Glacial water mass structure and rapid $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ changes during the last glacial termination in the Southwest Pacific

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Abstract

Changes in ocean circulation are thought to have contributed to lowering glacial atmospheric CO₂ levels by enhancing deep ocean sequestration of carbon that was returned to the atmosphere during glacial terminations. High-resolution benthic foraminiferal $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records from a depth transect of cores in the Southwest Pacific Ocean presented here provide evidence that both wind- and thermohaline-driven circulation drove CO₂ from the ocean during the last deglaciation. Shallow geochemical stratification in the glacial Southern Ocean was followed by a short pulse of rapid $\delta^{13}\text{C}$ enrichment to intermediate water depths during Heinrich Stadial 1, indicative of better-ventilated intermediate waters co-occurring with documented wind-driven upwelling in the Southern Ocean. Intermediate depth $\delta^{13}\text{C}$ enrichment paused at the start of the Antarctic Cold Reversal (~14.7 ka), implying a brief shallow restratification, while deeper layers were progressively flushed of $\delta^{13}\text{C}$ -depleted and $\delta^{18}\text{O}$ -enriched waters, likely caused by the increasing influence of deep waters sourced from the North Atlantic. The coincidence of atmospheric CO₂ increases with these geochemical shifts in both shallow and deep cores suggests that shifts in both atmospheric and oceanic circulation contributed to the deglacial rise of CO₂.

1. Introduction

Records of atmospheric CO₂ derived from Antarctic ice cores indicate that late Pleistocene glaciations were characterized not only by colder average temperatures but also by atmospheric CO₂ levels ~80-100 ppm lower than interglacial periods (e.g. Barnola et al., 1987; Monnin et al., 2001). Although no single mechanism can account for the full amplitude of past CO₂ variability, there is compelling evidence that during glacial intervals most of the missing CO₂ was sequestered in the deep ocean (Boyle, 1988; Broecker, 1982; Sigman and Boyle, 2000). Ocean circulation (both wind-driven and thermohaline) and the strength of the biologic pump all have the power to influence ocean-atmosphere CO₂ partitioning, and these processes are thought to have varied dramatically during past changes in climate, with each having a role in determining past atmospheric CO₂ levels (CO_{2atm}) (e.g. Denton et al., 2010; Jaccard et al., 2016; Schmittner and Lund, 2015; Sigman et al., 2010; Toggweiler et al., 2006).

The formation of cold, salty, dense North Atlantic Deep Water (NADW) is an essential process driving modern thermohaline circulation and ventilating the deep ocean today. In the past, changes in the Atlantic meridional overturning circulation (AMOC) are believed to have played an important role in reducing CO_{2atm}. Numerous lines of geochemical evidence indicate that the influence of northern-sourced waters was reduced during the last glacial maximum (LGM) and that the depth of AMOC-delivered, well-ventilated water masses shoaled to above 2000 m in the Atlantic (Curry and Oppo, 2005; Gebbie, 2014; Gherardi et al., 2009; Lund et al., 2011). In contrast, the volume of abyssal water masses sourced from the Antarctic appears to have increased measurably in the Atlantic basin (Curry and Oppo, 2005; Lynch-Stieglitz et al., 2007). The resulting rearrangement in the oceans' interior water masses is thought to have raised the depth of the boundary between well-ventilated and poorly-ventilated water masses, accompanied by changes in stratification and density distributions that contributed to sequestering CO₂ in the deep glacial ocean (Ferrari et al., 2014; Sigman et al., 2010; Toggweiler, 1999). On shorter, millennial timescales, abrupt variations in thermohaline circulation are thought to affect the distribution of heat between the northern and southern hemispheres (Stocker and Johnsen, 2003) as well as the distribution of carbon between the atmosphere and the ocean (Hain et al., 2014; Marcott et al., 2014; Schmittner and Lund, 2015).

At the end of the last glaciation, the transition to interglacial climate and ocean-atmosphere circulation conditions proceeded in several millennial-scale steps. Early in the deglaciation, AMOC-driven export of deep water that was shallower and had a diminished footprint during the LGM (Curry and Oppo, 2005) was even more constricted during Heinrich Stadial 1 (HS1; 18 – 14.5 ka) (Gherardi et al., 2009; McManus et al., 2004). AMOC subsequently recovered, reaching near modern-day strength during the Antarctic Cold Reversal/Bølling-Allerød (ACR/ BA; ~14.7 to 12.7 ka) only to suffer a second reduction in the Younger Dryas (YD; 12.9 – 11.7 ka) before reaching Holocene levels (Böhm et al., 2015; Gherardi et al., 2009; Lund et al., 2011; Lynch-Stieglitz et al., 2007; McManus et al., 2004). The synchrony of these millennial-scale ocean circulation variations with increases in CO_{2atm} concentration (Marcott et al., 2014; Monnin et al., 2001) links the rise in CO_{2atm} to a combination of physical and geochemical changes that released CO₂ from the deep ocean (reviewed in Sigman et al., 2010). Critically, it has been suggested that the frigid climatic conditions in the northern Atlantic that paused or altered AMOC in the glaciation, HS1, and the YD were linked to latitudinal shifts in atmospheric circulation, which in turn may have altered atmosphere-ocean CO₂ partitioning in critical regions of the Southern Ocean (Denton et al., 2010; Roberts et al., 2014; Toggweiler et al., 2006). The conundrum in deciphering the oceanic and atmospheric mechanisms initiating and propelling the CO₂ release (Denton et al., 2010; Hain et al., 2014; Shakun et al., 2012) is they are not mutually exclusive (Anderson and Carr, 2010), with both models and data suggesting they may be mechanistically linked (Anderson et al., 2009; Ferrari et al., 2014; Hain et al., 2014; Jaccard et al., 2016).

Air-sea gas exchange in the Southern Ocean plays a vital role in regulating atmospheric CO₂ (Takahashi et al., 2009). There, changes in the net flux of CO₂ in or out regulates the distribution of CO₂ between the ocean and atmosphere (Sigman and Boyle, 2000). Today, the downstream component of NADW, carbon-rich Circumpolar Deep Water (CDW; ~1600-3000 m), upwells in response to wind-driven divergence around Antarctica (e.g. Talley, 2013). Part of this upwelled CDW is transported northward as surface water, which warms and freshens while losing CO₂ to the atmosphere before sinking near the Subantarctic Front (SAF) to form Antarctic Intermediate Water (AAIW; 800-1600 m) (**Figure 1b**)(Orsi et al., 1995). Farther north, between the SAF and the northern

boundary of the Southern Ocean (the Subtropical Front; STF) (Belkin and Gordon, 1996), warmer, saltier and less dense Subantarctic Mode Water forms (SAMW; 400-800 m). North of the Southern Ocean, both AAIW and SAMW subduct and flow northward beneath the even saltier, but less dense, subtropical surface waters of the Pacific Ocean. During transport in the shallow subsurface interior, these water masses retain the geochemical signal of atmospheric CO₂ exchange in the Southern Ocean that is a function of wind strength, position, water temperature, biological utilization of CO₂, and time of exposure at the surface (Takahashi et al., 2009). The dynamic between winds and interior water formation in the modern Southern Ocean is becoming better constrained through increased coverage by drifter deployments (Sallée et al., 2010). Understanding the evolution of ocean CO₂ storage through the deglaciation has been hampered by the paucity of oceanic records with sufficient vertical and temporal resolution to permit detailed comparison to ice cores.

A valuable tracer for CO₂ provenance in subsurface water masses is the $\delta^{13}\text{C}$ value of dissolved inorganic carbon (DIC). DIC is added to ocean water via CO₂ exchange with the atmosphere, riverine input, the respiration of organic matter, and the dissolution of CaCO₃ shells. The $\delta^{13}\text{C}$ of DIC reflects the cumulative effect of the processes that fractionate the isotopic composition while adding or removing that DIC from seawater, which include water temperature and photosynthesis in addition to the factors above (Curry et al., 1988). Accordingly, the $\delta^{13}\text{C}$ composition of the water masses described above is distinct. SAMW and AAIW have relatively positive $\delta^{13}\text{C}$ values that reflect CO₂ exchange with the cold polar atmosphere and photosynthesis, both enrich $\delta^{13}\text{C}$ of DIC. Ventilation of these shallower water masses in the Southern Ocean is so thorough that $\delta^{13}\text{C}$ respiration signal values are fully reset by these processes (Bostock et al., 2010; Lynch-Stieglitz et al., 1994; Lynch-Stieglitz et al., 1995) (**Figure 1b**). The lower $\delta^{13}\text{C}$ values in CDW reflect the addition of $\delta^{13}\text{C}$ -depleted respired CO₂ that has accumulated during transport and isolation from the atmosphere after formation in the North Atlantic as NADW (Curry et al., 1988). This respiration signal is not fully reset by air-sea exchange in the Southern Ocean. The vertical range in the $\delta^{13}\text{C}$ in the diagnostic region

of our study provides a portrait of the different histories of these water masses (See supplementary material SI #1 and **figure S2**).

The structure and source of interior water masses in the past can be constrained by the record of seawater $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ preserved in the calcium carbonate tests of benthic foraminifera (Charles and Fairbanks, 1992; Charles et al., 2010; Curry and Oppo, 2005; Hodell et al., 2003; Mackensen, 2012; Ninnemann and Charles, 2002). $\delta^{13}\text{C}$ profiles provide a picture of atmosphere CO_2 exchange or isolation and addition via the biologic pump (also called the soft tissue pump). The speciation of DIC in the mixed layer can also impact the shape of $\delta^{13}\text{C}$ profiles by influencing the rate at which the DIC pool's composition is reset (Galbraith et al., 2015). Nonetheless, $\delta^{13}\text{C}$ profiles provide valuable insight into ocean storage of respired CO_2 , particularly where complementary oxygenation and/or $[\text{CO}_3^{2-}]$ data are available (Allen et al., 2015; Yu et al., 2008). The $\delta^{18}\text{O}$ of foraminiferal calcite is a function of temperature and seawater $\delta^{18}\text{O}$, which is linked to salinity in the surface ocean via preferential evaporation of fresh, isotopically light water (LeGrande and Schmidt, 2006). Once water is subducted below the sea surface, $\delta^{18}\text{O}$ is not affected by any process other than mixing, and thus it acts as a conservative water mass tracer that is linked to seawater density (Adkins, 2013; Lynch-Stieglitz et al., 2007).

2. Materials and Methods

2.1 Core locations and stratigraphy

The principal portion of the transect is composed of five jumbo piston cores (JPC) collected from the Bay of Plenty, north and east of the north island of New Zealand. Two cores had adjacent trigger cores (TC) that were spliced to provide a continuous record into the Holocene. The Bay of Plenty is proximal to the New Zealand Volcanic Zone, allowing for the use of tephrastatigraphy to generate robust independent chronologies (Samson et al., 2005; Schiraldi et al., 2014; Shane et al., 2006). These 5 cores: 87TC/87JPC, 79JPC, 83TC/83JPC, H214, and 125JPC form the heart of the depth transect spanning modern water depths of 663, 1165, 1627, 2045, and 2541 m, respectively. Core 41JPC (3836 m) was collected from Hawke Bay with stratigraphy based on one tephra. To attain resolution in the deeper portion of the depth transect in

this study, previously unpublished planktonic $\delta^{13}\text{C}$ data were used from cores for which tephrostratigraphy was unavailable. Stratigraphy for cores RS147-GC07 (3300 m) and core Z2112 (2858m) were generated by linearly interpolating between planktonic ^{14}C AMS dates and converting to calendar ages using IntCal13 (Reimer et al., 2013) updating the published stratigraphy (Samson, 1998; Sikes et al., 2009). See SI #1 for details.

Southern Ocean sourced waters, including the rapidly advected shallow-subsurface SAMW and AAIW, penetrate well northward of our study site (Bostock et al., 2010), ensuring our transect provides a high-resolution, proximal cross-section of southern-sourced water masses that exchange with the Pacific Ocean throughout the last deglaciation (**Figure 1**). Results from this regional ensemble are consistent with published records from the greater Australia-New Zealand region, including those based on different foraminiferal species (Bostock et al., 2004; Lynch-Stieglitz et al., 1994; McCave et al., 2008; Pahnke and Zahn, 2005; Pahnke et al., 2003; Rose et al., 2010) (**Figure 2**, see SI # 3 and **Figure S4& S5**).

2.2 Sample preparation and isotopic analyses

Cores were sampled at 1 or 2 cm intervals across the deglacial portion and at coarser resolution (4 cm) through the glacial and Holocene. Dried sediments were washed to $>63\mu\text{m}$ and up to five tests of the mono-specific epibenthic foraminifer species, *Cibicidoides wuellerstorfi* (*C. wuellerstorfi*), also called *Planulina wuellerstorfi* (*P. wuellerstorfi*), were handpicked from the $>150\mu\text{m}$ fraction for stable isotopic analyses, where available. When insufficient, *C. kullenbergi* were also used. The benthic foraminiferal samples for cores 87TC/87JPC, 79JPC, 83TC/83JPC, and 125JPC were analyzed using a Micromass Optima Mass Spectrometer equipped with an automated Multiprep 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 lab standard that is routinely calibrated with NBS-19 (1.95 ‰ $\delta^{13}\text{C}$, -2.20 ‰ $\delta^{18}\text{O}$) (Coplen et al., 1983). Samples from cores RS147-GC07, H214, and core Z2112 were analyzed at the Central Science Laboratory, University of Tasmania as previously described (Samson et al., 2005; Sikes et al., 2009). For further details see SI #2.

2.3 Contour plot generation

Visualization of the multitude of benthic foraminiferal $\delta^{13}\text{C}$ data is enhanced by the generation of a smoothed contour plot of data from the total suite of cores. The contoured plot includes benthic foraminiferal $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data from all sample intervals in all cores, linearly interpolated to yield a uniform resolution of 200 years, reducing high-frequency variability. Uniformly gridded data were contoured at 0.1 ‰ intervals in Matlab. Core chronologies in this study are largely based on independent tephra stratigraphy (without $\delta^{18}\text{O}$ -tuning or matching), allowing $\delta^{18}\text{O}$ differences to be used to isolate and assess temperature and $\delta^{18}\text{O}_{\text{sw}}$ changes. Comparing the $\delta^{18}\text{O}$ of 1 ka and 21ka time slices in anomaly plots ($21\text{ka } \delta^{18}\text{O} - 1\text{ ka } \delta^{18}\text{O} = \delta^{18}\text{O}$ anomaly; Fig. 3C) facilitates visualization of water-mass salinity and/or temperature structure.

2.4 Calculation of time-slice averages and vertical differences

Vertical profiles in benthic foraminiferal $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were determined by compiling isotopic data for key time intervals (indicated by grey bars in **Figure 2B** and **Figure 2D**) to quantitatively estimate changes in stratification. The identified time periods are: Glacial (19-23 ka), Heinrich Stadial 1 (H1, 15.0-17.5 ka), Antarctic Cold Reversal (ACR; 12.9-14.5 ka), and Holocene (0-10.5 ka). Time slices were chosen to include intervals in which high quality, monospecific isotopic data are available, and to span key climate periods identified by independent paleo-climate records. Isotopic differences between cores at different depths were calculated from isotope records that had undergone a 5-point smoothing and subsequent resampling at 100-year intervals.

3. Results and Discussion

3.1 The Last Glacial Period

During the last glacial period, our 4 km depth-transect of cores reveals that the high latitude Southwest Pacific had a shallower, more intensified subsurface geochemical ($\delta^{13}\text{C}$) boundary than today (**Figure 3a**). One way to assess the gradient across this depth transect is to calculate the $\delta^{13}\text{C}$ difference between a shallow core and a deeper core ($\Delta\delta^{13}\text{C}_{\text{S-D}}$ between 663 and 2050m, roughly the depths of SAMW and CDW today). The $\Delta\delta^{13}\text{C}_{\text{S-D}}$ during the LGM was more than double that of the Holocene (~1.5‰ and

~0.7‰, respectively) with more than half of the $\Delta\delta^{13}\text{C}$ difference occurring between SAMW-depth water and intermediate depth water (663 and 1165 m; $\Delta\delta^{13}\text{C}_{\text{S-I}} = 0.8\text{‰}$; **Figure 2d&4c**). This contrasts with the modern ocean where SAMW and AAIW $\delta^{13}\text{C}$ are similar and a large $\delta^{13}\text{C}$ shift occurs below these water masses, at about 1600m (**Figure 1b&2d**). The shoaled geochemical interface during the glaciation implies that the boundary between well-ventilated and isolated water was shallower. Models predict that an expansion of Antarctic sea ice would result in a proportional shoaling of the isopycnals separating the upper and lower branches of the overturning circulation in the Southern Ocean (Ferrari et al., 2014). Our results suggest a shoaling of this interface by around 500 m in the LGM. This has been estimated as equivalent to a northward shift in the formation zone by ~500 km (Ferrari et al., 2014)

LGM $\delta^{13}\text{C}$ values below 1600 m were almost 1.0‰ more negative than Holocene values (**Figure 2 d &3a**), reaffirming results from previous $\delta^{13}\text{C}$ studies in the region (McCave et al., 2008) (**Figure S4 &S5**). Both enhanced surface export and/or increased physical isolation of deep water can lead to $\delta^{13}\text{C}$ depletion in subsurface waters (e.g. Mackensen, 2012). Local records of extremely old (>2,000 year) radiocarbon ages at these depths during the glacial (Sikes et al., 2016; Sikes et al., 2000; Skinner et al., 2010) confirm that increased export of fresh, ^{14}C rich organic matter from the surface ocean cannot explain $\delta^{13}\text{C}$ patterns in this region. A record of B/Ca-derived carbonate ion ($[\text{CO}_3^{2-}]$) from a core within our New Zealand transect (83 JPC, at 1627m depth) provides independent corroboration that a large proportion of the deep $\delta^{13}\text{C}$ depletion observed here was due to increased storage of respired CO_2 (Allen et al., 2015), rather than a change in the temperature of air-sea gas exchange. The greater LGM $\Delta\delta^{13}\text{C}_{\text{S-D}}$ differences seen in our depth transect combined with high local ^{14}C reservoir ages and B/Ca together provide strong support for the idea that increased respired carbon storage in combination with increased isolation of deep water was the mechanism driving this deep, $\delta^{13}\text{C}$ -depleted signal.

Our new dataset places the base of the glacial geochemical divide (i.e., the depth of most rapid $\delta^{13}\text{C}$ change) at ~1,500m, approximately 1,000m shallower than it sat in the South Atlantic (Hodell et al., 2003). Here in the Pacific, the isotopic difference between shallow

and deep water masses, $\Delta\delta^{13}\text{C}_{\text{S-D}}$ was $\sim 0.5\text{‰}$ less than it was in the Atlantic (Charles et al., 2010; Curry and Oppo, 2005; Hodell et al., 2003) (**Figure 2d**; see supplemental information for calculations and discussion). These inter-ocean differences suggest that although deep waters in the LGM South Pacific and Southern Atlantic were both more isolated from the atmosphere, the two basins were also more isolated from each other, supporting the idea of cross-basinal differences in deep water formation and communication during the LGM (McCave et al., 2008).

3.2 The Deglaciation

3.2.1 Heinrich Stadial 1

The high-resolution time series in our cores reveal rapid deglacial $\delta^{13}\text{C}$ variations in subsurface Southern Pacific waters, some of which correspond to $\text{CO}_{2\text{atm}}$ increases seen in high-resolution ice core records (Marcott et al., 2014; Monnin et al., 2001). During the second half of HS1, from ~ 16.5 -14 ka, several episodes of $\delta^{13}\text{C}$ enrichment deepened the LGM geochemical front from SAMW to AAIW depths in short, intense pulses that extended deeper than 1100m but less than 1600. The injection of enriched $\delta^{13}\text{C}$ to intermediate depths reduced the average $\Delta\delta^{13}\text{C}_{\text{S-I}}$ from 0.8‰ (glacial) to 0.1‰ (HS1) (**Figure 3a and 4c**). Notably, the peak of this enrichment coincided with a period of rapidly rising atmospheric CO_2 interspersed with abrupt CO_2 peaks (at ~ 16.3 and 14.8 ka) (Marcott et al., 2014)(**Figure 4a and c**). The timing of the $\delta^{13}\text{C}$ increase in waters at AAIW-depths mirrors the abrupt decrease observed in atmospheric $\delta^{13}\text{C}$ (**Figure 4b to g**) (Schmitt et al., 2012). This suggests a direct transfer of this isotopic signal from intermediate layers of the ocean to the atmosphere in the early deglaciation, although terrestrial sources may have contributed in later stages of the deglaciation (Schmitt et al., 2012).

The $\delta^{13}\text{C}$ enrichment pulse expressed in our ~ 1100 m core in HS1 appears to be widespread but confined to these shallow waters, as it is observed in several other regional benthic $\delta^{13}\text{C}$ records at similar depths (900 and 1200m; **Figure 4e**)(Bostock et al., 2004; Pahnke et al., 2003). Somewhat less than half the regionally observed $\delta^{13}\text{C}$ signal is accounted for in model simulations of deglacial AMOC changes that may have

affected the efficiency of the biological pump, but the rapid rise in $\text{CO}_{2\text{atm}}$ at 16.5ka is not simulated (Schmittner and Lund, 2015). This suggests the need for an additional mechanism to account for the full scale of these abrupt changes. Evidence for enhanced upwelling and southward wind shifts in the Southern Hemisphere at the same time (Anderson et al., 2009; Jaccard et al., 2016; Lamy et al., 2010; Putnam et al., 2010) provide a straightforward explanation for our observed signal in both amplitude and timing: A sudden southward shift in the westerly winds would have placed the locus of wind-driven air–sea exchange in the Southern Ocean in a more optimal location for ventilation (Toggweiler et al., 2006). The associated retreat of sea ice cover (Shemesh et al., 2002; Wolff et al., 2006) would have both increased the area available for that exchange and changed the sea-ice freshwater transport affecting water-mass transformation, thereby accelerating the upper limb of the overturning circulation (Abernathy et al., 2016). The combination would have amplified the flushing of respired CO_2 and its negative isotopic signal from intermediate waters to the atmosphere. CO_2 release during this time was likely enhanced by a coincident drop in dust-borne nutrient delivery that weakened the Southern Ocean’s soft tissue pump in the South Atlantic sector at this time driving CO_2 from deeper layers of the ocean (Jaccard et al., 2016). Evidence in our Pacific cores suggest that changed dynamics in shallow layers of the Indo-Pacific region had an impact on shallow ventilation. These dynamics may have worked in concert with other mechanisms making them a contributing, if not the dominant driving mechanism in the rapid rise of atmospheric CO_2 from ~16.5-14 ka.

The onset of the abrupt shallow ventilation interval seen in our record occurred ~ 1.2 ka later than the well-documented AMOC reduction at the start of HS1 (~17.8 ka) and ~1.5 ka prior to AMOC resumption (Gherardi et al., 2009; McManus et al., 2004). Instead, the onset of the enrichment episode seen in these Pacific cores coincided with changes occurring in the Southern Hemisphere, such as the retreat of sea ice (Shemesh et al., 2002; Wolff et al., 2006), increase in opal export (Anderson et al., 2009) and an abrupt retreat of both New Zealand and Patagonian glaciers attributed to warming summertime conditions, and/or a shift in the mean position of the Westerly Winds (Kaplan et al., 2008; Putnam et al., 2013). Collectively, these results imply that the Atlantic thermohaline circulation was not directly or fully responsible for the enriched $\delta^{13}\text{C}$ signal

at intermediate to shallow depths in the Southwest Pacific during HS1. Instead, we argue that the Pacific $\delta^{13}\text{C}$ enrichment was the result of enhanced air-sea gas exchange occurring in the Southern Ocean, which drove the early release of respired CO_2 from the shallower layers of the glacial ocean (Anderson and Carr, 2010; Gnanadesikan, 1999; Hain et al., 2014; Toggweiler et al., 2006). (**Figure 4a&f**).

3.2.2 Antarctic Cold Reversal

At the end of HS1, the depth of the $\delta^{13}\text{C}$ geochemical divide in the Southwest Pacific shoaled back above ~1100 m. This shoaling coincided with the onset of the ACR and with the start of a prolonged pause in the deglacial $\text{CO}_{2\text{atm}}$ rise between 14.5 and 13 ka (Marcott et al., 2014; Monnin et al., 2001). The ACR was a period of Southern Hemisphere cooling that was attended by a northward shift of the Southern Westerly Winds (Lamy et al., 2010; Putnam et al., 2010), sea ice expansion (Shemesh et al., 2002; Wolff et al., 2006), and a sharp and temporary reduction in Southern Ocean upwelling (Anderson et al., 2009). The resulting glacial-like northward displacement of the intermediate water ventilation region is thought to have reduced air-sea exchange in the Southern Ocean (Anderson et al., 2009; Ferrari et al., 2014) providing a plausible wind-driven mechanism for the reduced $\delta^{13}\text{C}$ between ~660 and 1500 m that is not fully explained by direct ocean circulation changes in models (Schmittner and Lund, 2015). Our Southwest Pacific results provide support for winds contributing to the $\text{CO}_{2\text{atm}}$ plateau during the first part of the ACR: the shoaling of the $\delta^{13}\text{C}$ geochemical divide and a temporary increase in $\Delta\delta^{13}\text{C}_{\text{S-I}}$ (Figures 3 and 4) imply that there was a brief restratification in these shallow layers coinciding with the pause in the ascent of atmospheric CO_2 .

In contrast to the $\delta^{13}\text{C}$ record from the intermediate-depth core (79 JPC, 1100 m), which exhibits a rapid depletion during the ACR, all the deeper cores in our Southwest Pacific dataset (> 1500 m, $n = 6$) are characterized by $\delta^{13}\text{C}$ values that became increasingly enriched throughout the ACR (Figures 2 and 3), apparently unaffected by changes in the composition of overlying shallow and intermediate waters. The end of HS1 was notable for reinvigoration of AMOC-style circulation (Böhm et al., 2015; Lynch-Stieglitz et al., 2007), with data from the Atlantic indicating the thermohaline circulation at the time had

enhanced advection at 2000 m and above (Gherardi et al., 2009; McManus et al., 2004). The reduction of the $\Delta\delta^{18}\text{O}_{\text{S-I}}$ in our Pacific record from the ACR through the YD is consistent with this enhanced advection (**Figure 4d**). Radiocarbon evidence indicates shallow interior waters had become more ventilated at the start of the ACR as AMOC resumed (Sikes et al., 2016; Skinner et al., 2015). Our deep records from the Southwest Pacific indicate that the average $\delta^{13}\text{C}$ value of Southwest Pacific deep water rose during the ACR, consistent with an overall loss of deeply sequestered respired CO_2 . In the Atlantic, rapid increases in shallow $\delta^{13}\text{C}$ were attended by no changes at depth (Lund et al., 2015) and mirrored in the radiocarbon signal (Chen et al., 2015; Skinner et al., 2010) suggest repartitioning of CO_2 to the deep ocean in this sector. This inter-ocean contrast may in part explain the $\text{CO}_{2\text{atm}}$ plateau. We note that the rate of change of $\delta^{13}\text{C}$ in the Pacific was both gradual and larger than that observed for the deep Atlantic $\delta^{13}\text{C}$ (Lund et al., 2015). The mean shift in $\delta^{18}\text{O}$ in the deeper layers of our Southwest Pacific cores starts later than the shallower cores (**Figure 3**). Although these differences are more subtle than in the $\delta^{13}\text{C}$ data set, the slow ventilation of deeper water in Pacific during the ACR is supported by the steady shift in $\delta^{18}\text{O}$ in our deeper cores and importantly, by regional radiocarbon records (Ronge et al., 2016; Sikes et al., 2016; Skinner et al., 2015). Notably, the shift in $\delta^{18}\text{O}$ above 2000 m occurs notably later and moves more slowly than $\delta^{18}\text{O}$ changes observed in the South Atlantic (Lund et al., 2015).

We suggest that AMOC resumption and the resulting deep ventilation was responsible for much of the deglacial isotopic change observed in the deeper layers of the South Pacific. This was similar to the ventilation seen in the shallow Atlantic but the signal was possibly attenuated by mixing during transport via the ACC en route to our core sites. The mean shifts of deep $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in our record reflect the steady flushing of the deeper Southern Pacific caused by progressively deepening and strengthening AMOC that both data and modeling evidence suggest began in the ACR (Gherardi et al., 2009; Lund et al., 2015; Schmittner and Lund, 2015). The shift in $\delta^{18}\text{O}$ likely reflects both salinity and temperature changes, reflecting a net change in density and the erosion of the glacial stratification between deep water masses (Adkins, 2013). The fact that this deep $\delta^{13}\text{C}$ enrichment pattern also largely mirrors the depletion in atmospheric $\delta^{13}\text{C}$ from the

ACR through the YD (Schmitt et al., 2012) implies loss of CO₂ to the atmosphere from deeper layers of the ocean (**Figure 4b & c**).

3.2.3 Younger Dryas

Opal fluxes in the South Atlantic sector of the Southern Ocean were enhanced during the YD (12.9 – 11.7 ka), similar to HS1, indicating invigorated upwelling that is supported by lower resolution results from the Southwest Pacific (Anderson et al., 2009; Studer et al., 2015) (**Figure 4g**). Given this similarity, it could be expected that intermediate-depth isotope signatures in the Southwest Pacific during these two periods should also be similar, with the expectation of a strong $\delta^{13}\text{C}$ enrichment as was observed during HS1. Although the $\Delta\delta^{18}\text{O}_{\text{S-I}}$ return to levels similar to HS1, the $\delta^{13}\text{C}$ isotope values in our intermediate core (79 JPC), during the YD were not appreciably different from those of prior (ACR) or subsequent (early Holocene) intervals (**Figure 3**). In other words, the YD interval in this Pacific record contains few distinguishing characteristics in terms of benthic $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$. Instead, the shoaling of the $\delta^{13}\text{C}$ enrichment interface that reestablished during the ACR simply persisted into the early Holocene, and the $\Delta\delta^{13}\text{C}_{\text{S-D}}$ and the $\Delta\delta^{13}\text{C}_{\text{S-I}}$ steadily diminished as deep $\delta^{13}\text{C}$ values continued to rise on roughly the same trajectory as they had during the ACR.

From a broader Southern Hemisphere perspective, the absence of a YD signal here is not surprising. The reduction in AMOC during the YD was weaker and shorter than the reduction that occurred during HS1 (McManus et al., 2004), and deep transport was similar to the ACR (Gherardi et al., 2009). Notably, climate records from the Southern Hemisphere often do not contain YD signals (Alloway et al., 2007; Lamy et al., 2004; Samson et al., 2005; Sikes et al., 2013). Substantial warming in the Southern Hemisphere (Shakun et al., 2012), more northerly positions of Southern Ocean fronts (Sikes et al., 2009) and the resulting effect on shallow water mass structure (Ferrari et al., 2014) differentiate the YD from HS1 in the Southern Ocean. Other regional benthic $\delta^{13}\text{C}$ records from ~1000m that exhibited similar $\delta^{13}\text{C}$ enrichment (ventilation) signals during HS1 had diverging signals following the ACR that did not realign until the Holocene (**Figure 4e**) (Bostock et al., 2004; Pahnke et al., 2003). This suggests that the formation dynamics of Southern Ocean shallow water masses were regionally and temporally

variable during this time. Higher frequency variations in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in our shallowest core (~660 m) from the ACR to the Holocene may reflect highly variable Southern Ocean conditions (see supplemental material **Figure S3**). The divergence of intermediate $\delta^{13}\text{C}$ records after the ACR could be explained by several processes: vertical heaving of the boundary between intermediate and deep water masses in response to latitudinal shifts in formation zones, zonal differences in deep mixing (Sallée et al., 2010), sea ice effects (Abernathy et al., 2016), and/or variable air-sea CO_2 exchange during formation of different types or “flavors” of intermediate water (Bostock et al., 2013). There are also indications that the location of ocean CO_2 degassing may have shifted during the course of deglaciation, with increased rates of ventilation occurring in the East Equatorial Pacific (Martínez-Botí et al., 2015).

3.3 The Holocene

During the early Holocene, both shallow and deep isotope records achieved near-modern compositions. At ~9 ka, there was a second, sustained deepening of enriched $\delta^{13}\text{C}$ waters in our shallowest cores, creating a pattern resembling modern $\delta^{13}\text{C}$ profiles (**Figure 3**). This enrichment of shallow-intermediate $\delta^{13}\text{C}$ could be interpreted as an increase in ventilation, similar to HS1; however, the Holocene shift was distinguished from HS1 by the fact that the deepening progressed more slowly and persisted through the Holocene, consistent with thermohaline circulation as a fundamental driving mechanism. Evidence from other marine studies at similar depths in Drake Passage attribute the late deglacial $\text{CO}_{2\text{atm}}$ rise to transiently stronger-than-modern AMOC at the end of the YD (Chen et al., 2015); the $\delta^{13}\text{C}$ enrichment observed in the Southwest Pacific occurs ~1.5 ka too late to represent a ventilation signal corresponding to that final CO_2 rise. Rather, the gradual attainment of modern $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ likely reflects differences between the basins during the transition of the ocean-atmosphere system to its Holocene configuration in terms of AMOC, sea ice, Westerly Wind position, productivity, dust supply, and upwelling patterns.

Similarly, the attainment of modern $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in deep waters likely reflects the achievement of deep water sources similar to modern as deep water formation on the shelves surrounding Antarctica resumed during the early Holocene. Substantial warming

in the Southern Hemisphere and significant Antarctic ice sheet and sea ice melt-back (Mackintosh et al., 2011; Wolff et al., 2006) would have further altered southern water mass formation mechanisms, allowing such shelf-based deep water formation that could not have occurred during the glaciation (Hall et al., 2015)

4. Conclusions

During the last glacial period, a combination of depleted $\delta^{13}\text{C}$ and older ^{14}C ages in the deep Southwest Pacific (>1,500 m) indicate higher concentrations of deeply sequestered respired CO_2 than in the modern ocean (Ronge et al., 2016; Sikes et al., 2016; Sikes et al., 2000; Skinner et al., 2015). Our South Pacific depth transect (~600 – 4000 m) constrains the base of the glacial geochemical divide (i.e., the depth of most rapid $\delta^{13}\text{C}$ change) to ~1,500 m, approximately 1,000 m shallower than it sat in the South Atlantic (Hodell et al., 2003). This observation is consistent with the idea that mixing between deep water masses in the South Atlantic and South Pacific oceans may have been reduced compared to today (Charles et al., 1996; McCave et al., 2008).

Recent high-resolution ice core work has refined the timing of deglacial CO_2 changes in the atmosphere, revealing that deglacial CO_2 increases proceeded in both slow and rapid increments largely driven by release from the ocean (Marcott et al., 2014). In the South Pacific, enrichment in intermediate-depth $\delta^{13}\text{C}$ (~1,100 m) during HS1 coincided with increased opal fluxes in the Southern Ocean and rapid increases in $\text{CO}_{2\text{atm}}$, suggesting that intermediate waters forming in the Southern Ocean and flowing north into the Pacific Ocean were strongly influenced by wind-driven ocean ventilation in addition to any underlying ocean influences associated with thermohaline circulation changes. Pacific intermediate-depth $\delta^{13}\text{C}$ enrichment reversed and atmospheric CO_2 rise paused during the ACR when Southern Westerly Winds temporarily shifted north in the New Zealand region (Putnam et al., 2013), providing further evidence for atmospheric influence on intermediate ocean ventilation. Concurrently deeper waters (>1500 m) began a relatively steady rise toward modern $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, reflecting the strengthening influence of deep water from the North Atlantic, carrying the signatures of AMOC ventilation and meltwater input to the Southwest Pacific region.

Gradual deglacial CO_{2atm} increase following the ACR was accompanied by continued slow $\delta^{13}\text{C}$ shifts recorded in deeper waters that were likely associated with AMOC. The effect of wind-driven thickening of thermocline waters during AMOC shutdown as a delayed feedback to trigger deep water formation in ~1.5 ka (Hain et al., 2014) provides a mechanism to connect these different types of ventilation and CO₂ release. This has been predicted as the means for rapidly expelling CO₂ from the ocean at 16.3 and 11.7 ka (Hain et al., 2014). The details of the timing in our record for the 16.3 ka pulse in HS1 match this mechanism well. However, there is a poor match with the YD at 11.7 ka. The initiation of wind-driven mixing in the South Pacific (inferred from our $\delta^{13}\text{C}$ records) lags the end of the YD by at least ~2.5 ka. We suggest the lack of YD signal here may in part be attributed to the muted influence of the YD in the Southwest Pacific. Overall, we argue that the relative timing of oceanic geochemical changes compared with atmospheric CO₂ changes provides strong evidence to support the idea that wind-driven circulation coupled to the ocean's thermohaline circulation, played a crucial role in driving CO₂ back into the atmosphere during the deglaciation.

Our high-resolution records from the Southern Pacific Ocean document geochemical changes of water masses spanning 600 to 3800 m depth during the deglaciation in this region. These detailed records provide insight into the role that air-sea exchange in the Pacific sector of the Southern Ocean played in influencing the rise of deglacial CO₂. The implication is that multiple ocean-atmosphere processes (such as wind-driven shallow ventilation and deep water formation) in different combinations contributed to the release of CO₂ from the ocean during the deglaciation. Our results are consistent with a fundamental role for AMOC in the deglacial climate transition, but also support the theory laid out in modeling studies (Gnanadesikan, 1999; Hain et al., 2014) that atmospheric circulation played a critical role in the pattern of glacial–interglacial rise of atmospheric CO₂. In this framework, the Southern Ocean played a fundamental role in reorganizing ocean interior ventilation during the last deglaciation.

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505 [data](http://www.ncdc.noaa.gov/data-access/paleoclimatology-data)

506

Figure Captions

Figure 1: Ocean fronts and water-mass properties in the South Pacific and Southern Ocean. **A)** Core locations and schematic representation of front locations. Cores with new data presented in this paper are indicated by red circles; previously published cores discussed in the text are indicated by yellow circles. The Subtropical Front (STF, dotted line) typically lies between the 100m 10°C and 12°C contours; 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). $\delta^{13}\text{C}$ -depleted CDW upwells south of the APF in the Southern Ocean. North of the SAF, less salty and $\delta^{13}\text{C}$ -enriched Antarctic Intermediate Water (AAIW) forms after freshwater input (precipitation) and gas/heat exchange with the atmosphere. Warmer, saltier and more positive $\delta^{13}\text{C}$ Subantarctic Mode Water (SAMW) forms north of the SAF, moving north and sinking below subtropical waters at the STF **B)** Cross section along WOCE P15 transect represented by dotted line X-Y in panel A. Bathymetry along WOCE transect is shown in black and along 176° E is shown in grey; this represents the approximate bottom contour of the Bay of Plenty for perspective. Salinity contours (in practical salinity units), are denoted by black lines, and $\delta^{13}\text{C}$ values by color shading. In the Pacific, SAMW and AAIW have more positive $\delta^{13}\text{C}$ and sit above CDW, which carries a lower $\delta^{13}\text{C}$ signal from respired CO_2 (Curry et al., 1988). North Pacific Deep Water (NPDW) at mid-depths has low $\delta^{13}\text{C}$

Figure 2: Benthic $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ time series and profiles for each of the cores in the vertical transect. **A)** $\delta^{18}\text{O}$ of *Cibicidoides wuellerstorfi*. Each data point represents the analysis of 1-4 individuals, and solid lines are derived from 5-point running means calculated by the box method in IgorPro Version 6.22. Open symbols represent trigger-core (TC) data; solid points represent jumbo piston core (JPC) data. Horizontal grey bars designate the time slices averaged for vertical profiles in panels B and D. **B)** Vertical profiles of averaged $\delta^{18}\text{O}$ for selected time slices: Glacial (19-23ka), Heinrich Stadial 1 (15.0-17.5 ka), Antarctic Cold Reversal (12.9-14.5ka), and Holocene (2.0-10.5ka). Some of these time slices have been narrowed compared to their full lengths listed in the main text to achieve a more accurate average and avoid edge effects. Error bars = 1σ . Open circle in the LGM profile at 2050m indicates that for this core this time-slice is not fully constrained by tephra chronology (Samson et al., 2005). **C)** Carbon stable isotope records from *C. wuellerstorfi* ($\delta^{13}\text{C}$), same notation and methods as panel A. Note that during the LGM, $\delta^{13}\text{C}$ values in core JPC 79 sit midway between the shallow and deep cores. However, at the start of Heinrich Event 1 (~17.5ka) they bounce between values similar to the shallow core (~1.0 ‰) and deeper cores (~0.5 ‰). We suggest this is the signature of short pulses of intermediate-depth ventilation that served to trigger deeper water $\delta^{13}\text{C}$ enrichment. **D)** Vertical profiles of average $\delta^{13}\text{C}$, using the same time slices and methods as panel B. Diamonds represent published data from the South Atlantic during the LGM (Hodell et al., 2003; Ninnemann and Charles, 2002). Comparison with the depth transect from the South Atlantic demonstrates that the glacial $\delta^{13}\text{C}$ depletion in the Atlantic is more than 1‰ greater than the Pacific at depths below ~2000 m. The shallow gradient in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ provides evidence for a strong geochemical and density front between ~650m-1600m in the LGM. (see SI #2 for details on speciation and isotopic analyses).

Figure 3: Contoured depth-time plots of stable isotopes in the Southwest Pacific since the last glaciation. **A)** Linearly interpolated contour diagram of benthic $\delta^{13}\text{C}$ during the last deglaciation. Individual data points are shown (circles). Note the strong vertical stratification between 25ka-17ka, indicated by a sharp, shallow $\delta^{13}\text{C}$ gradient, and the weakening stratification through the termination, ending with more positive $\delta^{13}\text{C}$ values below 2 km in the Holocene. **B)** Linearly interpolated contour diagram of benthic $\delta^{18}\text{O}$ data during the last deglaciation. **C)** $\delta^{18}\text{O}$ anomalies were calculated by subtracting LGM values (defined here as 21 ka) from subsequent values (i.e., $\delta^{18}\text{O} - \delta^{18}\text{O}_{\text{LGM}} = \delta^{18}\text{O}$ anomaly). Prior to calculation, all $\delta^{18}\text{O}$ records were linearly interpolated at 500 year increments between 0 and 25 ka.

Figure 4: Paleorecords of atmospheric $\delta^{13}\text{CO}_2$ and CO_2 , benthic stable isotopes, and opal flux during the last deglaciation. **A)** CO_2 content of the atmosphere EPICA Dome core (EDC) (Monnin et al., 2001; Parrenin et al., 2013) and West Antarctic ice sheet core (WAIS) (Marcott et al., 2014). **B)** $\delta^{13}\text{C}$ of atmospheric CO_2 (Schmitt et al., 2012). **C)** Vertical difference in Southern Ocean $\delta^{13}\text{C}_{\text{DIC}}$ between shallow (663 m) and intermediate-depth (1170 m) waters ($\Delta\delta^{13}\text{C}_{\text{S-I}}$) and between shallow and deep waters (2050 m) ($\Delta\delta^{13}\text{C}_{\text{S-D}}$). **D)** Vertical difference in Southern Ocean $\delta^{18}\text{O}$ between shallow (663 m) and intermediate-depth (1170 m) waters ($\Delta\delta^{18}\text{O}_{\text{S-I}}$) and between shallow and deep waters (2050 m) ($\Delta\delta^{18}\text{O}_{\text{S-D}}$). **E)** Benthic $\delta^{13}\text{C}$ from regional AAIW depth cores: blue, RR0503-79, 1165 m; grey, FR197-GC12, 990 m (Bostock et al., 2004) and black, MD97-2120, 1010 m (Pahnke et al., 2003). **F)** Opal flux in deep sea core E27-23 in the Pacific sector of the Southern Ocean, see Figure 1a for location relative to our study area (Anderson et al., 2009). Opal flux is a proxy for wind-driven upwelling and productivity in the Southern Ocean; greater opal indicates greater supply of upwelled silicate. **G)** Opal flux in deep sea core TN057-13 in the Atlantic sector of the Southern Ocean (Anderson et al., 2009). Grey shaded area is HS1 and blue shaded area is the ACR. Orange vertical lines denote times of rapid CO_2 increases in the WAIS record. Note the initial drop in $\Delta\delta^{13}\text{C}_{\text{S-I}}$ coincides both with increased productivity and the drop in atmospheric $\delta^{13}\text{C}$. The timing suggests wind-driven ventilation of SAMW and AAIW in HS1 triggered the rapid, short-term release of $\delta^{13}\text{C}$ -depleted CO_2 to the atmosphere. Later release of CO_2 to the atmosphere traces the decrease in $\Delta\delta^{13}\text{C}_{\text{S-D}}$ suggesting slower, continued release from deeper layers of the ocean, perhaps under the influence of renewed NADW.

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