	67	20.6	20.4	20.9		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 JPC	68	69	21.8	21.5	22.0		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 JPC	76	77	21.6	21.3	21.8		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 JPC	107	108	23.3	23.0	23.5		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 JPC	106	108	22.1	21.9	22.3		Okareka tephra (recalculated with SHCAL13)
83 JPC	158	164	25.4	25.2	25.6		Kawakawa/Oruanui tephra (Vandergoes et al., 2012)
83 JPC	262	271.5	35	--	--		Hauparu tephra (Shane et al., 2006)
83 TC	9	10	0.63	0.61	0.65		Kaharoa tephra (Lowe et al., 2013)
83 TC	57	58	6.6	6.0	7.1		Tuhua tephra (Lowe et al., 2013)
83 TC	70	71	8.0	7.9	8.1		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 TC	72	73	8.0	7.9	8.1		Mamaku tephra (recalculated with SHCAL13)
83 TC	73	74	8.7	8.6	8.8		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 TC	74	75	8.9	8.8	9.0		Calculated from ¹⁴ C age BP (<i>G. inflata</i>), MARINE13
83 TC	125	134	14.0	13.8	14.2		Waiohau tephra (recalculated with SHCAL13)

Table 1. Age constraints for core RR0503-83 JPC and TC. Radiocarbon (¹⁴C) ages were calculated assuming a constant 400-year reservoir age for the surface ocean; 95% confidence bounds are 2σ age ranges derived using the MARINE13 calibration (Reimer et al., 2013). The ages of tephras in time intervals in which the INTCAL13 and INTCAL09 calibration curves do not significantly differ were not recalculated, and are taken from Lowe et al. (2013).

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Figure 1. (A) Location of sediment core RR0503-83 in the Bay of Plenty. (B) Salinity (black lines) and $[\text{CO}_3^{2-}]$ (colors) of the P15 transect from the World Ocean Circulation Experiment (drawn from “X” to “Y” on Panel A). The Subtropical Front (STF, dotted line) typically lies between 10°C and 12°C temperature contours at 100 m depth; the Subantarctic Front (SAF) can be approximated by the 7°C contour at 200 m depth in the Australian sector of the Southern Ocean, and the Antarctic Polar Front (APF) lies near the 2°C contour between 0-100 m depth (Belkin and Gordon, 1996). AAIW = Antarctic Intermediate Water; CDW = Circumpolar Deep Water; AABW = Antarctic Bottom Water; PDW = Pacific Deep Water. $[\text{CO}_3^{2-}]$ contours were calculated in Ocean Data View from the GLODAP dataset (Key et al., 2004).

Figure 2. Age models for RR0503-83 TC and JPC (black lines). Black circles indicate radiocarbon dates on planktonic foraminifera (*G. inflata*); gray vertical bars indicate volcanic tephras.

Figure 3. Geochemical records from site RR0503-83 (1627 m) in New Zealand's Bay of Plenty: A) ΔCO_3^{2-} reconstructed from B/Ca of *C. wuellerstorfi* calcite using the linear calibration of Yu et al. (2013), B) $\delta^{13}\text{C}$ and C) $\delta^{18}\text{O}$ from *Cibicidoides* specimens. Open symbols represent trigger-core (TC) data; closed (black) symbols represent jumbo piston core (JPC) data. Analytical uncertainties are based on replicate analysis of consistency standards ($\pm 1\sigma$). Between ~20-18 ka (gray vertical band), ΔCO_3^{2-} drops sharply, then rises through Heinrich Stadial 1 (HS1, yellow vertical band), eventually reaching the highest values of the record during the Antarctic Cold Reversal (ACR, blue vertical band). Average B/Ca values for the Holocene and LGM are 198 ± 2 and 194 ± 2 $\mu\text{mol/mol}$, respectively.

Figure 4. Relationships between benthic $\delta^{13}\text{C}$ and B/Ca-derived $[\text{CO}_3^{2-}]$ at site RR0503-83 since 26 ka. Green line is the average ‘Redfield’ slope at a rain ratio of $C_{\text{org}}:C_{\text{C}}$ of 4:1 (Yu et al., 2008). Observed changes in $\delta^{13}\text{C}$ exceed the whole-ocean $\delta^{13}\text{C}_{\text{DIC}}$ change ($\sim +0.34\text{‰}$; Peterson et al., 2014), indicating that this record reflects regional changes in the composition and/or extent of water masses in addition to the mean ocean $\delta^{13}\text{C}$ shift from LGM to Holocene. The mean shift can be largely explained by regrowth of the terrestrial biosphere (which preferentially incorporates light carbon); the diagonal dotted black line represents the expected change in seawater composition if 654 GtC are removed from the ocean (460 GtC to the biosphere, -24.3‰ , and 194 GtC to the atmosphere, -6.4‰). The general shift from low $[\text{CO}_3^{2-}]$, low $\delta^{13}\text{C}$ values during glacial times (dark blue symbols), to higher $[\text{CO}_3^{2-}]$, higher $\delta^{13}\text{C}$ values during the Holocene (red symbols), is consistent with a reduction in the inventory of ‘light’ respired CO_2 in the deep ocean, corresponding to a net transfer of CO_2 from the deep ocean to the atmosphere. Gray background symbols are modern ocean GLODAP data (Key et al., 2004) from the compilation of Schmittner et al. (2013). Water masses (yellow, green circles) are mean values derived from the WOCE P15 transect (see Fig. 1); LGM values = modern $- 0.34\text{‰}$.

Figure 5. Vertical profiles of carbonate ion concentration ($[\text{CO}_3^{2-}]$) for the LGM and Late Holocene reconstructed from B/Ca. Black diamonds represent averages from core RR0503-83 (this study) between 0 and 7 ka (filled symbol, $n = 7$) and 20 and 27 ka (open symbol, $n = 5$). Blue and green symbols have been previously published (Yu et al., 2013; Yu et al., 2008). Horizontal bars represent 1-sigma uncertainty of the mean. Figure modified from Yu et al. (2013).

Figure 6. Major shifts in $[\text{CO}_3^{2-}]$ of interior water (panel C, blue circles, reconstructed from benthic B/Ca at site 83, 1627 m depth) coincide with shifts in atmospheric CO_2 (panel B), implicating carbon transfer between ocean and atmosphere during the early termination. Between 20 – 18 ka, $[\text{CO}_3^{2-}]$ at site 83 drops rapidly, while the concentration of atmospheric CO_2 (red line) decreases by ~6 p.p.m. (WAIS Divide, Marcott et al., 2014) and the $\delta^{13}\text{C}$ of CO_2 (panel A, black circles) increases (Schmitt et al., 2012). These features are consistent with a temporary shoaling of the thermocline, intensification of ocean stratification, and a brief increase in ocean CO_2 storage. During Heinrich Stadial 1 (HS1), $[\text{CO}_3^{2-}]$ rises with CO_2 , while $\delta^{13}\text{C}$ of CO_2 falls, consistent with steady ventilation of isotopically-light CO_2 from the ocean interior to the atmosphere.

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