# AN INVESTIGATION OF THE OCEANIC REDISTRIBUTION OF CARBON DURING THE LAST DEGLACIATION

by

SEAN PATRICK BRYAN

B.A., Carleton College, 2004

M.S., University of Colorado, 2007

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written by Sean Patrick Bryan

has been approved for the Department of Geological Sciences

Dr. Thomas M. Marchitto

Dr. Scott J. Lehman

Date\_\_\_\_\_

The final copy of this thesis has been examined by the signatories, and we

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Bryan, Sean Patrick (Ph.D., Geological Sciences)

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Records from ice and marine sediment cores have revealed significant changes in the ocean and atmospheric carbon reservoirs at the end of the last glacial period: atmospheric CO<sub>2</sub> concentrations increased by ~50%, the atmospheric radiocarbon activity ( $\Delta^{14}$ C) declined by 190‰, the  $\Delta^{14}$ C of intermediate depth waters in the eastern North Pacific Ocean became extremely low relative to the contemporaneous atmosphere, and planktic foraminifera in the tropical and southern high latitude oceans experienced a negative excursion in  $\delta^{13}$ C. A promising theory for explaining these changes involves increased storage of carbon in the deep ocean during the last glacial period due to reduced upwelling and air-sea gas exchange in the Southern Ocean. Poor ventilation would have led this deep water mass to become extremely depleted in <sup>14</sup>C and <sup>13</sup>C. During deglaciation, as upwelling in the Southern Ocean increased, this isolated deep water would have been mixed back in to ocean surface, spreading low  $\Delta^{14}$ C and  $\delta^{13}$ C carbon into the upper ocean and atmosphere.

In this dissertation, I investigate this hypothesis by reconstructing intermediate water  $\Delta^{14}$ C during the last deglaciation using two marine sediment cores from the northern Arabian Sea and one core from the margin of southern Chile. The Arabian Sea  $\Delta^{14}$ C records demonstrate that intermediate waters become extremely old during the deglaciation. These results along with previous results from the North Pacific suggest that <sup>14</sup>C-depleted waters upwelled to the surface in the Southern Ocean and were transported northward as intermediate waters. Intermediate waters along the Chile margin, however, were similar to modern, indicating no

evidence for large <sup>14</sup>C depletions. These seemingly contradictory results can be explained by regional variability in upwelling and intermediate water formation in the deglacial Southern Ocean. I also examine the relationship between the deglacial  $\Delta^{14}$ C and  $\delta^{13}$ C minima using a compilation of published  $\Delta^{14}$ C and  $\delta^{13}$ C records from the deep ocean during the last glacial maximum and new measurements of  $\delta^{13}$ C in planktic foraminifera from the same Baja California and Arabian Sea cores that record the  $\Delta^{14}$ C minima. These data demonstrate that the distribution of  $\Delta^{14}$ C and  $\delta^{13}$ C in the glacial deep ocean was significantly different than in the modern ocean and indicate that the deep Southern Ocean could have supplied <sup>14</sup>C- and <sup>13</sup>C-depleted carbon to the upper ocean and atmosphere during the deglaciation. Declines in planktic  $\delta^{13}$ C are observed at the start of the deglaciation coincident with the decline in intermediate water  $\Delta^{14}$ C. However, the  $\delta^{13}$ C records are complicated by changes in local upwelling and productivity at these sites. In summary, the data presented here provide evidence for the redistribution of  ${}^{14}$ C- and  ${}^{13}$ Cdepleted carbon from the deep ocean to the upper ocean and atmosphere and are consistent with mechanisms involving changes in Southern Ocean stratification and upwelling during the last deglaciation.

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## **Chapter I: Introduction**

### 1. Glacial to Interglacial Carbon Cycle Changes

The overarching goal of this dissertation is to gain a better understanding of the mechanisms behind the carbon cycle changes that occurred over glacial – interglacial timescales. Analysis of gas bubbles trapped in the Antarctic ice cores has revealed variability in the concentration of CO<sub>2</sub> in the atmosphere of ~80-100 ppm over the past 800 kyr (Luthi et al., 2008; Petit et al., 1999; Siegenthaler et al., 2005) (Figure 1.1). Atmospheric CO<sub>2</sub> varied in step with changes in Antarctic temperature and global ice volume, with higher CO<sub>2</sub> during warm, interglacial intervals, and lower CO<sub>2</sub> during cold, glacial intervals. Soon after the initial discovery of the glacial to interglacial CO<sub>2</sub> shift, Broecker (1982) recognized that the cause of this change must lie within the ocean, since the ocean contains the largest reservoir of carbon that equilibrates with the atmosphere on millennial timescales. In the past 28 years, a number of hypotheses for explaining the glacial-interglacial  $CO_2$  changes have been presented (Archer et al., 2000; Sigman and Boyle, 2000). To this date, the exact mechanisms behind these changes remain unclear. It appears that there is no single process that can explain the entire glacial to interglacial change, although it is likely that the answer lies in some combination of processes acting synergistically (e.g., Peacock et al., 2006; Sigman and Boyle, 2000). The high latitude oceans, and the Southern Ocean in particular, appear to have played a prominent role, since the deep water masses that fill the majority of the ocean are formed at high latitudes (Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984). The strong westerly winds over the Southern Ocean drive Ekman divergence and upwelling, which brings nutrient and carbon-rich deep waters up to the sea surface. Incomplete utilization of upwelled nutrients allows some of the CO<sub>2</sub> that had been sequestered in the deep ocean to leak out to the

atmosphere. Most current hypotheses attempting to explain the glacial/interglacial  $CO_2$  changes focus on closing the Southern Ocean leak through some combination of biogeochemical and physical mechanisms. The most often mentioned mechanisms involve increasing the efficiency of nutrient utilization by phytoplankton (Francois et al., 1997; Martin, 1990), decreasing mixing between the surface of the Southern Ocean and the deep ocean (Francois et al., 1997; Toggweiler, 1999; Watson and Naveira Garabato, 2006), and reducing air-sea  $CO_2$  exchange by increasing sea ice coverage (Stephens and Keeling, 2000). Box models suggest that these processes in conjunction with a carbonate compensation feedback can explain the full glacial to interglacial  $CO_2$  change (Sigman et al., 2010).

These hypotheses make predictions about how ocean chemistry would have changed, which we can test using measurements on fossil shells recovered in ocean sediment cores. This dissertation focuses on changes related to the physical ocean circulation and the interaction between the atmosphere/surface ocean and the deep ocean. If ventilation of the glacial deep ocean was reduced by limited upwelling/mixing or increased sea ice coverage in the Southern Ocean, we would expect that the <sup>14</sup>C content of the glacial deep ocean would have been reduced, as these processes would have also restricted the uptake of <sup>14</sup>C by the ocean. A longer residence time of waters in the deep ocean would have also reduced the <sup>13</sup>C/<sup>12</sup>C of the deep ocean as deep waters accumulated low <sup>13</sup>C/<sup>12</sup>C organic carbon. In this dissertation, I use measurements of radiocarbon and the stable isotopes of carbon to track the redistribution of carbon from the deep ocean into the upper ocean and atmosphere during the last deglaciation.



**Figure 1.1:** Composite record of atmospheric  $CO_2$  (bottom) for the past 800 kyr measured in Antarctic ice cores, compared to Antarctic temperature anomaly (top). Figure from Lüthi et al. (2008).

## 2. Radiocarbon as a Tracer in the Ocean

Produced in the atmosphere cosmogenically by collision of thermal neutrons with atmospheric nitrogen, radiocarbon (<sup>14</sup>C) makes up about one part per trillion of the carbon on Earth. <sup>14</sup>C is radioactive and beta-decays with a half-life of 5730 years (Godwin, 1962). <sup>14</sup>C is oxidized to <sup>14</sup>CO<sub>2</sub> and enters the carbon cycle. Through most of this dissertation I refer to <sup>14</sup>C in  $\Delta^{14}$ C notation.  $\Delta^{14}$ C is defined as the per mil deviation of the <sup>14</sup>C to <sup>12</sup>C ratio in a sample from a standard, normalized to  $\delta^{13}$ C = -25‰ to correct for isotopic fractionation (Equation 1) (Stuiver and Polach, 1977). The oxalic acid standard is set to have the activity of the pre-industrial prenuclear atmosphere; thus the pre-industrial pre-nuclear atmosphere had a  $\Delta^{14}$ C = 0‰.

$$\Delta^{14}C = ({}^{14}C/{}^{12}C_{\text{sample}} / {}^{14}C/{}^{12}C_{\text{standard}} - 1) * 1000$$
 [Equation 1]

Much of what we know about <sup>14</sup>C in the ocean has come from measurements made during the large measurement campaigns of the Geochemical Ocean Section Study (GEOSECS) during the 1970's (Ostlund and Stuiver, 1980; Stuiver and Ostlund, 1980; Stuiver and Ostlund, 1983) and the World Ocean Circulation Experiment (WOCE) during the 1980's and 1990's (Key et al., 1996; Key et al., 2002). <sup>14</sup>C enters the ocean through air-sea exchange of CO<sub>2</sub>. Isotopic equilibration between atmospheric CO<sub>2</sub> and dissolved inorganic carbon in the ocean is sufficiently slow relative to the residence time of waters at the sea surface that nowhere on Earth does the sea surface reach isotopic equilibrium (Broecker and Peng, 1982). The relatively slow rate of equilibration is related to the particularities of carbon chemistry in the ocean, specifically that only ~1% of the carbon in the ocean is present as  $CO_2(aq)$ . To reach equilibrium, <sup>14</sup>C must exchange with the much larger bicarbonate and carbonate ion pools. Over most of the sea surface natural  $\Delta^{14}$ C (after removing the impact of bomb produced  $^{14}$ C) averages ~ -40 to -60% (Key et al., 2004; Rubin and Key, 2002); however, in regions where low- $\Delta^{14}$ C deep waters upwell to the surface and the residence time of surface waters is short, such as the Southern Ocean, surface  $\Delta^{14}$ C can be as low as -140‰ (Broecker et al., 1998). As soon as a water parcel leaves the sea surface as a part of an intermediate or deep water mass, its  $\Delta^{14}$ C begins to decline, as <sup>14</sup>C decays away without renewal from the atmosphere. These processes cause  $\Delta^{14}$ C to track the path of the large-scale deep ocean circulation, decreasing from the North Atlantic to the North Pacific (Matsumoto, 2007). The distribution of radiocarbon in the ocean is, therefore, controlled by the degree of air-sea equilibration and the time since a water mass has been in contact with the atmosphere.

## 3. $\delta^{13}$ C in the Ocean

Carbon-13 is a stable isotope of carbon and represents about 1% of the carbon on Earth. As with radiocarbon, our understanding of <sup>13</sup>C in the oceans developed from measurements made during the GEOSECS program (e.g., Craig, 1970; Kroopnick, 1980; Kroopnick et al., 1972; Kroopnick, 1985).  $\delta^{13}$ C (the <sup>13</sup>C to <sup>12</sup>C ratio relative to a standard) in the ocean is predominantly controlled by the mass-dependent fractionation that occurs during photosynthesis. Phytoplankton living in the sea surface preferentially take up  $^{12}$ C, leaving the sea surface dissolved inorganic carbon (DIC) pool enriched in <sup>13</sup>C. After the phytoplankton die and sink into the ocean interior, the organic carbon is remineralized by oxic respiration, returning the  ${}^{13}$ Cdepleted carbon to the DIC pool. This biological carbon pump causes  $\delta^{13}$ C to be high near the sea surface and lower at depth, a distribution similar to the macronutrient phosphate.  $\delta^{13}C$  is very useful as a tracer of ocean circulation for two reasons: deep waters formed in the North Atlantic and the Southern Ocean begin with different  $\delta^{13}$ C values, due to varying degrees of nutrient utilization in their source waters; and the longer a deep water mass resides within the ocean interior, the greater opportunity it will have to accumulate low- $\delta^{13}$ C organic carbon. These processes allow  $\delta^{13}$ C to track changes in the relative contributions of North Atlantic vs. Southern Ocean sourced deep waters, as well as, qualitatively, changes in the residence time of waters within the deep ocean.  $\delta^{13}$ C is additionally affected by fractionation between atmospheric CO<sub>2</sub> and DIC (e.g., Broecker and Maier-Reimer, 1992; Lynch-Stieglitz et al., 1995). CO<sub>2</sub> is depleted in <sup>13</sup>C relative to DIC and this fractionation increases at colder temperatures. This process tends to increase the  $\delta^{13}$ C of surface waters that undergo air-sea CO<sub>2</sub> exchange at cold temperatures. While this process complicates the interpretation of  $\delta^{13}C$  data, the air-sea signature on  $\delta^{13}$ C is a conservative tracer, which is only altered by mixing (Lynch-Stieglitz and

Fairbanks, 1994a). If the various influences on  $\delta^{13}$ C can be isolated, ocean  $\delta^{13}$ C measurements and paleo-reconstructions allow the investigation of changes in both the biological pump and CO<sub>2</sub> exchange between the ocean and atmosphere.

### 4. Dissertation Organization

The contents of this dissertation are organized into three chapters following this introduction. Each chapter is designed to be a stand-alone article. As such there is some overlap in the introduction and methods sections of the chapters. Chapter II presents reconstructions of intermediate water  $\Delta^{14}$ C from the Arabian Sea during the last deglaciation. These reconstructions take advantage of two sediment cores from the Oman margin in the northwest Arabian Sea, which have stratigraphies that can be correlated to the GISP2 ice core record, allowing us to develop calendar age models independent of <sup>14</sup>C. These core sites would have been influenced by intermediate water masses formed in the Southern Ocean during the deglaciation. These records allow us to test whether the low- $\Delta^{14}$ C intermediate waters previously observed in the eastern North Pacific (Marchitto et al., 2007) were formed in the Southern Ocean. This chapter has been published in the September 15, 2010 issue of *Earth and Planetary Science Letters*.

Chapter III presents reconstructions of deglacial intermediate water  $\Delta^{14}$ C using a sediment core from the margin of southern Chile. These reconstructions were an attempt to track the upwelling and northward propagation of low- $\Delta^{14}$ C intermediate waters closer to their hypothesized source in the Southern Ocean. Chapter IV explores the relationship between the deglacial minima in intermediate water  $\Delta^{14}$ C and minima in planktic foraminiferal  $\delta^{13}$ C that occur during deglaciations in many records from the tropics and southern high-latitudes. I

present new measurements of planktic foraminiferal  $\delta^{13}$ C from the Arabian Sea and Baja California sediment cores in which the intermediate water  $\Delta^{14}$ C minima were observed. Chapter IV also includes a compilation of paired  $\Delta^{14}$ C and  $\delta^{13}$ C measurements from the deep ocean during the last glacial maximum, which is used to determine whether a coupling between  $\Delta^{14}$ C and  $\delta^{13}$ C in the deglacial ocean should expected. Chapter V summarizes the main conclusions of Chapters II-IV and suggests future directions to build upon the work presented here. Following the main contents of the dissertation are a list of the references cited and three Appendices, which include a description of the method used to estimate the error in the calendar age models presented in Chapters II & III, a description of the method used to normalize reconstructed  $\Delta^{14}$ C gradients to allow direct comparison to modern gradients, and a list of the new  $\delta^{13}$ C data presented in Chapter IV.

# Chapter II: The release of <sup>14</sup>C-depleted carbon from the deep ocean during the last deglaciation: evidence from the Arabian Sea

### Abstract.

During the last deglaciation the concentration of CO<sub>2</sub> in the atmosphere increased and the radiocarbon activity ( $\Delta^{14}$ C) of the atmosphere declined in two steps corresponding in timing to Heinrich Stadial 1 and the Younger Dryas. These changes have been attributed to the redistribution of <sup>14</sup>C-depleted carbon from the deep ocean into the upper ocean and atmosphere. Recently, reconstructions of  $\Delta^{14}$ C in intermediate waters of the eastern tropical Pacific have revealed pulses of very old water during the deglaciation, consistent with the release of <sup>14</sup>Cdepleted carbon from the deep ocean at this time. Here, we present reconstructions of intermediate water  $\Delta^{14}$ C from the northern Arabian Sea near the coast of Oman. These reconstructions record significant aging of intermediate waters in the Arabian Sea during Heinrich Stadial 1 and, to a lesser extent, during the Younger Dryas. The timing and magnitude of <sup>14</sup>C depletion in the Arabian Sea during Heinrich Stadial 1 is very similar to that previously observed in the eastern North Pacific near Baja California, indicating that similar mechanisms were involved in controlling  $\Delta^{14}$ C at these two sites. The most parsimonious explanation of the  $\Delta^{14}$ C records from the Arabian Sea and Baja California remains the release of  $^{14}$ C-depleted carbon from the deep ocean by renewal of upwelling and mixing in the Southern Ocean. These <sup>14</sup>C-depleted waters would have been incorporated into thermocline and intermediate water masses formed in the Southern Ocean and spread northward into the Pacific, Indian and Atlantic Ocean basins.

### **1. Introduction**

During the last glacial termination (~18-10 kyr BP) the concentration of CO<sub>2</sub> in the atmosphere increased by ~50% in two steps corresponding in timing to Heinrich Stadial 1 (HS1) and the Younger Dryas (YD) (2001). Most attempts to explain the CO<sub>2</sub> rise involve changes in the distribution of carbon between the atmosphere and the deep ocean, since the deep ocean is the largest reservoir of carbon that can interact with the atmosphere on relevant timescales (e.g., Archer et al., 2000; Broecker, 1982; Sigman and Boyle, 2000). However, the exact mechanisms involved remain unclear. At the same time as CO<sub>2</sub> was rising, the radiocarbon activity ( $\Delta^{14}$ C) of the atmosphere decreased rapidly (e.g., Fairbanks et al., 2005; Hughen et al., 2004a; Hughen et al., 2006; Marchitto et al., 2007; Reimer et al., 2004; Reimer et al., 2009). The decline in atmospheric  $\Delta^{14}$ C cannot be entirely explained by changes in  $^{14}$ C production. Production of  $^{14}$ C was elevated at times during the last glacial period due to lower geomagnetic field strength, particularly during the Laschamp and Mono Lake excursions (Laj et al., 2002; Muscheler et al., 2004). However, reconstructions of <sup>14</sup>C production based on paleomagnetic records and <sup>10</sup>Be in ocean sediments indicate only a small decrease during the deglaciation (Frank et al., 1997; Laj et al., 2002), and reconstructions based on <sup>10</sup>Be in the Greenland Summit ice cores indicate very little change (Muscheler et al., 2004). Broecker and Barker (2007) estimated that a maximum of about 37‰ out of the ~190‰ decrease in  $\Delta^{14}$ C that occurred between ~17.5 kyr BP and ~14.5 kyr BP can be explained by <sup>14</sup>C production. These observations indicate that changes in the distribution of <sup>14</sup>C between the atmosphere and other carbon reservoirs must be responsible for much of the deglacial  $\Delta^{14}$ C decline (Broecker and Barker, 2007; Hughen et al., 2004a; Hughen et al., 2006; Muscheler et al., 2004). This hypothesis requires that during the last glacial period, ventilation of some portion of the deep ocean (the only carbon reservoir large enough to explain

the changes) was greatly reduced, allowing <sup>14</sup>C to decay away with limited renewal from the surface ocean. During the deglaciation, the <sup>14</sup>C-depleted carbon in this reservoir was mixed back into the rest of the ocean and atmosphere. The hypothesized isolated deep ocean reservoir may have been stabilized by very high salinity associated with sea ice formation and brine rejection in the Southern Ocean (Adkins et al., 2002). An isolated deep ocean reservoir may have also accumulated remineralized organic carbon, providing at least a partial explanation for the glacial-interglacial pCO<sub>2</sub> changes (Sigman and Boyle, 2000; Toggweiler, 1999; Watson and Naveira Garabato, 2006).

According to this hypothesis, the radiocarbon age of the isolated deep ocean reservoir should appear very old when compared to the contemporaneous atmosphere or surface ocean. While the extent of aged deep waters in the glacial ocean remains unclear, recent records have provided increasing evidence that some portion of the glacial deep ocean was very poorly ventilated. There is strong evidence that the glacial North Atlantic was significantly depleted in <sup>14</sup>C relative to the modern North Atlantic. Benthic – planktic foraminiferal age differences indicate that the glacial North Atlantic below 2.5 km was ~200-300‰ lower than the contemporaneous atmosphere (Keigwin, 2004; Keigwin and Schlegel, 2002; Robinson et al., 2005; Skinner and Shackleton, 2004). These measurements are consistent with a glacial Atlantic in which North Atlantic Deep Water (NADW) was a shallower water mass and deep waters sourced from high southern latitudes (hereafter southern source) filled the ocean below ~2500 m (cf. Curry and Oppo, 2005; Marchitto and Broecker, 2006), along with some additional aging of glacial southern source deep waters relative to modern. Recent work by Skinner et al. (2010) indicates that deep waters in the Atlantic sector of the Southern Ocean were ~470-520‰ lower than the atmosphere during the last glacial maximum. However, results from the Pacific have

generally shown deep ocean <sup>14</sup>C depletions similar to or only slightly greater than today's (Broecker et al., 2004a; Broecker et al., 2008a; Broecker et al., 2007; Broecker et al., 2004c; Galbraith et al., 2007; Shackleton et al., 1988), suggesting that the old reservoir was rather limited in spatial extent. One study, which used volcanic tephras as stratigraphic markers, has found glacial deep waters in the southwest Pacific that were ~300-500‰ lower than the atmosphere (Sikes et al., 2000). There is also some unpublished data indicating substantial <sup>14</sup>C depletion in waters below 3 km in the Eastern Equatorial Pacific (EEP) (Keigwin et al., 2006). The lack of consensus regarding the <sup>14</sup>C content of the deep ocean in the past may be due in part to low sedimentation rates, poor carbonate preservation, and bioturbation, all of which typify deep ocean sediments (Barker et al., 2007; Peng and Broecker, 1984).

Compelling evidence for a <sup>14</sup>C-depleted carbon reservoir in the glacial ocean was presented by Marchitto et al. (2007) using a reconstruction of  $\Delta^{14}$ C in intermediate waters near Baja California. The Baja California record shows two pulses of extremely old waters during the deglaciation that coincide in timing with the decreases in atmospheric  $\Delta^{14}$ C and the increases in atmospheric pCO<sub>2</sub>. Marchitto et al. (2007) proposed that the <sup>14</sup>C-depleted carbon must have been sourced from an isolated deep ocean water mass. Given the strong similarity between the timing of the deglacial carbon cycle changes and warming in Antarctica and the Southern Ocean, Marchitto et al. (2007) suggested that the old carbon was upwelled in the Southern Ocean and advected to the Baja California margin via Antarctic Intermediate Water (AAIW) and/or Subantarctic Mode Water (SAMW). The recent reconstruction of deep Southern Ocean ventilation age by Skinner et al. (2010) confirms that this ocean could have supplied old water to the upper ocean and atmosphere, but the extent of aging was still somewhat lower than required to explain the observations of Marchitto et al. (2007). If the old carbon observed at Baja California was indeed sourced from an isolated deep ocean water mass and upwelled in the Southern Ocean during the deglaciation, the depleted  $\Delta^{14}$ C signal should also be recorded in intermediate depth cores from other regions that are influenced by AAIW and SAMW. In this paper we test this hypothesis using sediment cores from intermediate depths in the Arabian Sea.

#### 2. Arabian Sea Study Site

Our new measurements come from two sediment cores collected in the northern Arabian Sea near the coast of Oman: RC27-14 and RC27-23 (Table 2.1; Figure 2.1). These cores were selected for two primary reasons: they contain stratigraphic information that can be used to develop age models that are independent of <sup>14</sup>C, and we expect that they would have been influenced by SAMW or AAIW during the deglaciation. The core sites sit within a strong oxygen minimum zone related in part to monsoon-driven coastal upwelling. Previous work on these sediment cores demonstrated that the  $\delta^{15}$ N of organic matter, which is influenced by denitrification in the water column, displays clear evidence of Dansgaard-Oeschger cycles and can therefore be correlated with  $\delta^{18}$ O records from the Greenland ice cores (Altabet et al., 2002). This relationship is mechanistically tied to the strength of the Southwest Indian Monsoon. On millennial timescales warmer Northern Hemisphere high-latitudes correspond to a stronger Southwest Indian Monsoon (e.g., Burns et al., 2003; Fleitmann et al., 2003; Sinha et al., 2005). Stronger monsoons drive increased upwelling and productivity in the northern Arabian Sea, increasing oxidant demand, and increasing denitrification (Altabet et al., 2002; Ganeshram et al., 2000; Ivanochko et al., 2005; Schulz et al., 1998). <sup>14</sup>N is preferentially removed during water column denitrification, leaving the remaining nitrogen pool and the organic matter that incorporates it enriched in <sup>15</sup>N (Brandes et al., 1998; Cline and Kaplan, 1975).



**Figure 2.1:** Location map of sediment core and coral  $\Delta^{14}$ C records discussed in this paper. Arabian Sea cores RC27-14 and RC27-23 (this study), Baja California core MV99-MC19/GC31/PC08 (Marchitto et al., 2007), EEP core VM21-30 (Stott et al., 2009), Chile margin core SO161-SL22 (De Pol-Holz et al., 2010), Brazil margin corals C1 and C2 (Mangini et al., 2010) and Drake Passage corals (Goldstein et al., 2001; Robinson and van de Flierdt, 2009) contain records of intermediate water  $\Delta^{14}$ C during the last deglaciation. The location of core MD07-3076 (Skinner et al., 2010) in the Atlantic sector of the Southern Ocean is also shown; this core (at 3770 m water depth) records the oldest last glacial maximum deep waters that have been published.

Location	Core	Latitude	Longitude	Water Depth (m)	Reference
Arabian Sea	RC27-14	18.3°N	57.6°E	596	This study
Arabian Sea	RC27-23 MV99-	18°N	57.6°E	820	This study
Baja California Eastern Equatorial	MC19/GC31/PC08	23.5°N	111.6°W	705	Marchitto et al., 2007
Pacific	VM21-30	1.2°S	89.7°W	617	Stott et al., 2009 De Pol-Holz et al.,
Chile Margin	SO161-SL22	36.2°S	73.7°W	1000	2010
Brazil Margin	C1 (corals)	22.4°S	40.1°W	621	Mangini et al., 2010
Brazil Margin	C2 (corals)	24.3°S	43.2°W	781	Mangini et al., 2010
Drake Passage	Coral	59.7°S	68.7°W	1125	Goldstein et al., 2001 Robinson and van de
Drake Passage	Coral	59.4°S	68.5°W	1125	Flierdt, 2009

Table 2.1: Location of intermediate water  $\Delta^{14}$ C sites discussed in this paper.

We apply the GISP2 calendar age model (Meese et al., 1997) to RC27-14 and RC27-23 by correlating the  $\delta^{15}$ N records from the two sediment cores to the GISP2  $\delta^{18}$ O record (Grootes and Stuiver, 1997). To do this, we established five tie points between the sediment cores and GISP2 and used a linear interpolation in between the tie points (Figure 2.2a). Since the Greenland- monsoon teleconnection is via the atmosphere, we assume that the transitions apparent in the  $\delta^{15}$ N and the  $\delta^{18}$ O records are synchronous within the resolution of the sediment cores. The resulting sedimentation rates range from 12.7 – 15.3 cm/kyr for RC27-14 and 10.5 – 13.0 cm/kyr for RC27-23. Error in our calendar ages was estimated using a Monte Carlo analysis including an estimated uncertainty in the placement of tie points of 200-500 years and a 10% uncertainty in the sedimentation rate between the sample depth and the nearest tie point (Appendix A). This error analysis does not include possible error in the GISP2 age model. However, the strong agreement between the GISP2 age model and the U-Th-dated Hulu Cave speleothem record (Wang et al., 2001) during the deglaciation indicates that possible errors in the GISP2 age model are small (<~100 yrs) during the time interval of interest here.

SAMW and AAIW ventilate much of the thermocline and intermediate waters of the Indian Ocean (McCarthy and Talley, 1999; Sloyan and Rintoul, 2001; You, 1998). These water masses are difficult to identify in the modern Arabian Sea due to mixing along isopycnals with high-salinity waters formed from Red Sea and Persian Gulf outflows (You, 1998). However, the volumetric contribution of the outflow waters to the Arabian Sea is small compared to that from intermediate waters entering from the south (Olson et al., 1993; Swallow, 1984), which are composed of Southern Ocean-sourced waters and intermediate waters formed in the Indonesian Seas (Swallow, 1984; Wyrtki, 1973; You, 1998). Lower sea level during the last glacial period would have substantially reduced or eliminated outflow from the marginal seas (Rohling and Zachariasse, 1996), likely increasing the relative proportion of AAIW and SAMW in the Arabian Sea. Stable isotope records from intermediate depths near the Oman margin are consistent with increased southern-sourced waters during glacial periods (Zahn and Pedersen, 1991). Changes in denitrification, aragonite preservation, organic geochemistry, and stable isotopes have also been interpreted to indicate increased presence of oxygen-rich SAMW/AAIW in the Arabian Sea during HS1 and the YD (e.g., Böning and Bard, 2009; Jung et al., 2009; Pichevin et al., 2007; Schulte et al., 1999), consistent with records from the SW Pacific and Atlantic Oceans which suggest enhanced advection of AAIW during these intervals (Pahnke et al., 2008; Pahnke and Zahn, 2005; Rickaby and Elderfield, 2005).



**Figure 2.2:** Arabian Sea sediment core stratigraphy and  $\Delta^{14}$ C: a) GISP2  $\delta^{18}$ O (Grootes and Stuiver, 1997) and Arabian Sea  $\delta^{15}$ N (Altabet et al., 2002) records for the last deglaciation used to construct calendar age models for the sediment cores RC27-14 (shown in green) and RC27-23 (blue). The triangles indicate tie points used to correlate between the sedimentary  $\delta^{15}$ N and the GISP2  $\delta^{18}$ O records. b) Arabian Sea intermediate water  $\Delta^{14}$ C reconstructed from RC27-14 (green squares) and RC27-23 (blue diamonds); planktonic  $\Delta^{14}$ C from RC27-23 (*G. ruber* data are filled orange circles; *G. ruber/G. sacculifer* data are open orange circles; and *N. dutertrei* data are orange triangles); and atmospheric  $\Delta^{14}$ C (gray line) (Reimer et al., 2009). Error bars on  $\Delta^{14}$ C values are based on error on the <sup>14</sup>C ages and the determination of calendar ages as described in Section 2. Anomalous  $\Delta^{14}$ C values are indicated by question marks. One RC27-23 planktic  $\Delta^{14}$ C value from 17,990 yr BP is off of the chart at 905‰. YD, BA, ACR and HS1 indicate the Younger Dryas, Bølling-Allerød, Antarctic Cold Reversal and Heinrich Stadial 1 intervals respectively.

### **3. Radiocarbon Methods**

Foraminifera for <sup>14</sup>C analysis were picked from the >250  $\mu$ m sized fraction of previously washed sediment samples. In a few cases benthic foraminifera from the 150-250  $\mu$ m size fraction were added to increase the sample size. Benthic samples consisted of mixed species of benthic foraminifera. These were mostly infaunal genera including *Globobulimina*, *Bulimina*, *Virgulina*, and *Uvigerina*. Samples did not include any *Pyrgo* spp., which may yield anomalous <sup>14</sup>C ages (Nadeau et al., 2001). Planktic samples were monospecifc samples of *G. ruber* or *N. dutertrei*, or mixed *G. ruber* and *G. sacculifer*. Graphite targets were prepared at the INSTAAR Laboratory for AMS Radiocarbon Preparation and Research (NSRL). Foraminifera were leached for 5 minutes using 0.001N HCl. Foraminifera were then hydrolyzed using H<sub>3</sub>PO<sub>4</sub>, and the resultant CO<sub>2</sub> was purified cryogenically. CO<sub>2</sub> was reduced to graphite using an Fe catalyst in the presence of H<sub>2</sub> (McNichol et al., 1992). Oxalic acid primary and secondary measurement standards, geologic control samples of consensus <sup>14</sup>C age, and process blanks were prepared along with foraminiferal samples at NSRL. Samples were analyzed for <sup>14</sup>C by accelerator mass spectrometry at the Keck Carbon Cycle AMS Facility, UC Irvine (KCCAMS). Results are reported following the conventions of Stuiver and Polach (1977) and corrected for isotopic fractionation using  $\delta^{13}$ C measurements of the graphite samples in the AMS. KCCAMS  $\delta^{13}$ C values are not suitable for paleoceanographic interpretation, as fractionation can occur during graphitization or AMS measurement, and are not reported here.

### 4. Results

Radiocarbon ages for RC27-14 and RC27-23 are given in Table 2.2. We calculated agecorrected  $\Delta^{14}$ C values (Figure 2.2b) by combining <sup>14</sup>C ages with calendar ages derived using the correlation of  $\delta^{15}$ N records to GISP2  $\delta^{18}$ O and applying the summary equation for initial  $\Delta^{14}$ C of Adkins and Boyle (1997):

$$\Delta^{14}C = (e^{-14C \operatorname{age}/8033} / e^{-\operatorname{cal} \operatorname{age}/8266} - 1) * 1000$$
 [Equation 1]

where 8033 and 8266 are the Libby and true mean lives of <sup>14</sup>C, respectively. Error bars on  $\Delta^{14}$ C values were calculated by combining the one-sigma error on the <sup>14</sup>C ages with the estimated error in the calendar ages given in Table 2.2. The  $\Delta^{14}$ C errors are dominated by the error in the calendar ages, which causes the error bars to be oriented in a diagonal direction that lies very close to a decay trajectory.

### 4.1 Evaluation of Data Quality

One sample depth from RC27-14 and two depths from RC27-23 produced what appear to be anomalous ages (Table 2.2).  $\Delta^{14}$ C values from these samples are either much higher or much lower than the samples immediately above and below in the cores. We are hesitant to interpret large excursions in the  $\Delta^{14}$ C data that are not confirmed by either multiple data points or similar patterns between the two cores. Furthermore, results from all three sample depths suggest physically implausible  $\Delta^{14}$ C relationships, exhibiting either benthic  $\Delta^{14}$ C higher than the atmosphere, planktic  $\Delta^{14}$ C *much* higher than the atmosphere, or planktic  $\Delta^{14}$ C lower than benthic  $\Delta^{14}$ C in the other core. In the case of the questionable samples from 212 cm (and 222 cm) in RC27-23, the paired planktic and benthic results are *both* much lower (or higher) than expected, suggesting a process such as lumpy mixing by deep burrowing organisms. If any of the other samples were impacted by deep burrowing, the most likely candidates are 217 cm from RC27-23, the interval in between the two anomalous intervals; and 192 cm in RC27-23, where the planktic  $\Delta^{14}$ C is ~290‰ lower than the atmosphere. It should be noted that the exclusion of these two additional intervals would not significantly affect our conclusions. The rest of the data are supported by planktic  $\Delta^{14}$ C close to atmospheric values, similar benthic  $\Delta^{14}$ C values between the two cores and/or similar benthic  $\Delta^{14}$ C values in samples immediately above or below within the core. We have plotted the anomalous values in Figures 2.2, 2.3, and 2.4, where they are indicated by question marks, but we do not interpret them as reflective of seawater  $\Delta^{14}$ C changes in the following discussion.

The impact of bioturbation of benthic foraminiferal abundance peaks appears to be minimal in RC7-23. Abundances of benthic foraminifera (>150 µm) in RC27-23 were relatively stable during the deglaciation, averaging 310±160 individuals/g (Anderson, 1991) (Figure 2.3). Importantly, abundances do not show a trend across the dramatic benthic  $\Delta^{14}$ C drop between 227 cm and 192 cm. There is one particularly high count in the benthic abundances at 152 cm, where values reach 870 individuals/g. This abundance peak does not appear to have significantly biased the  $\Delta^{14}$ C record. Notably, the benthic <sup>14</sup>C age reversal and resulting low  $\Delta^{14}$ C value at 142 cm (Table 2.2) cannot be explained by bioturbation of this abundance peak since the benthic <sup>14</sup>C age at 142 cm is ~600 years older than the benthic age at 152 cm. Abundances of benthic foraminifera were slightly higher during the LGM (440±110 individuals/g) and increased dramatically during the mid-Holocene (reaching a peak of 1110 individuals/g). Since the sedimentation rate in RC27-23 is relatively high (10.5-13.0 cm/kyr) it is unlikely that these abundance changes significantly affected the deglacial  $\Delta^{14}$ C record. Benthic foraminiferal abundances were not available in RC27-14.



**Figure 2.3**: Comparison of RC27-23 benthic foraminiferal abundances and intermediate water <sup>14</sup>C depletions. Benthic foraminiferal abundance data shown in gray open squares are from Anderson et al. (1991). Atmosphere – benthic  $\Delta^{14}$ C differences are shown in black filled diamonds. Atmospheric values are average Intcal09 (Reimer et al., 2009) values for the time interval surrounding each calendar age ± the calendar age errors. The modern Atmosphere – benthic  $\Delta^{14}$ C difference for ~800 m in the Arabian Sea is indicated by a dashed line. Benthic  $\Delta^{14}$ C values determined to be anomalous (see Section 4.1) are indicated by question marks. YD, BA, ACR and HS1 indicate the Younger Dryas, Bølling-Allerød, Antarctic Cold Reversal and Heinrich Stadial 1 intervals respectively.

## 4.2 Intermediate Water $\Delta^{14}C$ History

At ~18 kyr BP, coincident with the start of the atmospheric  $\Delta^{14}$ C decline and atmospheric CO<sub>2</sub> rise, intermediate water  $\Delta^{14}$ C began to decline at both of the core sites (Figure 2.2).  $\Delta^{14}$ C at the shallower core site, RC27-14, decreased by ~170‰, reaching a minimum of ~-40‰ at ~15.0 kyr BP. Intermediate water  $\Delta^{14}$ C at the RC27-14 core site was as much as ~390‰ lower than the contemporaneous atmosphere at ~16.6 kyr BP. For comparison, in the modern Arabian Sea at ~600 m  $\Delta^{14}$ C is only ~100‰ lower than the preindustrial atmosphere (Key et al., 2004).  $\Delta^{14}$ C at the deeper Arabian Sea core site, RC27-23, declined by ~440‰ at the beginning of the deglaciation, reaching a minimum of ~-250‰ at ~15.0 kyr BP, ~520‰ lower than the local preindustrial difference of ~120‰ between the atmosphere and ~800 m and is more than twice as large as the difference between the most <sup>14</sup>C-depleted region of the modern ocean (the North Pacific at ~2 km) and the preindustrial atmosphere. This low- $\Delta^{14}$ C interval correlates to Heinrich Stadial 1 (HS1) in the North Atlantic and to early deglacial warming in Antarctica.

During the Bølling-Allerød (B-A) and the synchronous Antarctic Cold Reversal (ACR), intermediate water  $\Delta^{14}$ C at both core sites increased, reaching values ~120-140‰ lower than the contemporaneous atmosphere, similar to modern gradients.  $\Delta^{14}$ C then declined to values ~220-250‰ lower than the atmosphere in RC27-14 and 260-280‰ lower than the atmosphere in RC27-23 during the Younger Dryas (YD), but in both records this transient <sup>14</sup>C depletion appears to continue into the earliest Holocene, when substantially lower  $\Delta^{14}$ C values were achieved. We note that the interpretation of the Arabian Sea intermediate water records becomes more complicated near the end of the deglaciation, since outflow from the Red Sea would have resumed as sea level rose. While we remain cautious in interpreting single point excursions, the earliest Holocene negative excursions occur at both core sites with similar timing (i.e., within the estimated error of the age models), and atmospheric  $\Delta^{14}$ C does continue to decline until ~9 kyr BP (Reimer et al., 2009). These data may thus reflect the mixing of the last remnants of the isolated glacial deep water mass into the upper ocean.

The planktic  $\Delta^{14}$ C from RC27-23 generally falls close to the INTCAL09 atmosphere, with the exception of the intervals corresponding to the largest benthic depletion (HS1) and just following the YD. The lowering of planktic  $\Delta^{14}$ C towards benthic values records the local influence of low  $\Delta^{14}$ C intermediate waters on the surface ocean. The Arabian Sea cores are located within a strong upwelling zone related to the Southwest Monsoon, and variability within the planktic  $\Delta^{14}$ C record can be explained by variability in the strength of upwelling, as well as variability in the  $\Delta^{14}$ C of the upwelled water. Following the YD, there is evidence for increased upwelling related to the strengthening of the Southwest Monsoon as indicated by high  $\delta^{15}N$  at this time (Altabet et al., 2002), which would increase the subsurface influence on planktic  $\Delta^{14}$ C values. Even though the planktic  $\Delta^{14}$ C values vary from the expected warm surface ocean values at times, the reduction in benthic  $\Delta^{14}$ C at RC27-23 during the HS1 interval is confirmed by very large benthic-planktic age differences, ranging from 1.7 to 3.0 kyr. We also note that the greater magnitude of the intermediate water  $\Delta^{14}$ C decline, compared to the atmospheric and planktic  $\Delta^{14}$ C decreases, indicates that the <sup>14</sup>C-depleted carbon observed during HS1 was sourced from the ocean, rather than reflecting equilibration with an atmospheric  $\Delta^{14}$ C change. Additionally, the smaller  $\Delta^{14}$ C decline recorded in RC27-14 during HS1, relative to RC27-23, indicates that the core of the low- $\Delta^{14}$ C water lay below the depth of RC27-14. The  $\Delta^{14}$ C values recorded by RC27-14 during HS1 reflect the mixing between low- $\Delta^{14}$ C waters below and higher- $\Delta^{14}$ C waters above.

Sample depth (cm)	Calendar age <sup>a</sup> (vears BP)	Calendar age error <sup>b</sup> (vears)	Taxa	Sample weight (mg)	<sup>14</sup> C age (years)	<sup>14</sup> C age error (vears)	Δ <sup>14</sup> C <sup>c</sup> (‰)	Accession #
		~ /				~ /		
RC27-14	(18° 15.2' N,	57° 39.3' E, 5	96 m water depth)					
67	8890	520	Mixed Benthics	4.5	9115	20	-58	CURL-10154
76	9480	540	Mixed Benthics	4.4	10540	25	-153	CURL-10155
76.5	9510	540	Mixed Benthics	6.5	11045	25	-201	CURL-9855
87	10190	240	Mixed Benthics	5.2	10105	25	-24	CURL-9906
97	10850	210	Mixed Benthics	6.4	13130	30	-275	CURL-9918
106	11440	190	Mixed Benthics	8	11425	25	-38	CURL-9827
117	12270	210	Mixed Benthics	7.2	11975	30	-6	CURL-9916
126	12980	240	Mixed Benthics	13.8	12980	25	-44	CURL-9833
128	13140	250	Mixed Benthics	4.9	12980	40	-26	CURL-10156
136	13770	220	Mixed Benthics	7.6	12725	25	85	CURL-10159
137.5	13890	210	Mixed Benthics	11.5	13450	30	6	CURL-9837
147	14630	200	Mixed Benthics	4.4	14435	35	-26	CURL-9910
152.5	15010	200	Mixed Benthics	10.3	14950	30	-44	CURL-9842
157	15320	200	Mixed Benthics	6.3	15180	30	-36	CURL-9923
167	16000	240	Mixed Benthics	9.5	15535	35	2	CURL-9907
176	16620	280	Mixed Benthics	11.5	16060	35	11	CURL-9843
187	17370	340	Mixed Benthics	5.5	15900	35	130	CURL-9915
197	18060	400	Mixed Benthics	7.1	16220	40	180	CURL-9914
203	18470	370	Mixed Benthics	6	17470	45	61	CURL-9830
207	18740	350	Mixed Benthics	6.3	17190	45	136	CURL-9920
225 <sup>d</sup>	19980	300	Mixed Benthics	8.4	16315	40	470	CURL-9828
240	21000	290	Mixed Benthics	7.8	18530	45	264	CURL-9836
275	23610	200	Mixed Benthics	7.9	21870	70	143	CURL-9852
BC27 23	(17º 50 6' N	57° 35 <i>1</i> ' F 8'	20 m watar danth)					
112	8630	57 <b>53.4 E, 8</b>	Mixed Benthics	5.6	9505	20	-130	CURI -10999
12	9400	510	Mixed Benthics	3.5	10525	20	-159	CURL-10991
122	9780	520	Mixed Benthics	6.1	10210	20	-84	CURL-10488
132	10170	250	Mixed Benthics	3.1	11170	30	-148	CURL-10993
132	10170	230	G ruher	3.9	10215	30	-6	CURL-11156
137	10560	230	Mixed Benthics	63	10215	25	-60	CURL-10484
142	10940	220	G ruher	4.2	10870	30	-29	CURL-11157
142	10940	220	Mixed Benthics	8	12835	25	-240	CURL-10466
147	11330	210	G ruher	4 1	10760	30	32	CURL-11158
147	11330	210	Mixed Benthics	5.6	11965	30	-112	CURL-10469
1.52	11730	210	Mixed Benthics	10.1	12255	25	-102	CURL-10487
157	12140	220	Mixed Benthics	6	12420	25	-74	CURL-10468

Table 2.2: Arabian Sea <sup>14</sup>C data.

Sample depth (cm)	Calendar age <sup>a</sup> (years BP)	Calendar age error <sup>b</sup> (years)	Taxa	Sample weight (mg)	<sup>14</sup> C age (years)	<sup>14</sup> C age error (years)	Δ <sup>14</sup> C <sup>c</sup> (‰)	Accession #
162	12560	230	G. ruber	4.1	11065	25	152	CURL-11151
162	12560	230	Mixed Benthics	8.1	12590	25	-47	CURL-9829
167	12980	250	Mixed Benthics	8.5	13325	30	-85	CURL-10465
172	13390	240	Mixed Benthics	7.1	13365	30	-43	CURL-10470
177	13810	210	Mixed Benthics	10.2	12930	30	63	CURL-10486
182	14230	200	G. ruber/G. sacculifer	5.8	12000	30	255	CURL-11137
182	14230	200	Mixed Benthics	11.1	13315	25	65	CURL-10483
187	14650	200	G. ruber/G. sacculifer	4.9	13240	30	132	CURL-11145
187	14650	200	Mixed Benthics	3.2	15595	40	-156	CURL-10464
192	15130	200	G. ruber/G. sacculifer	4.2	14750	35	-6	CURL-11148
192	15130	200	N. dutertrei	3	14695	45	0	CURL-10989
192	15130	200	Mixed Benthics	5.7	16965	50	-246	CURL-10160
197	15600	220	G. ruber/G. sacculifer	4.9	13190	35	278	CURL-11155
197	15600	220	N. dutertrei	3.5	13740	35	194	CURL-10992
197	15600	220	Mixed Benthics	8.8	16165	50	-117	CURL-10157
202	16080	250	G. ruber/G. sacculifer	3.8	14235	35	189	CURL-11146
202	16080	250	Mixed Benthics	8.3	15890	35	-32	CURL-10153
207	16560	280	G. ruber/G. sacculifer	4.1	14060	35	288	CURL-11154
207	16560	280	Mixed Benthics	7.7	15980	30	14	CURL-10481
212 <sup>d</sup>	17030	320	N. dutertrei	2.3	17340	70	-93	CURL-10983
212 <sup>d</sup>	17030	320	Mixed Benthics	9.3	19340	80	-293	CURL-10161
217	17510	360	G. ruber/G. sacculifer	3.6	14495	35	369	CURL-11147
217	17510	360	Mixed Benthics	7.2	16675	40	44	CURL-10474
222 <sup>d</sup>	17990	430	N. dutertrei	3.8	12305	30	905	CURL-10996
222 <sup>d</sup>	17990	430	Mixed Benthics	7.4	14950	35	370	CURL-10162
227	18470	400	Mixed Benthics	6.3	16450	35	205	CURL-10490
232	18940	360	N. dutertrei	3.1	16340	60	294	CURL-10982
232	18940	360	Mixed Benthics	5.4	17015	35	190	CURL-10463
237	19420	340	Mixed Benthics	5.5	17440	35	195	CURL-10477
242	19900	320	Mixed Benthics	7.9	17995	40	182	CURL-10480
262	21970	320	Mixed Benthics	6.5	18940	60	351	CURL-9850

a) Calendar ages derived from correlation between sediment  $\delta^{15}N$  and GISP2  $\delta^{18}O$  as described in Section 2.

b) Calendar age errors based on the precision of tie points and uncertainty in sedimentation rates as described in Section 2.

c)  $\Delta^{14}$ C calculated from <sup>14</sup>C ages and calendar ages using Equation 1.

d) These intervals yielded anomalously young or old  $^{14}$ C ages.

### 5. Discussion

<sup>14</sup>C-depleted intermediate waters during the deglaciation have been previously recorded at two sites in the eastern Pacific (Marchitto et al., 2007; Stott et al., 2009) (Table 2.1; Figure 2.1). Intermediate water  $\Delta^{14}$ C reconstructed for the Arabian Sea during the deglaciation is similar to that reconstructed for the eastern North Pacific near Baja California (Marchitto et al., 2007) (Figure 2.4). In particular, the timing and magnitude of <sup>14</sup>C depletion recorded in the deeper Arabian Sea core during the HS1 interval is almost identical to that of the Baja record, and the Arabian Sea and Baja California records rebound to similar values during the B-A. However, the appearance of the YD <sup>14</sup>C-depletion in the Arabian Sea is significantly different from that observed near Baja California. The Arabian Sea records do not reach values as low as those near Baja California, and while the Baja California record reaches a local minimum during the YD, the Arabian Sea records continue to decline, reaching minima after the YD. The  $\Delta^{14}$ C record from the EEP (Stott et al., 2009) exhibits a broad minimum without the millennial-scale features evident in the Arabian Sea and Baja California records. The  $\Delta^{14}$ C values in the EEP are also extremely low, with values reaching  $\sim 800\%$  lower than the atmosphere at times. These features suggest that the source of the low  $\Delta^{14}$ C values or the processes involved in transporting  $^{14}$ Cdepeted water to the EEP site were different than those responsible for the Arabian Sea and Baja California records. While it is possible that the low  $\Delta^{14}$ C values recorded at Baja California could be explained by episodic transport of low  $\Delta^{14}$ C waters from a proximate source in the EEP, it is very unlikely that this can explain the similar findings in the Arabian Sea.

The strong similarity between the deeper Arabian Sea record and the Baja California record during HS1 and the B-A suggests that similar mechanisms were involved in controlling



**Figure 2.4**: Comparison of the deglacial intermediate water  $\Delta^{14}$ C data: Arabian Sea records, shown in green squares (RC27-14) and dark blue diamonds (RC27-23), Baja California (red circles) (Marchitto et al., 2007), Eastern Equatorial Pacific (EEP) (purple triangles) (Stott et al., 2009), Chile Margin (black triangles) (De Pol-Holz et al., 2010), Brazil Margin corals (orange diamonds) (Mangini et al., 2010), and the Drake Passage corals (Robinson and van de Flierdt, 2009 - closed light blue circles; and Goldstein et al., 2001 - open light blue circle). The INTCAL09 atmospheric  $\Delta^{14}$ C record (Reimer et al., 2009) is also shown in gray. De Pol-Holz et al. (2010) used calibrated planktonic foraminiferal <sup>14</sup>C ages for calendar ages; these <sup>14</sup>C ages have been recalibrated here using MARINE09 (Reimer et al., 2009) (400 year reservoir age) to allow direct comparison with the INTCAL09 atmosphere. YD, BA, ACR and HS1 indicate the Younger Dryas, Bølling-Allerød, Antarctic Cold Reversal and Heinrich Stadial 1 intervals respectively.

the  $\Delta^{14}$ C at these two sites. The similar response at these distant sites also indicates that the cause of <sup>14</sup>C depletion is likely oceanographic in origin, rather than locally sourced <sup>14</sup>C-dead geologic CO<sub>2</sub>. In the following discussion we evaluate three different mechanisms that may have played a role in controlling the  $\Delta^{14}$ C of intermediate waters in the Arabian Sea and near Baja California: *in situ* aging of intermediate waters, local upwelling of low-<sup>14</sup>C carbon from the deep ocean, and advection of low-<sup>14</sup>C carbon to the sites via intermediate waters. We focus here on the  $\Delta^{14}$ C decline during the HS1 interval, since it is well defined at both sites and corresponds to the largest changes in atmospheric  $\Delta^{14}$ C and pCO<sub>2</sub>. While the same arguments can generally be applied to the YD interval, other processes such as differential water mass mixing or local upwelling likely led the Arabian Sea and Baja California to diverge during the YD.

An important constraint on the mechanisms involved in the  $\Delta^{14}C$  declines in the Arabian Sea and near Baja California is the apparent decoupling between  $\Delta^{14}C$  and  $[O_2]$  during HS1 and the YD. As was discussed above, the modern Arabian Sea contains a large oxygen minimum zone and undergoes significant denitrification. The  $\delta^{15}N$  records from RC27-14 and RC27-23 (Altabet et al., 2002) and other sites in the Arabian Sea (e.g., Pichevin et al., 2007) indicate reduced denitrification (and hence higher oxygen concentrations) during HS1 and the YD. Reduced organic carbon and sedimentary Mo concentrations in the Baja California core also indicate higher intermediate water oxygen concentrations during these intervals (Dean et al., 2006; Ortiz et al., 2004). Higher oxygen concentrations during intervals of lower  $\Delta^{14}C$  are somewhat counterintuitive. In general,  $\Delta^{14}C$  and  $[O_2]$  are well correlated in the ocean, with low  $\Delta^{14}C$  values corresponding to low  $[O_2]$ . Both <sup>14</sup>C and  $O_2$  are renewed in the surface ocean through gas exchange with the atmosphere. The longer a water mass resides within the ocean interior, the more <sup>14</sup>C is lost to decay and the more  $O_2$  is consumed by the oxidation of organic
matter. We would expect that an isolated deep water mass that is depleted in <sup>14</sup>C would also have very low [O<sub>2</sub>]. However,  $\Delta^{14}$ C and [O<sub>2</sub>] can become decoupled during the process of airsea gas exchange. This is due to the large difference in the timescale of air-sea oxygen exchange compared to that for isotopic equilibration of CO<sub>2</sub> (a month vs. a decade, respectively, for a mixed layer depth of 80 m) (Broecker and Peng, 1974). Thus, decoupling can occur for waterparcels with residence times at or near the surface that are close to the timescale for gas exchange, but significantly less than for carbon isotopic exchange. In the modern ocean this process occurs to varying degrees in the modern Southern Ocean in the formation region of AAIW, where [O<sub>2</sub>] is renewed to saturation but  $\Delta^{14}$ C is not fully equilibrated with the atmosphere (Key et al., 2004). This oxygen constraint plays a prominent role in our assessment of the possible mechanisms described below.

#### 5.1 In Situ Aging of Intermediate Waters

The rate of decline in intermediate water  $\Delta^{14}$ C that occurs near Baja California and in the Arabian Sea at the start of the deglaciation is similar to or slightly greater than the rate of <sup>14</sup>C decay. Both the Baja California and Arabian Sea sites are located in regions that are outside of direct thermocline ventilation (cf. Luyten et al., 1983). How much of the <sup>14</sup>C depletion may be explained simply by isolation and localized aging of the intermediate water at these sites? In the absence of lateral advection along isopycnals, the ventilation timescale will be set by the rate of turbulent diffusive mixing. Vertical diffusive mixing across the thermocline is relatively slow, given the strong density gradient. If we assume a typical vertical diffusion coefficient for the thermocline of 10<sup>-5</sup> m<sup>2</sup>/s, and a depth of 700 m for RC27-23 (incorporating a glacial reduction of sea level of 120 m (Fairbanks, 1989)) we can estimate a timescale for mixing of ~1500 years. If

vertical diffusion was the only mechanism of <sup>14</sup>C renewal, then aging may have explained a significant proportion of the  $\Delta^{14}$ C decline. However, these sites are not horizontally isolated from the rest of the ocean basin and rates of mixing along isopycnals are much more rapid than vertical mixing. For example, assuming a typical basin scale horizontal diffusion coefficient of 1000 m<sup>2</sup>/s, and a length scale of 1000 km, the mixing timescale is on the order of decades. A decadal timescale is consistent with CFC estimates of the ventilation age of modern Arabian Sea intermediate waters (Fine et al., 2008). In order to explain a significant portion of the  $\Delta^{14}$ C decline, the horizontal diffusion coefficient would need to be about 2 orders of magnitude smaller.

An *in situ* aging mechanism would also violate the oxygen constraint. Oxygen concentrations reflect the balance between oxygen supply and oxidant demand due to the remineralization of exported carbon from primary production. While there is some disagreement as to which factor dominates in the Arabian Sea and off Baja California, in order to explain both the isolation of waters for centuries to thousands of years and higher than modern oxygen concentrations, productivity would have to be essentially shut off. Reconstructions do indicate reduced productivity in the Arabian Sea (Altabet et al., 2002; Pourmand et al., 2007) and off Baja California (Ortiz et al., 2004) during HS1. However, productivity was not eliminated entirely, and without the renewal of oxygen from advection of intermediate and thermocline waters or horizontal diffusive mixing, O<sub>2</sub> concentrations should have been depleted rapidly. We therefore reject *in situ* aging of intermediate waters as a significant contributor to the HS1  $\Delta^{14}$ C decline.

# 5.2 Local Upward Mixing of <sup>14</sup>C-depleted Carbon

Another possible mechanism that may have contributed to the  $\Delta^{14}$ C decline is local upward mixing of <sup>14</sup>C-depleted carbon from the deep ocean. Since the deep <sup>14</sup>C-depleted waters would have to mix extensively with overlying, less <sup>14</sup>C-depleted waters, the signal would be substantially diluted by the time it reached our core sites, requiring the deep waters to be much more depleted than the largest depletion seen in our intermediate water cores. The absolute amount of depletion required will be dependent on the volume occupied by the deep water mass and the amount of mixing that occurred. Since the hypothetical <sup>14</sup>C-depleted deep ocean reservoir appears to be limited to deeper than ~3 km (Broecker et al., 2007), this deep water mass would have to be extremely old. This scenario also requires that the upward mixing of deep waters in the Indian and Pacific Oceans responded rapidly to a common trigger, increasing at the beginning of the deglaciation and shutting off at the start of the Bølling. The similarity between the Arabian Sea and Baja California records further requires that the deep water  $\Delta^{14}$ C and the amount of mixing with overlying waters be very similar between the northern Indian Ocean and the eastern North Pacific.

Local upward mixing of deep waters would also likely violate the local oxygen constraint. Extremely old deep waters would be expected to have very low oxygen concentrations (cf. Jaccard et al., 2009). These initially very low oxygen levels would be rapidly consumed by respiration in the intermediate depth ocean. While we cannot rule out some contribution of locally upwelled,  $low-\Delta^{14}C$  deep water to intermediate waters of the Arabian Sea and those off Baja California, this mechanism seems unlikely to be the primary control on intermediate water  $\Delta^{14}C$ .

# 5.3 Advection of <sup>14</sup>C-depleted Carbon via Intermediate Waters

The third possible mechanism that may explain the HS1  $\Delta^{14}$ C decline is the incorporation of <sup>14</sup>C-depleted deep sea carbon into an intermediate water mass and advection of that water to the Arabian Sea and Baja California core sites. Indeed, the easiest way to explain the strong similarity between the Arabian Sea and Baja California records is to invoke ventilation by a common water mass. The incorporation and transport of the aged carbon by such an intermediate water mass would also relieve the oxygen constraint. The relatively brief timescale required for conversion of upwelled deep waters to intermediate water by the addition of buoyancy may permit oxygen to be renewed without significantly influencing  $\Delta^{14}$ C. We also note that if the greater aragonite preservation observed by Böning and Bard (2009) in the Arabian Sea during HS1 is primarily a result of higher preformed intermediate water [CO<sub>3</sub><sup>2-</sup>], then the upwelled deep waters must have also released much of their excess CO<sub>2</sub> to the atmosphere during the conversion to intermediate waters. However, carbonate preservation may also be affected by changes in pore-water dissolution related to variability in organic carbon flux to the sediments (Emerson and Bender, 1981).

If we conclude that the advection of <sup>14</sup>C-depleted carbon to the Arabian Sea and Baja California via an intermediate water mass is the most likely explanation, the next question is where were the intermediate waters formed. A Southern Ocean source is supported by several observations: 1) The main connection between the Indian Ocean and the Pacific Ocean is through the Southern Ocean. In the modern ocean, well-oxygenated AAIW flows into each of the major ocean basins, ventilating the intermediate waters throughout the Southern Hemisphere and Northern Tropics (Sloyan and Rintoul, 2001; Talley, 1999). 2) The Southern Ocean is the only location in the modern ocean where carbon and nutrient rich deep waters upwell to the

surface. The direct incorporation of old deep water into intermediate waters with limited mixing would minimize the required age of the glacial <sup>14</sup>C-depleted deep water. 3) As we have already noted, the formation region of AAIW/SAMW in the Southern Ocean is the only region in the modern ocean where processes of deep to intermediate water mass conversion permit decoupling of performed [O<sub>2</sub>] and  $\Delta^{14}$ C. 4) The timing of the intermediate water  $\Delta^{14}$ C depletions is coincident with warming in Antarctica (Monnin et al., 2001) and increased upwelling in the Southern Ocean (Anderson et al., 2009), providing a mechanism for the return of old deep waters to the upper ocean (Figure 2.5). The increasing depletion of <sup>14</sup>C during HS1 observed in the Arabian Sea and near Baja California is likely related to a combination of increasing deep upwelling in the Southern Ocean, which tapped progressively into deeper, more depleted waters, and the continued aging of the densest deep waters. 5) Modeling studies have shown a see-saw type behavior in the NADW and AAIW overturning circulations (Keeling and Stephens, 2001; Saenko et al., 2003; Schulte et al., 1999; Sijp and England, 2006), in which a decrease in the NADW production, as occurred during HS1 and the YD (McManus et al., 2004), leads to an enhancement of AAIW production. These results are consistent with paleoceanographic observations that indicate increased advection of AAIW during HS1 and the YD (e.g., Bostock et al., 2004; Pahnke et al., 2008; Pahnke and Zahn, 2005; Rickaby and Elderfield, 2005), as well as a tight coupling between NADW and AAIW formation for the past 340 kyr (Pahnke and Zahn, 2005).

The input of nutrient and carbon rich waters into SAMW and AAIW is consistent with the widespread minima in  $\delta^{13}$ C recorded in planktonic foraminifera and intermediate depth benthic foraminifera from the southern hemisphere and northern tropics during deglaciations (e.g., Curry and Crowley, 1987; Ninnemann and Charles, 1997; Oppo and Fairbanks, 1987; Spero and Lea, 2002), as well as the deglacial increases in productivity and oxidant demand in the Eastern Equatorial Pacific (e.g., Loubere and Bennett, 2008; Martinez and Robinson, 2010; Robinson et al., 2009). Unfortunately the infaunal benthic foraminifera that dominate the assemblages in the Arabian Sea and Baja California cores do not allow us to assess the preformed  $\delta^{13}$ C signal that should be associated with the low  $\Delta^{14}$ C values.

A challenge to Southern Ocean upwelling of <sup>14</sup>C-depleted carbon is the lack of a  $\Delta^{14}$ C decline in the intermediate waters along the Chile margin (De Pol-Holz et al., 2010). This site is ventilated by AAIW in the modern ocean, and if <sup>14</sup>C-depleted waters were upwelled in Southern Ocean we would expect to see low  $\Delta^{14}$ C values at this site. Yet there is no evidence for the influx of <sup>14</sup>C-depleted waters during the deglaciation at this site. In fact, intermediate water  $\Delta^{14}$ C values recorded at this site *increase* during the deglaciation and follow the atmosphere closely (Figure 2.4), which is unexpected for waters sourced in the Southern Ocean, especially at a time of increased Southern Ocean upwelling (Anderson et al., 2009). The waters that bathed the Chile margin must have spent enough time at the surface to become isotopically well equilibrated with the atmosphere.

It is possible that a Southern Ocean source of low-  $\Delta^{14}$ C intermediate waters may be reconciled with the lack of <sup>14</sup>C depletion along the Chile margin if there were multiple regions of AAIW formation in the deglacial Southern Ocean. The intermediate waters that bathed the Chile margin likely formed in the southeast Pacific, just west of the Drake Passage, where the majority of modern AAIW is forms today (McCartney, 1977; Talley, 1996). Corals from intermediate waters in the Drake Passage record only a small decrease in  $\Delta^{14}$ C during HS1 relative to modern gradients (Goldstein et al., 2001; Robinson and van de Flierdt, 2009) (Figure 2.4), consistent with the formation of relatively well-ventilated intermediate waters in the southeast Pacific. Coral records from intermediate waters along the Brazil margin also agree well with those from the Drake Passage during HS1 (Mangini et al., 2010), suggesting that the Brazil margin waters were also formed in the southeast Pacific. Thus, the available records appear to limit the regions of deep-to-intermediate water mass conversion under conditions of poor carbon isotopic equilibration to the Atlantic, Indian and southwest Pacific sectors of the Southern Ocean. Today, much of the <sup>14</sup>C depletion signal carried to the areas of upwelling in the EEP originates in the southwest Pacific sector, off of Tasmania (Toggweiler et al., 1991). This is compatible with an influence of the southwest Pacific sector on the Baja Margin, while an influence of the Atlantic and Indian Ocean sectors on the Arabian Sea sites is also to be expected. Additional records from or downstream of these areas will be needed in order to test this hypothesis.

A less likely possibility is that the low- $\Delta^{14}$ C waters at both the Baja Margin and in the Arabian Sea were sourced from the North Pacific. The reconstructed increase in North Pacific Deep Water (NPDW) ventilation during the deglaciation suggests that the North Pacific may have been a source of at least some <sup>14</sup>C-depleted carbon to the upper ocean and atmosphere during deglaciation (e.g., Galbraith et al., 2007; Okazaki et al., 2010), although the reconstructed NPDW  $\Delta^{14}$ C values are not low enough to explain the Arabian Sea or Baja California results. If low- $\Delta^{14}$ C deep waters did upwell to the surface of the North Pacific, O<sub>2</sub> could have been renewed during the conversion to North Pacific Intermediate Water (NPIW) in a process analogous to the modern deep-intermediate water conversion in the Southern Ocean. This hypothetical deglacial version of NPIW would likely need to form farther east than modern NPIW, since benthic-planktic <sup>14</sup>C pairs from cores in the northwest Pacific indicate young, <sup>14</sup>Cequilibrated intermediate waters during the deglaciation (e.g., Ahagon et al., 2003; Duplessy et al., 1989; Okazaki et al., 2010). While the incorporation of low- $\Delta^{14}$ C waters into NPIW may have influenced Baja California record, it is difficult to explain the Arabian Sea results in this manner. The North Pacific signal would need to reach the Arabian Sea via the Indonesian Throughflow (ITF). In the modern ITF, the lower thermocline and intermediate waters are sourced from the South Pacific, and the ITF waters undergo intense mixing as they cross the various sills in the Indonesian Seas (e.g., Gordon and Fine, 1996; Gordon et al., 2003; Talley and Sprintall, 2005). These features make it unlikely that a North Pacific signal could reach the Arabian Sea without significant dilution. Lower sea level would have also reduced the maximum sill depths within the Indonesian Seas, restricting the passage of the densest through-flow waters.



**Figure 2.5**: Compilation of carbon cycle and climate changes during the last deglaciation: a) Atmospheric CO<sub>2</sub> concentration measured in the Dome C ice core (black diamonds) (Monnin et al., 2001), placed on the GISP2 timescale using methane synchronization (Marchitto et al., 2007). b) INTCAL09 atmospheric  $\Delta^{14}$ C record (gray line) (Reimer et al., 2009). c) Baja California intermediate water  $\Delta^{14}$ C (red circles) (Marchitto et al., 2007). d) Arabian Sea intermediate water  $\Delta^{14}$ C from RC27-14 (green squares) and RC27-23 (blue diamonds). e) Southern Ocean opal flux (orange triangles) indicating the strength of Southern Ocean (SO) upwelling (Anderson et al., 2009). f) Antarctic Dome C  $\delta$ D (gray line) (Jouzel et al., 2007) placed on the GISP2 timescale (Marchitto et al., 2007). YD, BA, ACR and HS1 indicate the Younger Dryas, Bølling-Allerød, Antarctic Cold Reversal and Heinrich Stadial 1 intervals respectively.

## 6. Conclusion

In this study we have reconstructed the  $\Delta^{14}$ C at intermediate depths in the Arabian Sea during the last deglaciation. These reconstructions reveal intermediate waters that were very depleted in <sup>14</sup>C relative to the contemporaneous atmosphere, with the deeper core site recording lower  $\Delta^{14}$ C values than the shallower site. The timing of the low  $\Delta^{14}$ C intervals is coincident with increases in atmospheric pCO<sub>2</sub> and decreases in atmospheric  $\Delta^{14}$ C. The  $\Delta^{14}$ C reconstructed for the Arabian Sea is similar to that previously recorded in the eastern North Pacific near Baja California, particularly during Heinrich Stadial 1. The similarity in the  $\Delta^{14}$ C records between these two distant sites suggests that similar mechanisms were responsible for the observations and that the processes involved are likely oceanographic in origin rather than geologic.

The intermediate water  $\Delta^{14}$ C records in the Arabian Sea and near Baja California are most readily consistent with the upwelling of <sup>14</sup>C-depleted deep water up to the surface of the Southern Ocean as this ocean warmed and destratified during the deglaciation. These <sup>14</sup>Cdepleted waters must have spent enough time near the surface of the Southern Ocean to gain buoyancy and renew oxygen concentrations, but not enough time to significantly alter  $\Delta^{14}$ C, before being incorporated into thermocline or intermediate waters such as Subantarctic Mode Water or Antarctic Intermediate Water.

At this time, significant outstanding questions remain. It is unclear why <sup>14</sup>C-depleted waters are not observed along the Chile margin (De Pol-Holz et al., 2010). It is also unclear how the  $\Delta^{14}$ C record from the intermediate Eastern Equatorial Pacific (Stott et al., 2009) is related to the records from the Arabian Sea or Baja California. The difference in timing and structure as well as the much lower  $\Delta^{14}$ C values suggests that the mechanisms involved in transporting <sup>14</sup>Cdepleted carbon to the EEP site were different. The spatial and temporal coverage of  $\Delta^{14}$ C records from the glacial and deglacial ocean remains very sparse. Effort should be made to reconstruct intermediate water  $\Delta^{14}$ C from other sites, especially from the southern high latitudes. Mapping of the glacial <sup>14</sup>C-depleted deep reservoir also remains a major priority.

# Chapter III: Ventilation of intermediate waters along the Chile margin during the last deglaciation and implications for the release of <sup>14</sup>C-depleted CO<sub>2</sub>

### Abstract.

Most current models explaining the glacial/interglacial variability in atmospheric  $CO_2$ focus on processes acting in the Southern Ocean. The decline in atmospheric  $\Delta^{14}$ C and minima in intermediate water  $\Delta^{14}$ C during the deglaciation have been interpreted to represent the upwelling of <sup>14</sup>C-depleted, carbon-rich deep waters in the Southern Ocean. This scenario has recently been challenged by the absence of anomalous <sup>14</sup>C depletion in an intermediate water record from the Chile margin. However, modern Antarctic Intermediate Waters flow away from the Chile margin at mid-latitudes, following the path of the South Pacific subtropical gyre, leaving open the possibility that low- $\Delta^{14}$ C intermediate waters bypassed this site. We test this hypothesis using a reconstruction of deglacial intermediate water  $\Delta^{14}$ C from ~53°S along the Chile margin. Our  $\Delta^{14}$ C results confirm that the intermediate waters occupying the depth range of modern Antarctic Intermediate Water in the southeast Pacific were relatively well equilibrated with the atmosphere during the deglaciation. These results indicate that if low- $\Delta^{14}$ C intermediate waters were formed in the Southern Ocean during the deglaciation, the mechanisms involved in their formation must have been significantly different from those responsible for modern Antarctic Intermediate Water formation. We suggest that low- $\Delta^{14}$ C waters upwelled in the Southern Ocean may have been incorporated into relatively deep and dense intermediate waters formed through subduction at the Polar Front. Our  $\Delta^{14}$ C results also reveal atmosphere to intermediate water  $\Delta^{14}$ C offsets that are significantly higher than modern during the Last Glacial Maximum and the latter half of the Antarctic Cold Reversal, indicating a shoaling and/or

northward shift of the  $\Delta^{14}$ C gradients in the southeast Pacific at these times. These shifts in  $\Delta^{14}$ C gradients would be consistent with northward displacement of the Southern Ocean frontal zones.

#### 1. Introduction

Soon after it was discovered that atmospheric CO<sub>2</sub> concentrations were reduced during the last glacial period (Berner et al., 1980; Delmas et al., 1980), researchers recognized the importance of Southern Ocean processes in regulating atmospheric CO<sub>2</sub> (Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984). Strong westerly winds over the Southern Ocean drive Ekman divergence and upwelling, which bring nutrient and carbon-rich deep waters up to the sea surface. Incomplete utilization of upwelled nutrients allows some of the CO<sub>2</sub> that had been sequestered in the deep ocean to leak out to the atmosphere. Most current hypotheses attempting to explain the glacial/interglacial CO<sub>2</sub> changes focus on closing the Southern Ocean leak through some combination of biogeochemical and/or physical mechanisms. The most often mentioned mechanisms involve increasing the efficiency of nutrient utilization by phytoplankton (Francois et al., 1997; Martin, 1990), decreasing mixing between the surface of the Southern Ocean and the deep ocean (Francois et al., 1997; Toggweiler, 1999; Watson and Naveira Garabato, 2006), and reducing air-sea CO<sub>2</sub> exchange by increasing sea ice coverage (Stephens and Keeling, 2000) (see Sigman et al., 2010 for a review).

If ventilation of the glacial deep ocean was reduced by limited upwelling/mixing or increased sea ice coverage in the Southern Ocean, we would expect that the <sup>14</sup>C content of the glacial deep ocean would have been reduced, as these processes would have also restricted the uptake of <sup>14</sup>C by the ocean. This prediction appears to be consistent with reconstructions of atmospheric radiocarbon activity ( $\Delta^{14}$ C), which indicate higher atmospheric  $\Delta^{14}$ C during the last glacial period, followed by a steep decline in  $\Delta^{14}$ C during the deglaciation (Broecker and Barker, 2007; Fairbanks et al., 2005; Hughen et al., 2004a; Hughen et al., 2006). The deglacial atmospheric  $\Delta^{14}$ C changes are coincident with the two-step rise in atmospheric CO<sub>2</sub> (Marchitto et al., 2007), suggesting that the CO<sub>2</sub> released from the ocean was very depleted in <sup>14</sup>C. Records of deep ocean  $\Delta^{14}$ C also generally support <sup>14</sup>C depletion of the deep ocean during the last glacial period (Broecker et al., 2004; Galbraith et al., 2007; Keigwin, 2004; Keigwin and Schlegel, 2002; Shackleton et al., 1988; Sikes et al., 2000; Skinner et al., 2010; Skinner and Shackleton, 2004), although the spatial extent and age of the glacial deep ocean low- $\Delta^{14}$ C reservoir remains unclear.

Minima in intermediate water  $\Delta^{14}$ C have also been observed during the last deglaciation (Bryan et al., 2010; Marchitto et al., 2007; Stott et al., 2009), and suggested to record the release of <sup>14</sup>C-depleted CO<sub>2</sub> from the deep ocean. The timing of  $\Delta^{14}$ C minima, during intervals of Antarctic warming, atmospheric CO<sub>2</sub> rise, and increased upwelling in the Southern Ocean (Anderson et al., 2009; Bryan et al., 2010; Marchitto et al., 2007), along with the decoupling between intermediate water  $\Delta^{14}$ C and O<sub>2</sub> (Bryan et al., 2010), and the Nd isotope signature of the Baja California margin intermediate waters (Basak et al., 2010) all point strongly to the Southern Ocean as the locus of <sup>14</sup>C-depleted CO<sub>2</sub> release. However, the upwelling of low- $\Delta^{14}$ C deep waters in the Southern Ocean was recently challenged by De Pol-Holz et al. (2010), who found no evidence for <sup>14</sup>C-depleted intermediate waters along the Chile margin during the last deglaciation. We argue that the results from the Chile margin are not necessarily inconsistent with upwelling of low- $\Delta^{14}$ C waters in the Southern ocean. In the modern ocean, Antarctic Intermediate Water formed in the southeast Pacific Ocean flows northward along the Chile margin before turning westward, following the path of the wind-driven subtropical gyre (Iudicone et al., 2007; Sloyan and Rintoul, 2001). It is possible that the core of the low- $\Delta^{14}$ C deglacial intermediate water mass turned away from the Chile margin prior to reaching the De Pol-Holz et al. (2010) core site at 36° S. Alternatively, it is possible that the distribution and/or mechanisms responsible for the formation of low- $\Delta^{14}$ C intermediate waters during the deglaciation were substantially different from those responsible for modern Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) formation. In this study, we test the first hypothesis, that low- $\Delta^{14}$ C waters were incorporated into intermediate waters similar to modern SAMW/AAIW, but these intermediate waters were guided away from the margin by the subtropical gyre prior to reaching the De Pol-Holz et al. core site, using a reconstruction of intermediate water  $\Delta^{14}$ C from farther south (53° S) along the Chile margin. We show that intermediate waters at this site were relatively well equilibrated with the atmosphere during the deglaciation and indicate no evidence for the incorporation very low- $\Delta^{14}$ C waters. This evidence, along with other recently published intermediate water records from southern high latitudes, allows us to reject the first possibility, indicating instead that very low- $\Delta^{14}$ C waters were not incorporated into deglacial water masses similar to modern SAMW/AAIW. We discuss how the formation of low- $\Delta^{14}$ C intermediate waters during the deglaciation may have differed from the modern mechanisms of SAMW/AAIW formation.

#### 2. Materials and Methods

New radiocarbon measurements in this study come from sediment core MD07-3128. MD07-3128 was recovered from a water depth of 1032 m along the margin of southern Chile (Table 3.1; Figure 3.1). In the modern ocean, this site lies near the base of the salinity minimum associated with AAIW and close to one of the primary regions of AAIW formation in the southeast Pacific (McCartney, 1977; Sallee et al., 2010; Talley, 1996). In the southeast Pacific, gradients in natural  $\Delta^{14}$ C are oriented along density gradients, with denser waters having lower  $\Delta^{14}$ C values. Natural  $\Delta^{14}$ C refers to estimates of  $\Delta^{14}$ C prior to nuclear weapons testing and addition of fossil fuel CO<sub>2</sub> (Rubin and Key, 2002). Upwelling to the south of the core site causes isopycnals to be near vertical, resulting in horizontal  $\Delta^{14}$ C gradients. The natural  $\Delta^{14}$ C value at ~1000 m near the core site is ~-115‰ (Key et al., 2004). The SO161-SL22 core site, studied by De Pol-Holz et al. (2010), is located at a similar position near the base of the salinity minimum and along the  $\Delta^{14}$ C gradient to MD07-3128 (Figure 3.1 c & d) but ~17° to the north.

For a for  ${}^{14}C$  analysis were picked from the >250  $\mu$ m size fraction of washed sediment samples. Benthic samples consisted of genera-specific samples of *Cibicidoides* or Uvigerina or mixed Cibicidoides and Uvigerina in few cases. Planktic samples were monospecific samples of G. bulloides or N. pachyderma (s) or mixed species. Graphite targets were prepared at the INSTAAR Laboratory for AMS Radiocarbon Preparation and Research (NSRL). Foraminifera were leached for 5 minutes using 0.001N HCl. Foraminifera were then hydrolyzed using H<sub>3</sub>PO<sub>4</sub>, and the resultant CO<sub>2</sub> was purified cryogenically. CO<sub>2</sub> was reduced to graphite using an Fe catalyst in the presence of H<sub>2</sub> (McNichol et al., 1992). Oxalic acid primary and secondary measurement standards, geologic control samples of consensus <sup>14</sup>C age, and process blanks were prepared along with foraminiferal samples at NSRL. Samples were analyzed for <sup>14</sup>C by accelerator mass spectrometry at the Keck Carbon Cycle AMS Facility, UC Irvine (KCCAMS). Results are reported following the conventions of Stuiver and Polach (1977) and corrected for isotopic fractionation using  $\delta^{13}$ C measurements of the graphite samples in the AMS. KCCAMS  $\delta^{13}$ C values are not suitable for paleoceanographic interpretation, as fractionation can occur during graphitization or AMS measurement, and are not reported here.

## 3. Calendar Age Model

Derivation of an age model independently of measured <sup>14</sup>C ages is preferred, so that reconstructed intermediate water  $\Delta^{14}$ C values are independent of any possible changes in surface reservoir ages. During the deglaciation, the calendar age model for MD07-3128 is based on the stratigraphic correlation of N. pachyderma (s)  $\delta^{18}$ O to the  $\delta$ D record of Antarctic temperature from the Epica Dome C (EDC) ice core (Jouzel et al., 2007) (Table 3.2; Figure 3.2). Previous studies have demonstrated that sea surface temperatures at southern high latitude sites increased during the deglaciation at the same time as Antarctic temperature (e.g., Kaiser et al., 2005; Lamy et al., 2007). Comparison of the temperature records from the EDC, Dronning Maud Land and Byrd ice cores also indicates that the intervals of deglacial warming are coincident between the Antarctic records (Barbante et al., 2006). The EDC  $\delta D$  record used for this correlation has been placed on the GISP2 timescale via methane synchronization (Marchitto et al., 2007) in order to allow direct comparison to previously published intermediate water  $\Delta^{14}$ C records (Bryan et al., 2010; Marchitto et al., 2007). Outside of the deglaciation when there are no suitable tie points, we use planktic foraminiferal <sup>14</sup>C ages calibrated to Marine09 (Reimer et al., 2009) assuming a  $\Delta R$  of 270±100 yr. Error in our calendar ages was estimated using a Monte Carlo analysis including an estimated uncertainty in the placement of tie points of 400-500 years and a 10% uncertainty in the sedimentation rate between the sample depth and the nearest tie point (see Appendix A for a description of this method). The sedimentation rates are 10-27 cm/kyr during the deglaciation. Sedimentation rates are much higher during the last glacial maximum (LGM) (~140 cm/kyr) and much lower during the Holocene (~2-4 cm/kyr). The large changes in sedimentation rates are related to the core site's proximity to fjords along the southern Chile

margin. When the alpine glaciers were at their maximum extent, terrigenous sediment flux to the core site was high, and as the glaciers retreated the sediment load decreased. The very low sedimentation rates during the Holocene have two important consequences for the  $\Delta^{14}$ C record: the *N. pachyderma* (s)  $\delta^{18}$ O record has a much lower resolution during this section resulting in greater uncertainty in the stratigraphic correlation; and the greatly reduced terrigenous input results in much higher concentrations of foraminifera, which may be mixed downward within the core by bioturbation, biasing the <sup>14</sup>C ages (this issue is discussed further in Section 4).



**Figure 3.1**: Location and oceanographic setting of intermediate water  $\Delta^{14}$ C records. a. Location map showing the location of MD07-3128 along with other deglacial intermediate water  $\Delta^{14}$ C sites discussed in this paper. See Table 3.1 for locations and references. b. Location along the Chile margin of MD07-3128 and the SO161-SL22 core site from De Pol-Holz et al. (2010). c. Section of salinity along the Chile margin, showing the location of MD07-3128 (green dot) near the base of the salinity minimum associated with Antarctic Intermediate Water. The location of SO161-SL22 is also shown (black diamond). d. Section of natural  $\Delta^{14}$ C along the Chile margin showing that core site records  $\Delta^{14}$ C values equilibrated in the Southern Ocean with little modification along transport. Salinity and natural  $\Delta^{14}$ C data are from the GLODAP v.1.1 data set (Key et al., 2004). Small blue dots in (c) indicate the location of measurements in the GLODAP dataset. Maps and sections were created using Ocean Data View Software.

Location	Core	Latitude	Longitude	Water Depth (m)	Reference
S. Chile Margin	MD07-3128	52.7°S	75.6°W	1032	This study
Arabian Sea	RC27-14	18.3°N	57.7°E	596	Bryan et al., 2010
Arabian Sea	RC27-23	18°N	57.6°E	820	Bryan et al., 2010
Baja California	MV99- MC19/GC31/PC08	23.5°N	111.6°W	705	Marchitto et al., 2007
Eastern Equatorial Pacific	VM21-30	1.2°S	89.7°W	617	Stott et al., 2009
N. Chile Margin	SO161-SL22	36.2°S	73.7°W	1000	De Pol-Holz et al., 2010
Brazil Margin	C1 (corals)	22.4°S	40.1°W	621	Mangini et al., 2010
Brazil Margin	C2 (corals)	24.3°S	43.2°W	781	Mangini et al., 2010
Drake Passage	Coral	59.7°S	68.7°W	1125	Goldstein et al., 2001
Drake Passage	Coral	59.4°S	68.5°W	1125	Robinson and van de Flierdt, 2009
Bay of Plenty	RR0503-JPC64	37.4°S	177.0°E	651	Rose et al., 2010
Chatham Rise	MD97-2120	43.5°S	174.9°E	1210	Rose et al., 2010

Table 3.1: Location of intermediate water  $\Delta^{14}$ C sites discussed in this paper.



**Figure 3.2**: MD07-3128  $\delta^{18}$ O stratigraphy. *N. pachyderma(s)* (red dots), *G. bulloides* (green dots), *Cibicidoides* (green diamonds) and *Uvigerina* (purple diamonds)  $\delta^{18}$ O values are compared to the Epica Dome C  $\delta$ D record (Jouzel et al., 2007), placed on the GISP2 age model (Marchitto et al., 2007). The MD07-3128 age model during the deglaciation was constructed by correlating the *N. pachyderma(s)*  $\delta^{18}$ O record to the EDC  $\delta$ D record. Tie points are indicated by black triangles (Table 3.2). Calendar ages before the oldest tie point and after the youngest tie point are based on calibrated planktic radiocarbon ages, assuming a constant reservoir age of 675±100 years.

Depth in	Calendar Age						
Core (cm)	(years BP)	Age Control					
3	2940	calibrated planktic <sup>14</sup> C <sup>a</sup>					
19	10550	EDC stratigraphic correlation <sup>b</sup>					
25	11900	EDC stratigraphic correlation <sup>b</sup>					
49	12850	EDC stratigraphic correlation <sup>b</sup>					
67	14600	EDC stratigraphic correlation <sup>b</sup>					
163	18200	EDC stratigraphic correlation <sup>b</sup>					
393	19820	calibrated planktic <sup>14</sup> C <sup>a</sup>					

## Table 3.2: MD07-3128 Age Model

a. Mixed planktic <sup>14</sup>C ages calibrated to Marine09 (Reimer et al., 2009) using the OxCal 4.1.6 program,  $\Delta R = 270\pm100$ 

b. *N. pachyderma(s)*  $\delta^{18}$ O correlated to Epica Dome C  $\delta$ D (Jouzel et al., 2007) placed on the GISP2 age model by methane synchronization (Marchitto et al., 2007)

## 4. Results

Planktic and benthic foraminiferal conventional <sup>14</sup>C ages from MD07-3128 are given in Table 3.3. We calculated age-corrected  $\Delta^{14}$ C values (Figure 3.3) by combining <sup>14</sup>C ages with interpolated calendar ages and applying the summary equation for initial  $\Delta^{14}$ C of Adkins and Boyle (1997):

$$\Delta^{14}C = (e^{-14C \operatorname{age}/8033} / e^{-\operatorname{cal} \operatorname{age}/8266} - 1) * 1000$$
 [Equation 1]

where 8033 and 8266 are the Libby and true mean lives of <sup>14</sup>C, respectively. Error bars on  $\Delta^{14}$ C values were calculated by combining the one-sigma error on the <sup>14</sup>C ages with the estimated error in the calendar ages given in Table 2. The  $\Delta^{14}$ C errors are dominated by the error in the calendar ages, which causes the error bars to be oriented in a diagonal direction that lies very close to a decay trajectory.

#### 4.1 Evaluation of data quality

Most of the  $\Delta^{14}$ C data follow the atmospheric trend in  $\Delta^{14}$ C with atmosphere to surface water (planktic) and intermediate water (benthic) offsets that are relatively constant. However, there are several planktic and two benthic  $\Delta^{14}$ C values that are higher than Intcal09 atmospheric values (Reimer et al., 2009). The cause of these anomalously high  $\Delta^{14}$ C values is likely the downward mixing of younger Holocene foraminifera into the late deglacial section of the core. The low sedimentation rates in the Holocene section of the core lead to very high foraminiferal concentrations in the Holocene section of the core and the bioturbation of concentration changes can lead to biases in the <sup>14</sup>C ages (Keigwin, 2004; Keigwin and Schlegel, 2002).



**Figure 3.3**: MD07-3128  $\Delta^{14}$ C values.  $\Delta^{14}$ C for benthic foraminifera (green circles), *N. pachyderma(s)* (red diamonds), and *G. bulloides* (blue diamonds) was calculated using Equation 1. The Intcal09 atmospheric record (Reimer et al., 2009) is shown for comparison.  $\Delta^{14}$ C values that are higher than atmospheric values (open symbols) are suspected to be affected by the bioturbation of younger foraminifera and are excluded from the interpretation of deglacial  $\Delta^{14}$ C. YD, B-A, ACR, HS1 and LGM indicate the Younger Dryas, Bølling-Allerød, Antarctic Cold Reversal, Heinrich Stadial 1, Last Glacial Maximum intervals respectively.

It is likely that the G. bulloides  $^{14}$ C ages are more susceptible to these biases than the N. pachyderma (s) or benthic <sup>14</sup>C ages, since the surface conditions (and species assemblages) are more polar-like during the last glacial maximum and the abundance of G. bulloides increases proportionally more than N. pachyderma (s) during the Holocene (based on qualitative estimates, specific counts were not made) (U. S. Ninnemann, personal communication, 2010). This interpretation is supported by the pattern of <sup>14</sup>C ages with depth in the core (Figure 3.4). The samples from 31 cm and 41 cm yield the same planktic and benthic <sup>14</sup>C ages suggesting homogenization of the sediment by bioturbation. Below these depths, down to ~110 cm, the benthic and N. pachyderma (s) <sup>14</sup>C ages generally increase with depth, while the G. bulloides ages remain more similar, consistent with the preferential bioturbation of G. bulloides. Below  $\sim$ 110 cm, with the exception of one *N. pachvderma* (s) age, all of the ages increase with depth, and the G. bulloides and N. pachyderma (s) ages agree well. It appears that the section below ~110 cm is far enough below the Holocene foraminiferal concentration increase and sedimentation rates are high enough that the effect of bioturbation is minimized. Since Holocene *N. pachyderma* (s) and benthic foraminiferal concentrations do not increase as much as G. bulloides, it appears that their ages are reliable below  $\sim 50$  cm (with the exception of the N. pachyderma (s) age at 179 cm).

An alternative explanation for the elevated  $\Delta^{14}$ C values is that the calendar ages determined from the stratigraphic correlation are too old. If we make the assumption that all of the <sup>14</sup>C ages are reliable, we can construct an age model using the youngest calibrated planktic <sup>14</sup>C ages. This "young" age model was constructed using ten of the planktic foraminiferal <sup>14</sup>C ages, calibrated using Marine09 (Reimer et al., 2009) and a constant  $\Delta$ R of 270±100 years. The <sup>14</sup>C ages included in the age model were selected to prevent reversals in calendar age and  $\Delta^{14}$ C values higher than the Intcal09 atmosphere; these <sup>14</sup>C ages are indicated in Table 3.3. This interpretation would imply that at times there are very large surface reservoir ages (>2000 yr) and very old intermediate waters at the core site (Figure 3.5a). While such large surface reservoir ages and old intermediate waters are theoretically possible given the core site's proximity to the Southern Ocean and the proposed upwelling of very old deep waters, the implications of the "young" age model for the  $\delta^{18}$ O stratigraphies are more problematic (Figure 3.5b). If the young age model were correct, the beginning of the deglacial *N. pachyderma* (s)  $\delta^{18}$ O decrease (which we interpret as primarily a sea surface temperature increase) would be delayed until ~16.4 kyr BP, well after temperatures in Antarctica (e.g., Jouzel et al., 2007) and sea surface temperatures at other sites along the Chile margin (Lamy et al., 2007; Mohtadi et al., 2008) began to increase. The young age model also implies that  $\delta^{18}$ O decrease (warming) at this site continued through the Antarctic Cold Reversal (ACR) and then paused during the second interval of Antarctic warming, a pattern that is out of phase with the Antarctic ice cores and other sea surface temperature records from southern high latitudes. For these reasons, we conclude that the young age model is very unlikely to be correct. In the rest of this paper, we use the stratigraphic age model, based on the expected pattern of climate development for the region, and attribute  $\Delta^{14}$ C values higher than the Intcal09 atmosphere (open symbols in Figure 3.2) to bioturbation. We exclude these values from our interpretation of intermediate water  $\Delta^{14}$ C history.

		Calendar						
	Calendar	Age		Sample		<sup>14</sup> C Age		
Depth in	Age <sup>a</sup>	Error		Weight	<sup>14</sup> C Age	Error	$\Delta^{14}C^{d}$	
core (cm)	(year BP)	(year)	Taxa	(mg)	(year)	(year)	(‰)	Accession #
2-4 <sup>b,c</sup>			Mixed planktics		3405	25		
30-32 <sup>b</sup>	12140	390	G. bulloides	6.6	9050	25	407	CURL-11831
30-32 <sup>b</sup>	12140	390	Cibicidoides	6	10410	25	188	CURL-11823
34-36 <sup>c</sup>			Mixed planktics		9945	45		
40-42	12530	410	G. bulloides	7.3	9050	20	476	CURL-11814
40-42	12530	410	Cibicidoides	10.8	10430	35	243	CURL-11818
50-52	13040	410	G. bulloides	7.1	11805	35	115	CURL-11822
50-52	13040	410	Cibicidoides	5.5	12930	35	-31	CURL-11830
54-56 <sup>b</sup>	13430	410	G. bulloides	7.4	11600	30	199	CURL-11813
54-56	13430	410	Cibicidoides	9.3	13475	40	-51	CURL-11821
60-62	14020	380	G. bulloides	6.3	12540	30	144	CURL-11820
60-62	14020	380	Cibicidoides	5.5	12990	35	82	CURL-11819
64-66	14410	380	G. bulloides	6.8	11940	30	292	CURL-11828
64-66	14410	380	Cibicidoides	6.3	13540	35	59	CURL-11815
70-72	14760	380	G. bulloides	6.2	12750	35	220	CURL-11832
70-72	14760	380	N. pachyderma (s)	3.6	13375	35	129	CURL-11133
70-72	14760	380	Cibicidoides	8.5	13820	35	68	CURL-11131
74-76 <sup>°</sup>			Mixed planktics		8140	40		
94-96 <sup>b</sup>	15740	400	G. bulloides	6.7	12370	35	439	CURL-11824
94-96	15740	400	N. pachyderma (s)	3.2	13705	35	219	CURL-11139
94-96	15740	400	Cibicidoides	6.4	14140	35	154	CURL-11136
108-110 <sup>b</sup>	16310	420	G. bulloides	6.7	12760	35	469	CURL-11829
108-110	16310	420	mixed benthics	3.3	14605	50	167	CURL-11817
130-132	17200	510	N. pachyderma (s)	3.6	14435	35	328	CURL-11134
130-132	17200	510	mixed benthics	8.1	14945	35	247	CURL-11132
150-152	18010	490	G. bulloides	6.3	15185	35	335	CURL-11856
150-152	18010	490	N. pachyderma (s)	3.1	15205	40	331	CURL-11140
150-152	18010	490	Uvigerina	4.1	15870	40	226	CURL-11152
154-156 <sup>c</sup>			Mixed planktics		15460	70		
164-166	18510	490	G. bulloides	6.1	15700	35	330	CURL-11858
164-166	18510	490	Uvigerina	5.5	16440	60	213	CURL-11827
178-180 <sup>b</sup>	18590	490	N. pachyderma (s)	3.4	14740	35	513	CURL-11135
178-180	18590	490	Uvigerina	5.4	16615	45	198	CURL-11142
220-222 <sup>b</sup>	18830	490	N. pachyderma(s)	3.5	16105	40	315	CURL-11138
220-222	18830	490	Uvigerina	4.3	17045	45	169	CURL-11153
300-302	19290	520	Uvigerina	3.8	18020	70	95	CURL-11816
392-394 <sup>b,c</sup>			Mixed planktics		17330	130		

Table 3.3: MD07-3128 <sup>14</sup>C data

a: Calendar ages linearly interpolated from the stratigraphic age model in Table 3.2.
b: <sup>14</sup>C ages used to create the "young" age model.
c: <sup>14</sup>C ages obtained from U. S. Ninnemann.
d: Δ<sup>14</sup>C values higher than the Intcal09 atmosphere are italicized.



**Figure 3.4**: MD07-3128 <sup>14</sup>C ages. Conventional <sup>14</sup>C ages for benthic foraminifera: *Cibicidoides* (dark green circles), *Uvigerina* (light green circles), and mixed genera (yellow circles); and planktic foraminifera: *N. pachyderma* (s) (red diamonds), *G. bulloides* (blue diamonds) and mixed species (purple diamonds) are plotted with depth in the sediment core. The <sup>14</sup>C ages that correspond to  $\Delta^{14}$ C values higher than atmospheric values in Figure 3.3 are shown as open symbols. The lack of an increase in *G. bulloides* <sup>14</sup>C ages that matches the increase in *N. pachyderma* (s) and benthic <sup>14</sup>C ages in the top ~1 m of the core suggests the downward bioturbative mixing of younger *G. bulloides* associated with very high abundances in the Holocene section of the core.



**Figure 3.5**: Implications of the "young" age model. a. Intermediate water (green open circles) and surface (*N. pachyderma* (s), red open diamonds; *G. bulloides*, green open diamonds)  $\Delta^{14}$ C values calculated using an age model based on the youngest calibrated <sup>14</sup>C ages.  $\Delta^{14}$ C values calculated using the "stratigraphic" age model are shown as closed symbols. b. Same as Figure 2, except the calendar ages were calculate using the "young" age model.

# *4.2 Intermediate water* $\Delta^{14}C$ *history*

At the end of the LGM and the beginning of the deglaciation, intermediate water  $\Delta^{14}$ C at MD07-3128 steadily increased by ~140‰, reaching a maximum of ~220‰ at ~17.0 kyr BP (Figure 3.3). From ~17.0 to ~14.7 kyr BP intermediate water  $\Delta^{14}$ C declined by ~160‰. This interval corresponds to Heinrich Stadial 1 (HS1) in the North Atlantic and the first interval of Antarctic warming. The  $\Delta^{14}$ C decline is also observed in the planktic foraminifera record and was very similar in timing and magnitude to the decline in atmospheric  $\Delta^{14}$ C during this interval (Hughen et al., 2006; Hughen et al., 2004b; Reimer et al., 2009). From ~14.7 to ~14.0 kyr BP, during the first part of the ACR, intermediate water  $\Delta^{14}$ C reached a plateau, before declining again by ~140‰ between ~14.0 and ~13.5 kyr BP. The similarity between the decline in intermediate water  $\Delta^{14}$ C and the decline in atmospheric  $\Delta^{14}$ C during HS1 suggests that the intermediate waters at this site were relatively well equilibrated with the atmosphere and do not record the influence of anomalously <sup>14</sup>C-depleted waters.

We can examine the degree of atmosphere to intermediate water  $\Delta^{14}$ C equilibration in more detail by subtracting the reconstructed  $\Delta^{14}$ C values for surface and intermediate waters from Intcal09 atmospheric  $\Delta^{14}$ C values (Reimer et al., 2009) (Figure 3.6). The largest atmosphere to intermediate water  $\Delta^{14}$ C offsets ( $\Delta\Delta^{14}C_{A-IW}$ ) occurred at the beginning of the record, during the last glacial maximum, when the  $\Delta^{14}$ C offset was as high as ~300‰. From the beginning of the record into the start of HS1,  $\Delta\Delta^{14}C_{A-IW}$  decreased steadily to ~170‰ at ~17.0 kyr BP. During HS1,  $\Delta\Delta^{14}C_{A-IW}$  increased to ~220‰ at ~16.2 kyr BP, after which  $\Delta\Delta^{14}C_{A-IW}$ decreased to ~170‰ and remained relatively constant until the end of HS1. During the beginning of the B-A/ACR,  $\Delta\Delta^{14}C_{A-IW}$  decreased to a minimum of ~100‰ at ~14.0 kyr BP, before increasing to 235-255‰ during the second half of the B-A/ACR. The  $\Delta^{14}C$  offset between the atmosphere and surface waters ( $\Delta\Delta^{14}C_{A-SW}$ ) remained relatively constant during the LGM and HS1;  $\Delta\Delta^{14}C_{A-SW}$  decreased from ~120‰ to ~90‰ at the start of HS1 but then increased back to ~120‰ at the end of HS1.  $\Delta\Delta^{14}C_{A-SW}$  decreased during the B-A/ACR, ranging from 5 to 90‰, possibly indicating reduced reservoir ages. However, it is also possible that the *G*. *bulloides* <sup>14</sup>C ages during this time exhibit a modest young bias as a result of downward bioturbation of younger foraminifera.

These  $\Delta^{14}$ C offsets are not directly comparable to modern offsets since there was a larger inventory of  ${}^{14}$ C in the glacial and deglacial atmosphere. Due to the exponential nature of  ${}^{14}$ C decay, the same physical processes will result in greater  $\Delta^{14}$ C offsets when the <sup>14</sup>C inventory is larger. In order to meaningfully compare present and past physical processes such as mixing and air-sea isotopic equilibration, we, therefore, normalize the  $\Delta^{14}$ C results to what they would be at pre-industrial, pre-nuclear atmospheric <sup>14</sup>C activity (i.e. Fraction Modern (Fm) = 1 or  $\Delta^{14}C = 0$ ) by accounting for initial Fm (see Appendix B) (Figure 3.6 – open symbols). The normalized  $\Delta^{14}$ C offsets are smaller than the absolute offsets, though the trends are the same. The normalized atmosphere to intermediate water  $\Delta^{14}$ C offsets were similar to or slightly larger during HS1 and the first part of the ACR than modern values near the core site. During the LGM and the second half of the ACR, normalized  $\Delta \Delta^{14} C_{A-IW}$  values were higher than modern, indicating reduced equilibration with the atmosphere and/or the incorporation of more <sup>14</sup>Cdepleted source water. Benthic foraminiferal  $\delta^{13}$ C values (U. S. Ninnemann, unpublished data) suggest that increased  $\Delta \Delta^{14}C_{A-IW}$  during the LGM reflects the replacement of AAIW by Circumpolar Deep Water (CDW) at the core site. The  $\Delta\Delta^{14}C_{A-IW}$  value at ~19.3 kyr BP suggests that CDW may have been more <sup>14</sup>C-depleted during the LGM, relative to modern values (~150‰, not shown). Although the MD07-3128 age model is less well constrained during this

interval and more data is needed to confirm this observation. It is unclear at this time if the increase in  $\Delta\Delta^{14}C_{A-IW}$  at ~14.0 indicates a shift back to CDW at the core site or the injection of <sup>14</sup>C-depleted deep waters into AAIW. Since a decline in  $\Delta^{14}C$  is not observed farther north along the Chile margin at this time (De Pol-Holz et al., 2010) (Figure 3.7), it is probable that the MD07-3128 core site is recording CDW. Normalized  $\Delta\Delta^{14}C_{A-SW}$  values were similar to modern values near the core site during most of the record, with the exception of during the B-A, which as previously noted, may have been affected by bioturbation.



**Figure 3.6**: MD07-3128  $\Delta\Delta^{14}$ C. The  $\Delta^{14}$ C offset between the Intcal09 atmosphere (Reimer et al., 2009) and the intermediate waters (green circles). The offset between the atmosphere and the surface ocean (*N. pachyderma* (s) values are red diamonds; *G. bulloides* values are blue diamonds) is also shown. Closed symbols represent the absolute  $\Delta\Delta^{14}$ C, while open symbols have been normalized to preindustrial atmosphere-intermediate water  $\Delta^{14}$ C offset near the core site is indicated by a green dotted line, and the preindustrial atmosphere-surface ocean  $\Delta^{14}$ C offset is indicated by a purple dotted line. YD, B-A, ACR, HS1 and LGM indicate the Younger Dryas, Bølling-Allerød, Antarctic Cold Reversal, Heinrich Stadial 1, Last Glacial Maximum intervals respectively.

## 5. Discussion

The atmosphere to intermediate water offsets recorded by MD07-3128 during HS1 indicate that the atmospheric equilibration of the intermediate waters in the depth range occupied by modern AAIW was not substantially different from modern equilibration. The lack of anomalously large atmosphere to intermediate water  $\Delta^{14}$ C offsets at the core site also indicates that the very low  $\Delta^{14}$ C intermediate waters observed along the Baja California margin and in the Arabian Sea were not sourced from intermediate waters formed in the southeast Pacific by processes similar to those responsible for modern AAIW. These observations allow us to reject the hypothesis that low- $\Delta^{14}$ C intermediate waters were formed locally and flowed away from the Chile margin prior to reaching the De Pol-Holz et al. (2010) core site.

The deglacial intermediate water  $\Delta^{14}$ C history reconstructed from MD07-3128 is similar to the  $\Delta^{14}$ C history reconstructed farther north along the Chile margin (36°S, 1000 m) (De Pol-Holz et al., 2010) (Figure 3.7). At both sites,  $\Delta^{14}$ C increased at the end of the LGM, followed by a decline during HS1 that was similar in timing and magnitude to the decline in atmospheric  $\Delta^{14}$ C. Throughout the record,  $\Delta^{14}$ C from MD07-3128 is consistently slightly lower than the site farther north. In the modern ocean, there is no significant  $\Delta^{14}$ C gradient between the two sites (Figure 3.1d). Regardless of the slightly increased  $\Delta^{14}$ C offset between the two sites, both sites are relatively well equilibrated with the atmosphere during HS1. If this difference is not an artifact of either age model, it suggests that the  $\Delta^{14}$ C gradients in the southeast Pacific were shifted such that the MD07-3128 core site was closer to a low- $\Delta^{14}$ C water mass. The Chile margin  $\Delta^{14}$ C values during HS1 are also similar to values from intermediate depths within the Drake Passage (Goldstein et al., 2001; Robinson and van de Flierdt, 2009) and along the Brazil margin (Mangini et al., 2010) (Figure 3.7). The similarity between these sites is consistent with the modern pattern of AAIW formation in the southeast Pacific and the Drake Passage and with northward transport of AAIW along either side of South America (Sallee et al., 2010).

Consequently, there is no evidence in AAIW formed in the vicinity of the Drake Passage (AAIW<sub>DP</sub>) for the very low intermediate water  $\Delta^{14}$ C values observed near Baja California and in the Arabian Sea during HS1 (Bryan et al., 2010; Marchitto et al., 2007) (Figure 3.8). Recent intermediate water  $\Delta^{14}$ C reconstructions from the Chatham Rise and the Bay of Plenty (Rose et al., 2010) also indicate relatively well-ventilated intermediate waters during HS1. While the intermediate waters at ~1200 m on the Chatham Rise had lower  $\Delta^{14}$ C values than AAIW<sub>DP</sub> during HS1, the values were still much higher than those observed near Baja California and in the Arabian Sea. These records from the Bay of Plenty and Chatham Rise along with the records from the Drake Passage region provide strong evidence that low  $\Delta^{14}$ C waters were not incorporated into the mode/intermediate waters formed in the southwest or southeast Pacific sectors of the Southern Ocean at similar depths to modern SAMW/AAIW.



**Figure 3.7**: Drake Passage AAIW. Comparison of intermediate water  $\Delta^{14}$ C from MD07-3128 (green circles) with intermediate water  $\Delta^{14}$ C from farther north along the Chile margin (black triangles) (De Pol-Holz et al., 2010), within the Drake Passage (blue circles; closed circles from Robinson and van de Flierdt (2009), open circle from Goldstein et al. (2001)) and the Brazil margin (yellow diamonds) (Mangini et al., 2010). YD, B-A, ACR, HS1 and LGM indicate the Younger Dryas, Bølling-Allerød, Antarctic Cold Reversal, Heinrich Stadial 1, Last Glacial Maximum intervals respectively.




If the low- $\Delta^{14}$ C waters observed along the Baja California margin and in the Arabian Sea were indeed sourced from the Southern Ocean, the formation mechanisms and the depth distribution of low- $\Delta^{14}$ C intermediate waters must have been significantly different from those of modern SAMW/AAIW. In the modern Southern Ocean, SAMW form near the Subantarctic Front along the northern edge of the ACC, in regions with deep winter mixed layers, such as the southeast Indian, southwest Pacific and southeast Pacific Oceans (Dong et al., 2008; Sallee et al., 2010). SAMW becomes progressively colder and fresher moving from the SE Indian to the SE Pacific, transformed by air-sea fluxes and the incorporation of Antarctic Surface Water, as the ACC is guided southward by the underlying topography (Dong et al., 2008; Sallee et al., 2010). AAIW formed in the southeast Pacific is commonly thought of as the coldest, freshest and densest variety of SAMW (England et al., 1993; McCartney, 1977; Talley, 1996; Talley, 1999). Cross frontal mixing between subantarctic waters and subtropical waters, as well as air-sea gas exchange, cause SAMW/AAIW to be well equilibrated with the atmosphere relative to upwelled Circumpolar Deep Water.

This current understanding of SAMW/AAIW formation differs from the traditional view proposed by Sverdrup et al. (1942), whereby AAIW is formed through subduction of Antarctic Surface Waters near the Polar Front by the addition of buoyancy. The formation of intermediate waters directly from Antarctic Surface Waters in a process similar to that proposed by Sverdrup et al. provides the most straightforward mechanism to maintain a low  $\Delta^{14}$ C signature from upwelled deep waters. We suggest that these two modes of intermediate water formation were both active during the deglaciation, with relatively well-equilibrated intermediate waters formed through wintertime mixing near the Subantarctic Front and poorly-equilibrated, denser intermediate waters forming through subduction at the Polar Front. The intermediate water  $\Delta^{14}$ C records from the Chile margin, Drake Passage, Brazil margin, and New Zealand are all within the depth range of modern SAMW/AAIW, and sample well-equilibrated intermediate waters.

The formation of relatively deep AAIW during HS1 is consistent with the model proposed by Keeling and Stephens (2001), which suggested that during extreme cold events in the North Atlantic, such as Heinrich Events, AAIW would be denser than deep waters formed in the North Atlantic. In this situation AAIW would directly overlie Antarctic Bottom Water and may sink to the depth of the sills spanning the Drake Passage (1500-2500 m) (Keeling and Stephens, 2001). Below this depth AAIW would recirculate back to the south as a geostrophic flow caused by the pressure gradient against the sills (Toggweiler and Samuels, 1995). Keeling and Stephens (2001) explicitly note that their model assumes that AAIW forms from Antarctic Surface Waters at the Polar front. There is strong evidence that North Atlantic Intermediate/Deep Water was weak during HS1 (e.g., McManus et al., 2004) (Figure 3.9). We also expect that low- $\Delta^{14}$ C deep waters upwelled in the Southern Ocean would have been denser than today (Adkins et al., 2002). Precipitation and the glacial meltwater fluxes would have provided the buoyancy required to convert upwelled deep waters to intermediate waters. The greater depth of the hypothesized low- $\Delta^{14}$ C intermediate water mass, relative to modern AAIW, would have facilitated the transmission of the low- $\Delta^{14}$ C farther north to the Baja California and Arabian Sea sites. The greater depth would have reduced the influence of the windblown subtropical gyres on intermediate water flow, and since the intermediate water would directly overlie AABW, mixing along the boundary between these water masses would likely not have increased the <sup>14</sup>C content of the intermediate water mass. While this explanation remains speculative at this time, it is consistent with the available  $\Delta^{14}$ C records, and can be tested with



**Figure 3.9:** Deglacial climate and carbon cycle changes. a. GISP2  $\delta^{18}$ O (Grootes and Stuiver, 1997) indicating temperature in Greenland. b. Pa/Th from a North Atlantic sediment core (McManus et al., 2004) indicating changes in North Atlantic Deep Water export. Light blue squares are based on <sup>238</sup>Th, and dark blue squares based on <sup>232</sup>Th. c. Intcal09 atmospheric  $\Delta^{14}$ C record (gray line) (Reimer et al., 2009) with selected intermediate water  $\Delta^{14}$ C records from this study (green circles), northern Chile margin (black triangles) (De Pol-Holz et al., 2010), Chatham Rise (orange squares) (Rose et al., 2010), Drake Passage (blue circles) (Robinson and van de Flierdt, 2009), Arabian Sea (blue diamonds) (Bryan et al., 2010) and Baja California (red circles) (Marchitto et al., 2007). d. Atmospheric pCO<sub>2</sub> measured in the Epica Dome C ice core (Monnin et al., 2001) placed on the GISP2 timescale via methane synchronization (Marchitto et al., 2007). e. Sediment core opal flux data from the Atlantic sector of the Southern Ocean (Anderson et al., 2007) placed on the GISP2 timescale (Marchitto et al., 2007), indicating the strength of upwelling in the Southern Ocean. f. Epica Dome C  $\delta D$  (Jouzel et al., 2007) placed on the GISP2 timescale (Marchitto et al., 2007), indicating Antarctic temperature.

## 6. Conclusion

We have reconstructed  $\Delta^{14}$ C values from ~1000 m on the margin of southern Chile during the last deglaciation. During Heinrich Stadial 1 and the beginning of the Antarctic Cold Reversal,  $\Delta^{14}$ C at the core site tracks the atmospheric decline in  $\Delta^{14}$ C and remains relatively well equilibrated with the atmosphere, consistent with previous  $\Delta^{14}$ C records from regions influenced by Antarctic Intermediate Water formed in the Drake Passage. This record shows no evidence during HS1 for the very low  $\Delta^{14}$ C values observed along the Baja California margin or in the Arabian Sea. Consequently, the lack of very low  $\Delta^{14}$ C values at the Chile margin site of De Pol-Holz et al. (2010) cannot be explained by the routing of low- $\Delta^{14}$ C intermediate waters away from the margin by the subtropical gyre. The intermediate water  $\Delta^{14}$ C records from the Chile margin along with other recently published records from the Drake Passage, Brazil margin and near New Zealand indicate that the intermediate waters occupying the depth range of modern SAMW and AAIW were relatively well equilibrated with the atmosphere, consistent with formation processes similar to modern SAMW/AAIW. We suggest that low- $\Delta^{14}$ C intermediate waters may have formed through subduction at the Polar Front. These intermediate waters would have been relatively dense and flowed at greater depth than modern SAMW/AAIW. Our new  $\Delta^{14}$ C record also shows larger atmosphere to intermediate water  $\Delta^{14}$ C offsets during the LGM and the latter half of the ACR, indicating a shoaling and/or northward shift of the  $\Delta^{14}$ C gradients in the southeast Pacific at these times. These shifts in  $\Delta^{14}$ C gradients would be consistent with the northward movement of the Southern Ocean frontal zones.

# Chapter IV: On the relationship between minima in $\delta^{13}$ C and $\Delta^{14}$ C of dissolved inorganic carbon during the last deglaciation

## Abstract.

During the transition from the last glacial interval into the Holocene (~18-11 kyr BP), the Earth's carbon cycle underwent significant changes, as illustrated by the  $\sim$ 50% increase in the concentration of  $CO_2$  in the atmosphere. While the exact mechanisms responsible for the deglacial increase in atmospheric CO<sub>2</sub> remain unclear, it is thought that the redistribution of carbon from the deep ocean into the upper ocean and atmosphere played a significant role. Minima in the  $\delta^{13}$ C values recorded by planktic foraminifera have been widely observed during the most recent as well as previous deglaciations. Recently, minima in the  $\Delta^{14}$ C of intermediate waters have also been observed during the last deglaciation. It has been proposed that these minima in upper ocean  $\delta^{13}$ C and  $\Delta^{14}$ C represent the redistribution of  $^{13}$ C and  $^{14}$ C-depleted carbon from the deep ocean as upwelling increased in the Southern Ocean. In this paper we investigate the relationship between the deglacial minima in  $\delta^{13}$ C and  $\Delta^{14}$ C, by compiling paired  $\delta^{13}$ C and  $\Delta^{14}$ C measurements from the deep ocean during the last glacial maximum and presenting new planktic foraminiferal  $\delta^{13}$ C measurements from two of the cores in which the intermediate water  $\Delta^{14}$ C minima have been observed. The compilation of last glacial maximum  $\delta^{13}$ C and  $\Delta^{14}$ C data suggests that the general correlation between  $\delta^{13}C$  and  $\Delta^{14}C$  in the modern ocean was maintained. The slope of the LGM  $\delta^{13}$ C -  $\Delta^{14}$ C relationship appears to be higher than modern, suggesting reduced remineralization rates in the deep ocean. It is also evident that the region of the lowest  $\delta^{13}$ C and  $\Delta^{14}$ C values shifted from the North Pacific to the Atlantic sector of the Southern Ocean at this time, indicating that the glacial deep Southern Ocean could have provided a source of <sup>13</sup>C and <sup>14</sup>C-depleted carbon to the upper ocean during the deglaciation. The planktic foraminiferal records from the Arabian Sea and the Baja California margin do show declines in  $\delta^{13}$ C at the same times as the declines in intermediate water  $\Delta^{14}$ C. However, it is difficult to isolate possible changes in the preformed  $\delta^{13}$ C<sub>DIC</sub> from local changes in productivity, upwelling and nutricline structure that occurred during the deglaciation, preventing us from assessing the relationship between preformed  $\delta^{13}$ C and  $\Delta^{14}$ C in these records. An examination of published  $\delta^{13}$ C records indicates that in some records the  $\delta^{13}$ C minima occur in two pulses with similar timing to the intermediate water  $\Delta^{14}$ C minima, intervals of warming in Antarctica, atmospheric CO<sub>2</sub> rise, and increased upwelling in the Southern Ocean. These observations are consistent with the interpretation that the deglacial  $\delta^{13}$ C and  $\Delta^{14}$ C minima are controlled by similar processes and that the upwelling of deep waters in the Southern Ocean likely plays an important role.

### **1. Introduction**

Minima in planktic foraminiferal  $\delta^{13}$ C during deglaciations have been recognized in many records from the subantarctic and tropical oceans (e.g., Curry and Crowley, 1987; Loubere and Bennett, 2008; Loubere et al., 2007; Ninnemann and Charles, 1997; Oppo and Fairbanks, 1989; Schneider et al., 1992; Shackleton et al., 1983; Shackleton and Pisias, 1985; Spero and Lea, 2002; Spero et al., 2003). The distribution of these records suggests that the  $\delta^{13}$ C minima originate from the Southern Ocean and are transferred to the low-latitude ocean via Subantarctic Mode Water and/or Antarctic Intermediate Water (AAIW) (Ninnemann and Charles, 1997; Oppo and Fairbanks, 1989), consistent with the dominant role of SAMW in transporting nutrients to low latitudes in the modern ocean (Sarmiento et al., 2004; Toggweiler et al., 1991). Spero and Lea (2002) observed that the  $\delta^{13}$ C minimum during the last deglaciation in the Eastern Equatorial Pacific (EEP) begins at the same time as Antarctic warming and a decrease in atmospheric  $\delta^{13}CO_2$ , and argued that the planktic foraminiferal  $\delta^{13}C$  records a preformed signal originating in the Southern Ocean from the upwelling of low- $\delta^{13}C$  deep waters.

This mechanism has also been recently invoked to explain minima in intermediate water  $\Delta^{14}$ C from the low-latitude eastern North Pacific and northwest Indian Oceans (Bryan et al., 2010; Marchitto et al., 2007). These minima record the spread of very low- $\Delta^{14}$ C intermediate waters during intervals of Antarctic warming, atmospheric CO<sub>2</sub> increase, atmospheric  $\Delta^{14}$ C decline and increased Southern Ocean upwelling (Anderson et al., 2009; Hughen et al., 2004; Jouzel et al., 2007; Marchitto et al., 2007; Monnin et al., 2001). Marchitto et al. (2007) and Bryan et al. (2010) argued that these very low- $\Delta^{14}$ C waters could only have been sourced from a poorly-ventilated deep ocean water mass. In this paper we explore the relationship between the deglacial  $\delta^{13}$ C and  $\Delta^{14}$ C minima in the upper ocean, in an effort to determine if these two signals record the same processes and what they can tell us about the ventilation of the glacial and deglacial ocean.

#### 2. Background

# 2.1. $\delta^{13}C$ and $\Delta^{14}C$ in the modern ocean

Before exploring the relationship between  $\delta^{13}C$  and  $\Delta^{14}C$  in the deglacial ocean it is instructive to look at their distributions in the modern ocean. The  $\delta^{13}C$  and  $\Delta^{14}C$  of dissolved inorganic carbon (DIC) have broadly similar distributions in the world oceans: high values at the sea surface and lower values in the ocean interior, with values decreasing along the path of the large scale overturning circulation from the North Atlantic to the North Pacific (Figure 4.1). The distributions of  $\delta^{13}C_{\text{DIC}}$  and  $\Delta^{14}C_{\text{DIC}}$  are similar despite being controlled by different processes. The distribution of  $\delta^{13}C_{DIC}$  is principally controlled by the mass-dependent fractionation during carbon uptake by phytoplankton, which preferentially removes <sup>12</sup>C from the DIC pool, leaving the surface ocean enriched in <sup>13</sup>C. This <sup>13</sup>C-depleted carbon is then returned to the DIC pool by oxic respiration within the ocean interior, decreasing  $\delta^{13}C_{DIC}$  in the deep ocean. As deep waters flow from the North Atlantic to the North Pacific, they accumulate remineralized low- $\delta^{13}$ C carbon (Kroopnick, 1985). These processes cause  $\delta^{13}C_{DIC}$  to be strongly correlated with the nutrient phosphate (Broecker and Peng, 1982). A secondary influence in  $\delta^{13}C_{DIC}$  is the thermodynamic fractionation that occurs during air-sea gas exchange (Broecker and Maier-Reimer, 1992; Charles et al., 1993; Lynch-Stieglitz et al., 1995). At equilibrium, the isotopic composition of the surface ocean DIC is enriched relative to atmospheric  $CO_2$  and the fractionation between DIC and atmospheric CO<sub>2</sub> increases at colder temperatures (Mook et al., 1974; Zhang et al., 1995). However, surface ocean DIC does not reach isotopic equilibrium due to the long timescale of equilibration relative to the residence time of water within the mixed layer (Broecker and Peng, 1974; Lynch-Stieglitz et al., 1995). Additionally, since atmospheric  $CO_2$  is isotopically light relative to ocean DIC,  $CO_2$  invasion will tend to decrease  $\delta^{13}C_{DIC}$  and  $CO_2$  outgassing will increase  $\delta^{13}C_{DIC}$  (Lynch-Stieglitz et al., 1995).



**Figure 4.1**: Depth profiles of  $\delta^{13}C_{DIC}$  and Natural  $\Delta^{14}C_{DIC}$  in the modern ocean. Profiles from the North Atlantic (blue x's), tropical North Atlantic (teal pluses), South Atlantic (red circles), Southern Ocean (green squares and light purple open circles), Equatorial Pacific (pink diamonds), and North Pacific (black squares, brown triangles and gray inverted triangles) show the progression of  $\delta^{13}C_{DIC}$  and Natural  $\Delta^{14}C_{DIC}$  along the path of the meridional overturning circulation from the North Atlantic to the North Pacific and the difference in the depth  $\delta^{13}C_{DIC}$  and Natural  $\Delta^{14}C_{DIC}$  and the difference in the depth  $\delta^{13}C_{DIC}$  and Natural  $\Delta^{14}C_{DIC}$  minima in the North Pacific. Data from the GLODAP v1.1 data set (Key et al., 2004). The map (c) shows the location of  $\delta^{13}C_{DIC}$  data in the GLODAP data set (blue dots), along with the location of the profiles shown in (a) and (b).

<sup>14</sup>C is also affected by isotopic fractionation; however, by definition  $\Delta^{14}$ C values are normalized to  $\delta^{13}C = -25\%$ , removing this influence (Stuiver and Polach, 1977). However, even without the  $\delta^{13}$ C normalization, the impact of radioactive decay would dominate the distribution of <sup>14</sup>C. <sup>14</sup>C is cosmogenically produced in the atmosphere and enters the ocean through air-sea gas exchange. Once a water parcel leaves the ocean surface, its  $\Delta^{14}C_{DIC}$  begins to decline as  ${}^{14}C$ decays with a half-life of 5730 years (Godwin, 1962). The distribution of  $\Delta^{14}C_{DIC}$  is therefore controlled by the degree of isotopic equilibration between surface waters and the atmosphere and the length of time waters have been away from the surface (Key et al., 2004; Matsumoto, 2007; Ostlund and Stuiver, 1980; Stuiver and Ostlund, 1980; Stuiver and Ostlund, 1983). The broad similarity in the distributions of the two isotopes originates from the accumulation of <sup>13</sup>Cdepleted remineralized carbon over the time the water in the interior of the ocean has been away from the surface. A scatter plot of  $\delta^{13}C_{DIC}$  and  $\Delta^{14}C_{DIC}$  in the modern ocean illustrates this broad relationship (Figure 4.2). There are some important differences between the distributions of  $\delta^{13}C_{DIC}$  and  $\Delta^{14}C_{DIC}$ . The strong influence of the depth of remineralization of organic matter on  $\delta^{13}C_{\text{DIC}}$  causes the minimum in the North Pacific to occur at a shallower depth (~500-1500 m) than the minimum in  $\Delta^{14}C_{DIC}$  (>~1500 m) (Figure 4.1). Organic carbon remineralization rates are highest just below the euphotic zone and decrease with depth (Feely et al., 2004). Separating the paired  $\delta^{13}C_{DIC}$  and  $\Delta^{14}C_{DIC}$  measurements into bins according to water depth indicates that the relationship between the two tracers varies with depth (Figure 4.2), i.e.  $\delta^{13}C_{DIC}$  decreases proportionally more than  $\Delta^{14}C_{DIC}$  in the upper 1.5 km of the ocean, while  $\Delta^{14}C_{DIC}$  decreases more than  $\delta^{13}C_{DIC}$  at greater depths. These observations suggest that while  $\delta^{13}C_{DIC}$  and  $\Delta^{14}C_{DIC}$  are broadly correlated due to their decrease along the path of the large scale overturning circulation, we should not necessarily expect them to maintain a strict linear relationship.

# 2.2. $\delta^{13}C_{DIC}$ and $\Delta^{14}C_{DIC}$ in the LGM ocean

Planktic and benthic foraminifera record the  $\Delta^{14}C_{DIC}$  and  $\delta^{13}C_{DIC}$  of the seawater in which they live. Paleoceanographers have taken advantage of this to reconstruct changes in the patterns and rates of deep ocean circulation in the past. A great deal of effort has been put into the reconstruction of changes in water mass distribution during the last glacial maximum (LGM) (~19-23 kyr BP) using  $\delta^{13}$ C in benthic foraminifera. The distribution of  $\delta^{13}$ C<sub>DIC</sub> in the LGM ocean indicates that the distribution of deep water masses very different from that in the modern ocean. In the deep Atlantic Ocean,  $\delta^{13}C_{DIC}$  was much lower than in the modern ocean, and there was a strong  $\delta^{13}C_{DIC}$  gradient at ~2500 m water depth (Curry and Oppo, 2005; Duplessy et al., 1988; Oppo and Lehman, 1993; Sarnthein et al., 1994). These changes have been interpreted to indicate reduced and/or shallower flow of North Atlantic Deep Water (NADW) and increased incursion of Southern Ocean sourced deep waters into the LGM Atlantic (Curry and Oppo, 2005). Data coverage is sparser for the LGM Pacific and Indian Oceans. However, the available data suggest a deepening of the  $\delta^{13}C_{DIC}$  minimum in these basins with a strong  $\delta^{13}C_{DIC}$  gradient near 2000 m water depth (Duplessy et al., 1988; Herguera et al., 1992; Kallel et al., 1988; Keigwin, 1998; Matsumoto et al., 2002). These changes have been interpreted as an increase in North Pacific Intermediate Water ventilation during the LGM. Perhaps the most remarkable difference in the distribution of  $\delta^{13}C_{DIC}$  in the LGM ocean is the shift of the lowest values from the mid-depth North Pacific to the deep Atlantic sector of the Southern Ocean (Charles et al., 1996; Curry et al., 1988; Ninnemann and Charles, 2002). It is unclear how much of the  $\delta^{13}C_{DIC}$ decrease in the Atlantic sector of the Southern Ocean represents an increase in nutrient concentrations and how much is due to reduced air-sea CO<sub>2</sub> exchange. Measurements of Cd/Ca in benthic foraminifera do not support increased nutrient concentrations in the LGM Southern

Ocean (Rosenthal et al., 1997), although benthic foraminiferal Cd/Ca can also be affected by changes in the carbonate ion saturation state (Marchitto et al., 2005; McCorkle et al., 1995). A comparison between  $\delta^{13}$ C and Cd/Ca in the LGM Atlantic Ocean also suggests a low  $\delta^{13}$ C air-sea signature in Southern Ocean sourced deep waters (Marchitto and Broecker, 2006). Box modeling results suggest that very low  $\delta^{13}$ C<sub>DIC</sub> in the Southern Ocean are consistent with reduced ventilation of Southern Ocean sourced deep waters (Toggweiler, 1999; Toggweiler et al., 2006).

Reconstructions of  $\Delta^{14}C_{DIC}$  in the LGM ocean also indicate significant changes from the modern ocean. Results from the North Atlantic indicate lower  $\Delta^{14}C_{DIC}$  below ~2.5 km, consistent with increased incursion of Southern Ocean sourced deep waters (Keigwin, 2004; Keigwin and Schlegel, 2002; Robinson et al., 2005; Skinner and Shackleton, 2004). Reconstructions from the deep Pacific indicate  $\Delta^{14}C_{DIC}$  similar to or moderately lower than the modern Pacific (Broecker and Clark, 2010; Broecker et al., 2004a; Broecker et al., 2008; Broecker et al., 2007; Broecker et al., 2004b; Galbraith et al., 2007; Shackleton et al., 1988). Recent results from the Atlantic sector of the Southern Ocean indicate that this region contained the lowest  $\Delta^{14}C_{DIC}$  in the LGM ocean, indicating a pattern similar to the  $\delta^{13}C_{DIC}$  distribution (Skinner et al., 2010).



**Figure 4.2**: Paired  $\delta^{13}C_{DIC}$  and Natural  $\Delta^{14}C_{DIC}$  measurements in the modern ocean (>500 m water depth) from the GLODAP v1.1 data set (Key et al., 2004). The global distribution of measurements is shown in Figure 4.1c. The data are grouped into bins according to water depth: 500-1000 m (black), 1000-1500 m (blue), 1500-2000 m (green), 2000-3000 m (red), 3000-4000 m (purple), 4000-6000 m (yellow).

We have compiled paired  $\delta^{13}C_{DIC}$  and  $\Delta^{14}C_{DIC}$  reconstructions from the LGM ocean (Table 4.1; Figure 4.3).  $\Delta^{14}$ C data are from Broecker et al. (2004a; 2008; 2004b), Galbraith et al. (2007), Keigwin and Schlegel (2002), Keigwin (2004), Robinson et al. (2005), Skinner and Shackleton (2004), and Skinner et al. (2010).  $\delta^{13}$ C data are either from the same cores as the  $\Delta^{14}$ C records or from nearby cores (Herguera et al., 2010; Hodell et al., 2003; Keigwin, 2004; Matsumoto et al., 2002; Mix et al., 1991; Ninnemann and Charles, 2002; Skinner and Shackleton, 2004). We calculated  $\Delta^{14}C_{DIC}$  using conventional <sup>14</sup>C ages and the equation for initial  $\Delta^{14}$ C from Adkins and Boyle (1997). Calendar ages were based on planktic foraminiferal <sup>14</sup>C ages calibrated using Marine09 (Reimer et al., 2009) or stratigraphic age models from the original publications. The offset between deep ocean  $\Delta^{14}$ C and the Intcal09 atmosphere (Reimer et al., 2009) was calculated and is shown as  $\Delta \Delta^{14}$ C in Figure 4.3. This compilation suggests that the general relationship of decreasing  $\Delta^{14}C_{DIC}$  with decreasing  $\delta^{13}C_{DIC}$  in the modern ocean is maintained in the LGM ocean. Importantly, it is evident that the Atlantic sector of the Southern Ocean has shifted from values midway between the Atlantic and Pacific to the lowest values in the ocean. If we normalize the atmosphere to deep ocean  $\Delta^{14}$ C gradients for the effect of higher glacial atmospheric  $\Delta^{14}$ C (see Appendix B) and subtract the whole-ocean  $\delta^{13}$ C<sub>DIC</sub> change of -0.3‰ (Duplessy et al., 1988), which is related to a transfer of terrestrial carbon to the ocean, we can directly compare the LGM  $\delta^{13}C_{DIC}$  -  $\Delta^{14}C_{DIC}$  relationship to the modern data (Figure 4.4).

There are significant differences between the modern and LGM  $\delta^{13}C_{DIC}$  and  $\Delta^{14}C_{DIC}$ relationships. The range of both  $\Delta^{14}C_{DIC}$  and  $\delta^{13}C_{DIC}$  in the LGM North Atlantic Ocean data is expanded relative to the modern Atlantic. The slope of the LGM Atlantic  $\delta^{13}C_{DIC}$  -  $\Delta^{14}C_{DIC}$  data is similar to or slightly lower than the modern Atlantic, suggesting increased remineralization and aging in the deep LGM Atlantic. The LGM Pacific indicates lower  $\Delta^{14}C_{DIC}$  without a significant decrease in  $\delta^{13}C_{DIC}$ . The Southern Ocean  $\delta^{13}C_{DIC} - \Delta^{14}C_{DIC}$  data are both much lower than the modern Southern Ocean, indicating that deep waters in this region experienced greatly increased aging, greatly reduced air-sea equilibration, and/or increased remineralization. These results suggest that the deep Southern Ocean could have supplied low- $\Delta^{14}C$  and  $\delta^{13}C$  carbon to the upper ocean and atmosphere during the deglaciation. However, at this time the LGM Southern Ocean is only constrained by one core site. A significant portion of the  $\Delta^{14}C$  decrease in this record, from Skinner et al. (2010), is associated with a large increase in the surface reservoir age. Assuming, LGM surface reservoir ages similar to modern ages near this core site, the deep ocean  $\Delta^{14}C_{DIC}$  would be ~100% higher than shown; this  $\Delta^{14}C_{DIC}$  value would still be ~100% lower than values in the modern Southern Ocean.

Overall, the LGM  $\delta^{13}C_{DIC} - \Delta^{14}C_{DIC}$  relationship is steeper than the modern relationship, with  $\Delta^{14}C_{DIC}$  decreasing proportionally more than  $\delta^{13}C_{DIC}$ . Assuming the average isotopic fractionation during photosynthesis did not change, the greater slope indicates that the rate of organic carbon remineralization in the deep ocean was reduced during the LGM. Deep ocean remineralization rates could be lowered by reducing primary productivity and/or increasing remineralization rates in the upper ocean. The available evidence indicates that export production was generally higher during the LGM than the late Holocene (Kohfeld et al., 2005), suggesting that upper ocean remineralization rates, particularly in the Pacific, must have been higher during the LGM. This change may have been related to better ventilation, and hence higher oxygen concentrations, of the mid-depth Pacific (e.g., Keigwin, 1998; Matsumoto et al., 2002).

Table 4.1	1: Compila	ition o	<b>FLGM</b>	$^{14}$ C and $\delta^{1}$	<sup>13</sup> C data									
Location	Core	Ref. <sup>ª</sup>	Depth (m)	Cal. Age (kyr BP)	Cal. Age Method <sup>b</sup>	$\Delta \mathbf{R}^{\mathbf{c}}$	Benthic <sup>14</sup> C Age	Benthic $\Delta^{14}$ C	Intcal09 $\Delta^{14}{ m C}$	$\Delta \Lambda^{14} C$	Norm. AA <sup>14</sup> C <sup>d</sup>	δ <sup>13</sup> C	δ <sup>13</sup> C Core <sup>e</sup>	Ref.
W Eq. Pacific	MD98- 2181	-	2100	19183	planktic 14C age	200	18050	76	388	312	224	-0.05	δ <sup>13</sup> C section	7
				19135	wood 14C age		17690	119	387	268	193	-0.05	δ <sup>13</sup> C section	٢
				19108	planktic 14C age	200	17690	116	387	271	196	-0.05	δ <sup>13</sup> C section	Г
				19700	planktic 14C age	200	18350	104	378	274	199	-0.05	δ <sup>13</sup> C section	٢
W Eq. Pacific	MD97- 2138	-	1900	21625	planktic 14C age	200	20590	54	436	382	266	0.00	δ <sup>13</sup> C section	7
				21896	planktic 14C age	200	20590	89	441	352	244	0.00	δ <sup>13</sup> C section	7
W Eq. Pacific	MD01- 2386	2	2820	19022	planktic 14C age	160	17850	82	394	312	224	-0.10	δ <sup>13</sup> C section	7
				19267	planktic 14C age	160	18550	22	371	349	255	-0.10	δ <sup>13</sup> C section	٢
E Eq. Pacific	V19-27	3	1370	18278	planktic 14C age	200	17140	91	410	319	226	0.10	same core	4
				20980	planktic 14C age	200	19353	137	418	281	198	0.10	same core	4
E Eq. Pacific	RC11- 238	3	2570	19184	planktic 14C age	200	18455	24	386	362	261	0.00	δ <sup>13</sup> C section	7
				20834	planktic 14C age	200	20160	11	409	398	283	0.00	δ <sup>13</sup> C section	Г
E Eq. Pacific	V21-40	3	3180	20882	planktic 14C age	200	20370	-10	412	422	299	-0.43	avg of 4 cores	5
NE Pacific	ODP 887	9	3647	18972	planktic 14C age	550	18290	18	392	374	268	-0.30	δ <sup>13</sup> C section	7
				18843	planktic 14C age	550	18290	3	397	394	282	-0.30	δ <sup>13</sup> C section	٢
				20309	planktic 14C age	550	19580	20	390	370	266	-0.30	δ <sup>13</sup> C section	7
NW Atlantic	HU7202 1-3	8	2470	19504	planktic 14C age	0	17750	162	367	205	150	0.60	δ <sup>13</sup> C section	6
NW Atlantic	KNR140 -39GGC	10	2975	19664	planktic 14C age	0	18150	127	372	245	179	0.32	same core	11

3 <sup>13</sup> C 3 <sup>13</sup> C Ref.	).36 same 11 core 11	0.36 same 11 core 11	0.85 same 11 core 11	0.16 same 11 core 11	0.49 same 11 core 11	0.26 same 11 core 11	0.00 same 12 core 12	0.80 avg of 4 14 cores	0.80 avg of 4 14 cores 14	0.80 avg of 4 14 cores 14	0.80 avg of 4 14 cores 14	I. (1991); 5. Herguers ppo (2005); 10. 10); 14. Hodell et al.	-2334K age model 04). The MD07-3070	l Mg/Ca records from	
Norm. ΔΔ <sup>14</sup> C	133	176 0	118 (	175 -	211 -	- 202	209 (	365 -	377 -	351 -	311 -	4. Mix et a Jurry and O ler et al. (20	The MD99 tckleton, 20	records and	
$\Delta \Lambda^{14} C$	187	252	168	242	296	285	305	485	524	477	469	(2004b); 005); 9. C 13. Skinn	., 2009). r and Sha	tice core	
Intcal09 $\Delta^{14}$ C	404	433	430	384	404	409	461	364	405	374	463	cker et al. n et al. (2 1 (2004);	imer et al d (Skinne	Antarctic	1
$\begin{array}{c} Benthic \\ \Delta^{14}C \end{array}$	217	181	262	142	108	124	156	-121	-119	-103	-9	); 3. Broe . Robinso shackletor	curve (Re	records to	endix B).
Benthic <sup>14</sup> C Age	16550	19300	18950	17650	17300	17150	20370	19530	19870	20800	22270	al. (2008) (2002); 8 iner and S	dibration e GISP2 8	l Mg/Ca 1	<sup>14</sup> C (Appe
ΔR	0	0	0	0	0	0						ker et et al. 2. Skir	e09 ca to the	nıfera	$\operatorname{eric}_{2^{12}}\Delta$
Cal. Age Method	planktic 14C age	original age model	original age model	original age model	original age model	original age model	a); 2. Broec Matsumoto n (2004); 12	o the Marin inifera δ <sup>18</sup> C	nktic foram et al., 2010)	is. ier atmosph					
Cal. Age (kyr BP)	18653	21235	21421	19257	18652	18617	22161	19028	19398	20509	22870	t al. (2004 (2007); 7. 1. Keigwi	alibrated to ktic foram	slating plai (Skinner (	ublication nt for high
Depth (m)	2972		2590	3845	4250	4712	3146	3770				roecker e ith et al. ( (2002); 1	C ages c ting plan	1 by corre 057-21)	original p to accou
Ref.	10		11	11	11	11	12	13				o 1. Bı Jalbra ılegel (	feral <sup>14</sup> sorrela	tructec re (TN	m the ( alized
Core	KNR140 -37JPC		KNR140 -43GGC	KNR140 -26GGC	KNR140 -12JPC	KNR140 -22JPC	MD99- 2334K	MD07- 3076				nces refer to (2010); 6. ( vin and Sch	c foraminit tructed by c	ediment con	ues are froi ffsets norm
Location	NW Atlantic		NW Atlantic	NW Atlantic	NW Atlantic	NW Atlantic	NE Atlantic	Southern Ocean				a. Referen et al. ( Keigv (2003	b. Plankti was const	age mode another se	c. $\Delta \mathbf{R}$ val d. $\Delta^{14} \mathbf{C}$ o



**Figure 4.3**: Compilation of paired  $\delta^{13}$ C and  $\Delta^{14}$ C published data from the last glacial maximum from the Atlantic (blue), Pacific (red) and Southern Ocean (black).  $\Delta^{14}$ C data are the average difference from the Intcal09 atmosphere (Reimer et al., 2009) reconstructed from each sediment core for the interval 18-23 calendar kyr BP.  $\Delta^{14}$ C data are from Broecker et al. (2004a; 2008; 2004b), Galbraith et al. (2007), Keigwin and Schlegel (2002), Keigwin (2004), Robinson et al. (2005), Skinner and Shackleton (2004), and Skinner et al. (2010).  $\delta^{13}$ C data are either from the same cores as the  $\Delta^{14}$ C records or from nearby cores (Herguera et al., 2010; Hodell et al., 2003; Keigwin, 2004; Matsumoto et al., 2002; Mix et al., 1991; Ninnemann and Charles, 2002; Skinner and Shackleton, 2004).



**Figure 4.4**: Comparison of modern and LGM  $\delta^{13}$ C and  $\Delta^{14}$ C data. Modern data are from water depths greater than 1200 m and are grouped by ocean basin: Atlantic (blue), Pacific (red), Indian (green) and Southern Ocean (black). LGM  $\Delta^{14}$ C offsets have been normalized to atmospheric Fm = 1 to account for higher atmospheric  $\Delta^{14}$ C during the LGM (see Appendix B), and 0.3 has been added to the LGM  $\delta^{13}$ C values to account for the addition of terrestrial carbon (Duplessy et al., 1988). LGM symbols are as shown in Figure 4.3. Remineralization of organic carbon in the deep ocean moves values to the right; while aging of deep waters moves values down. The slope of this relationship is controlled by the rate of remineralization in the deep ocean. Modern end member values are from Curry et al. (1988) and Broecker and Peng (1982).

# **3.** $\delta^{13}$ C Methods

New planktic foraminiferal stable isotope measurements in this study come from sediment cores RC27-23 in the northern Arabian Sea (18°N, 57.6°E, 820 m) and MV99-GC31/PC08 from the Baja California margin (23.5°N, 111.6°W, 705 m). The calendar age models for RC27-23 and MV99-GC31/PC08 come from the stratigraphic correlation of  $\delta^{15}$ N and reflectance data, respectively, to the GISP2  $\delta^{18}$ O record (Bryan et al., 2010; Marchitto et al., 2007). Four species of planktic foraminifera, Globigerinoides ruber (white), Globigerinoides sacculifer, Globorotalia menardii and Neogloboquadrina dutertrei, were picked from washed sediment samples. G. ruber and G. sacculifer (without sac chamber) samples were picked from the 250-355 µm size fraction. G. menardii specimens had shell lengths 600-850 µm, and N. *dutertrei* specimens had shell lengths >500 µm. Large *G. menardii* and *N. dutertrei* were chosen to minimize isotopic variability related to shell size (Billups and Spero, 1995; Bouvier-Soumagnac and Duplessy, 1985; Kroon and Darling, 1995). Samples consisted of 10 individuals for G. ruber, 7-10 individuals for G. sacculifer and 3 individuals for G. menardii and N. *dutertrei*. Stable isotope measurement was performed at the Woods Hole Oceanographic Institution Mass Spectrometry Facility on a Finnigan MAT253 outfitted with a Kiel III Carbonate Device. The analytical precision determined from repeat analysis of the NBS19 calcite standard is  $\pm 0.07$  for  $\delta^{18}$ O and  $\pm 0.03$  for  $\delta^{13}$ C. A second set of G. ruber and N. dutertrei samples consisting of 9-30 individuals and 6-12 individuals, respectively, was analyzed at the University of California, Davis Stable Isotope Laboratory on a GVI Optima Stable Isotope Ratio Mass Spectrometer. Analytical precision was  $\pm 0.05\%$  for  $\delta^{18}$ O and  $\pm 0.04\%$   $\delta^{13}$ C, based on repeat analyses of the NBS19 calcite standard. The samples analyzed at UC Davis were sonicated in methanol for a few seconds prior to being sent out for stable isotope analysis. In all

of the following figures we show the mean of the two sets of measurements weighted by the number of individuals in each measurement. All measurements are reported relative to the Vienna Pee Dee Belemnite (VPDB) standard.

# 4. Planktic $\delta^{13}$ C Results

#### 4.1 Arabian Sea

The planktic foraminiferal stable isotope results from Arabian Sea core RC27-23 are shown in Figures 4.5 and 4.6. We have also included the RC27-23 *G. bulloides* records from Anderson (1991). All new stable isotope data are listed in Appendix C.  $\delta^{18}$ O in all of the species generally decreased across the deglaciation (Figure 4.5). The LGM to early Holocene  $\delta^{18}$ O change was ~1.5‰ for *G. ruber*, ~1.3‰ for *G. menardii* and *N. dutertrei*, ~1.2‰ for *G. sacculifer* and ~1.1‰ for *G. bulloides*. These changes indicate some warming or decrease in salinity in addition to the ~1.0‰ change related to global ice volume (Schrag et al., 2002). If the additional decrease in  $\delta^{18}$ O was solely due to temperature, it would represent a ~1-2°C temperature rise (Bemis et al., 1998; Bouvier-Soumagnac and Duplessy, 1985; Mulitza et al., 2003). There is also some millennial-scale structure evident in the  $\delta^{18}$ O records. All of the species recorded an increase in the slope of the  $\delta^{18}$ O decrease at the start of the Bølling-Allerød (B-A), indicating warming/decreased salinity, followed by an increase in  $\delta^{18}$ O just prior to or during the Younger Dryas (YD), indicating cooling/increased salinity.



**Figure 4.5**: Planktic foraminiferal  $\delta^{18}$ O from Arabian Sea core RC27-23 during the last deglaciation for (a) *G. ruber*, (b) *G. sacculifer*, (c) *G. menardii*, (d) *N. dutertrei* and (e) *G. bulloides*. *G. bulloides* data are from Anderson (1991). Thick lines are three point moving averages connected by Microsoft Excel's smoothing function, which uses Bezier curves. All values are referenced to the VPDB standard. HS1, B-A, ACR and YD correspond to the Heinrich Stadial 1, Bølling-Allerød, Antarctic Cold Reversal and Younger Dryas intervals, respectively.

The Arabian Sea  $\delta^{13}$ C records (Figure 4.6) show evidence for high-frequency (centennial to millennial-scale) variability superimposed upon broader trends. The source of the high-frequency variability is unclear. It is possible that it was caused by weather-related noise; since individual foraminifera only live for a few weeks, we may not have sampled enough foraminifera to record an adequate climatological mean. However, at least some of the higher frequency variability is consistent between several species, suggesting that at least some of the variability reflects real centennial-scale changes in the thermocline nutrient content or structure. Interestingly, the variability appears to be greater during the LGM and Heinrich Stadial 1 (HS1) than later on in the records, suggesting that the nutrient content and structure of the thermocline may have been more variable during cold times. Unfortunately many of the high-frequency changes are only constrained by one data point. Higher resolution would be needed to confirm and interpret the possible centennial-scale variability.

Focusing on the broader-scale features in the  $\delta^{13}$ C records, illustrated by the 3-point running means in Figure 4.6, it appears that *G. sacculifer*, *G. menardii*, *N. dutertrei* and *G. bulloides* record similar trends during the deglaciation.  $\delta^{13}$ C in these species increased from the start of the records, ~21-22 kyr BP, to a local maximum just prior to the start of HS1.  $\delta^{13}$ C then declined during HS1 to values similar to or slightly lower than values seen at the beginning of the record. The amplitude of these changes was ~0.3-0.6‰.  $\delta^{13}$ C in *G. sacculifer* and *G. menardii* reached minimum values near the end of HS1 and began to increase gradually into the early Holocene.  $\delta^{13}$ C in *N. dutertrei* and *G. bulloides* remained low until the end of the YD, after which  $\delta^{13}$ C increased to the end of the records.  $\delta^{13}$ C in *G. ruber* recorded a different pattern during the deglaciation. *G. ruber*  $\delta^{13}$ C remained relatively constant from the LGM into HS1.



**Figure 4.6**: Planktic foraminiferal  $\delta^{13}$ C from Arabian Sea core RC27-23 during the last deglaciation for (a) *G. ruber*, (b) *G. sacculifer*, (c) *G. menardii*, (d) *N. dutertrei* and (e) *G. bulloides*. *G. bulloides* data are from Anderson (1991). Thick lines are three point moving averages connected by Microsoft Excel's smoothing function. All values are referenced to the VPDB standard. HS1, B-A, ACR and YD correspond to the Heinrich Stadial 1, Bølling-Allerød, Antarctic Cold Reversal and Younger Dryas intervals, respectively.

At the end of HS1 and the start of the B-A. G. ruber  $\delta^{13}$ C increased by ~0.25‰. G. ruber  $\delta^{13}$ C remained relatively constant through the B-A and Younger Dryas (YD) before increasing again by ~0.3‰ at the start of the Holocene. The difference in the deglacial  $\delta^{13}$ C trends between G. *ruber* and the rest of the species is likely related to differences in the seasonal and/or depth habitat of the species. Sediment trap studies from the northwest Arabian Sea indicate that foraminiferal fluxes, in general, and the fluxes of G. bulloides, N. dutertrei and G. menardii, in particular, are several orders of magnitude higher during the summer monsoon upwelling season than during the rest of the year. (Conan and Brummer, 2000; Curry et al., 1992; Peeters et al., 2002). In contrast, G. ruber lives through out the year, during upwelling and nonupwelling seasons (Curry et al., 1992; Peeters et al., 2002). G. ruber, G. sacculifer, and G. bulloides live within the surface mixed layer; while G. menardii and N. dutertrei live deeper within the thermocline near the chlorophyll maximum (Fairbanks et al., 1982; Fairbanks et al., 1980; Peeters et al., 2002; Ravelo and Fairbanks, 1992; Ravelo et al., 1990). G. sacculifer is commonly regarded as a warm, mixed layer dweller; however, Spero and Lea (1993) found that smaller G. sacculifer, which were used in this study, record stable isotopic values consistent with growth in low light, suggesting that G. sacculifer may at times live in a deep mixed layer or upper thermocline habitat. The  $\delta^{13}$ C results presented here are consistent with smaller G. sacculifer in the northwest Arabian Sea living near the base of the mixed layer and/or predominantly during the summer upwelling season.

The interpretation of planktic foraminiferal  $\delta^{13}$ C values is not simple. While planktic foraminifera do record changes in the  $\delta^{13}C_{DIC}$  of the seawater in which they live (Spero, 1992), they do not calcify in isotopic equilibrium with DIC. Planktic foraminiferal  $\delta^{13}$ C can be offset from  $\delta^{13}C_{DIC}$  by the influence of photosynthetic symbiotic algae (Spero and Williams, 1988), the

incorporation of respired CO<sub>2</sub> (Spero and Lea, 1996), temperature (Bemis et al., 2000) and carbonate ion concentration (Spero et al., 1997). While the offsets are not as large as for  $\delta^{13}$ C, disequilibria between planktic foraminiferal  $\delta^{18}$ O and seawater  $\delta^{18}$ O have been observed and are likely related to varying influences from photosynthesis, respiration and carbonate ion concentrations (Bemis et al., 1998; Spero et al., 1997; Spero and Lea, 1996). The  $\delta^{18}$ O disequilibrium between planktic foraminifera and seawater varies between species (e.g., Niebler et al., 1999), and has lead to the development of species-specific  $\delta^{18}$ O-temperature equations (Bemis et al., 1998). In order to compare the records from different species to each other in a hydrographically meaningful way, it is necessary to apply correction factors, placing results for each species on a common scale. Following Spero et al. (2003), we normalized  $\delta^{18}$ O results to G. ruber values and normalized  $\delta^{13}$ C results to  $\delta^{13}$ C<sub>DIC</sub> (Figure 4.7; Table 4.2). These offsets were determined using measurements on foraminifera grown in culture and collected in plankton tows (Spero et al., 2003). While these correction factors allow a comparison of the relative  $\delta^{18}$ O and  $\delta^{13}$ C values between the different species, it is important to keep in mind that the correction factors are empirically derived and likely incorporate the impacts of multiple processes; therefore, the true offsets may vary in space and time. The relative  $\delta^{18}$ O values of the different species in the Arabian Sea records are consistent with the expected seasonal habitat of each species. G. ruber has lowest  $\delta^{18}$ O values consistent with a warm, non-upwelling, mixed layer habitat. G. menardii, N. dutertrei and G. bulloides  $\delta^{18}$ O values are similar and are the highest of the species analyzed, representative of the cooler, summer upwelling season. G. sacculifer  $\delta^{18}$ O falls in between the values of G. ruber and the values of G. menardii and N. dutertrei.

The normalized  $\delta^{13}$ C records confirm our interpretations based on the deglacial trends of the different species (Figure 4.7b). *G. ruber* has the highest  $\delta^{13}$ C values and is distinct

from the other species, which group together. Based on these observations we take the *N*. *dutertrei*, *G. menardii* and *G. bulloides*  $\delta^{13}$ C records to be indicative of  $\delta^{13}C_{DIC}$  changes within the thermocline and mixed layer during the summer monsoon upwelling season. We interpret *G. ruber*  $\delta^{13}$ C as reflecting the  $\delta^{13}C_{DIC}$  of the mixed layer during the non-upwelling season. It appears that *G. sacculifer* mostly records conditions during the upwelling season. Our objective for constructing these records was to determine if there is a preformed  $\delta^{13}C_{DIC}$  decrease during the deglaciation and how the  $\delta^{13}C_{DIC}$  signal is related to the intermediate water  $\Delta^{14}$ C decline observed in this core. It is apparent that there is a broad minimum across the deglaciation in the upwelling season foraminifera. The magnitude of the  $\delta^{13}$ C decrease is ~0.5‰, similar to deglacial minima at other sites (Spero and Lea, 2002).



**Figure 4.7**: RC27-23 normalized planktic foraminiferal  $\delta^{18}$ O (a) and  $\delta^{13}$ C (b) data. *G. ruber* data are indicated by blue diamonds; *G. sacculifer* data are green squares; *G. menardii* data are black triangles, *N. dutertrei* data are red circles, and *G. bulloides* data are purple open diamonds. Thick lines represent three point moving averages connected by Microsoft Excel's smoothing function.  $\delta^{18}$ O data have been normalized to *G. ruber* values and  $\delta^{13}$ C have been normalized to  $\delta^{13}$ C<sub>DIC</sub> following the methods of Spero et al. (2003). All values are referenced to the VPDB standard. HS1, B-A, ACR and YD correspond to the Heinrich Stadial 1, Bølling-Allerød, Antarctic Cold Reversal and Younger Dryas intervals, respectively.

<b>Table 4.2</b> : 0 U af	id o C Normalization Fac	lors
Species	$\delta^{18}$ O normalization <sup>b</sup>	$\delta^{13}$ C normalization
G. ruber	0	+0.94
G. sacculifer	-0.11	-0.73
G. menardii	0	0
N. dutertei	+0.61	-0.50
G. bulloides <sup>c</sup>	+0.95	+2.70

**Table 4.2**:  $\delta^{18}$ O and  $\delta^{13}$ C Normalization Factors<sup>a</sup>

a.  $\delta^{18}$ O values are normalized to *G. ruber* and  $\delta^{13}$ C values are normalized to  $\delta^{13}$ C<sub>DIC</sub> following Spero et al. (2003).

b. *G. ruber* and *G. sacculifer*  $\delta^{18}$ O values are normalized using the 25°C corrections in Spero et al. (2003). *G. menardii* and *N. dutertrei* values use the 15°C corrections.

c. Normalization factors from Spero and Lea (1996), using the equations for 22°C and assuming a mean shell size of 300  $\mu$ m.

Comparison of the planktic foraminiferal  $\delta^{13}$ C records to records of intermediate water  $\Delta^{14}$ C from RC27-23 and a nearby core from ~600 m water depth, RC27-14 (Bryan et al., 2010) (Figure 4.8), indicates that the beginning of the decline in  $\delta^{13}$ C is coincident with the decline in intermediate water  $\Delta^{14}$ C.  $\delta^{13}$ C in *G. sacculifer* and *G. menardii* reached a minimum at the same time as the minimum in intermediate water  $\Delta^{14}$ C. Following HS1,  $\delta^{13}$ C in *G. sacculifer* and *G. menardii* began to increase around the same time as intermediate water  $\Delta^{14}$ C; however the  $\delta^{13}$ C in *C. sacculifer* and *G. menardii* began to increase around the same time as intermediate water  $\Delta^{14}$ C; however the  $\delta^{13}$ C in *C. sacculifer* and *G. bulloides* 

remained low during this interval. The second decrease in intermediate water  $\Delta^{14}$ C, just prior to the YD, is not observed in the  $\delta^{13}$ C records.

In addition to changes in the preformed  $\delta^{13}C_{DIC}$  of upwelled waters, planktic for a miniferal  $\delta^{13}$ C may also have been affected by changes in the strength of upwelling during the deglaciation (e.g., Bouvier-Soumagnac and Duplessy, 1985; Peeters et al., 2002). Here we use the  $\delta^{15}$ N record from RC27-23 (Altabet et al., 2002) as a qualitative representation of upwelling strength.  $\delta^{15}$ N in the Arabian Sea reflects the extent of water column denitrification. which is related to low oxygen concentrations (Ganeshram et al., 2000). Low oxygen concentrations can be related to low oxygen supply and/or oxygen consumption during respiration (Olson et al., 1993); however, the RC27-23  $\delta^{15}$ N record has been interpreted to primarily reflect changes in monsoon-driven upwelling and productivity (Altabet et al., 2002). The decrease in  $\delta^{13}$ C during HS1 was not accompanied by a significant shift in upwelling strength, supporting the interpretation of this change as a decrease in preformed  $\delta^{13}C_{DIC}$ . At the start of the B-A,  $\delta^{15}$ N increased abruptly, indicating an increase in upwelling. It is unclear if any changes in preformed  $\delta^{13}C_{DIC}$  occurred during the B-A and YD. It is possible that changes may have been obscured by changes in nutrient supply and carbonate ion concentration related to upwelling strength.



**Figure 4.8**: Comparison of RC27-23 planktic foraminiferal  $\delta^{13}$ C to records of intermediate water  $\Delta^{14}$ C and upwelling strength. a.  $\delta^{15}$ N of organic matter from RC27-23 (Altabet et al., 2002); higher values indicate increased summer monsoon upwelling. b. Normalized planktic foraminiferal  $\delta^{13}$ C (as in Figure 7b): *G. ruber* (blue diamonds), *G. sacculifer* (green squares), *G. menardii* (black triangles), *N. dutertrei* (red circles), *G. bulloides* (purple open diamonds). Thick lines are three point moving averages connected by Microsoft Excel's smoothing function. c.  $\Delta^{14}$ C offsets between surface/thermocline waters and the Intcal09 atmosphere. *G. ruber* data are blue circles; mixed *G. ruber* and *G. sacculifer* data are open green circles; *N. dutertrei* data are red circles; and *G. bulloides* data are purple circles. The *N. dutertrei* data indicated by open red circles and the *G. bulloides* data are from Anderson (1991). Intermediate water  $\Delta^{14}$ C offsets at 820 m water depth (RC27-23 - dark blue closed diamonds) and at 596 m water depth (RC27-14 - dark blue open diamonds) are also shown (Bryan et al., 2010). Higher values indicate greater <sup>14</sup>C depletion in the surface/thermocline and intermediate waters. HS1, B-A, ACR and YD correspond to the Heinrich Stadial 1, Bølling-Allerød, Antarctic Cold Reversal and Younger Dryas intervals, respectively.

## 4.2 Baja California

The planktic foraminiferal stable isotope results from MV99-GC31/PC08 are shown in Figures 4.9 and 4.10. The LGM to early Holocene  $\delta^{18}$ O change in *G. ruber*, *G. sacculifer* and *N. dutertrei* was ~1.0‰ (Figure 4.9), although the pattern of  $\delta^{18}$ O decrease differs between the species. While *N. dutertrei*  $\delta^{18}$ O decreased gradually across the deglaciation, *G. ruber*  $\delta^{18}$ O increased slightly during HS1, indicating cooling or increased salinity. *G. ruber*  $\delta^{18}$ O decreased at the start of the B-A back to values similar to the LGM. Almost all of the LGM to Holocene  $\delta^{18}$ O decrease in *G. ruber* occurs after the YD.  $\delta^{18}$ O in *G. sacculifer* remained relatively constant until the end of the HS1, after which it decreased into the early Holocene. *G. menardii*  $\delta^{18}$ O oscillates during the deglaciation, without any trend in the mean values, suggesting that the habitat of *G. menardii* was sensitive to changes in the structure of the thermocline (c.f. Spero et al., 2003).

Each of the species recorded distinct trends in  $\delta^{13}$ C through the deglaciation (Figure 4.10). *G. ruber* recorded two minima in  $\delta^{13}$ C, which occurred during HS1 and the YD. *G*.

sacculifer  $\delta^{13}$ C remained relatively constant through the deglaciation, with the exception during the B-A, when  $\delta^{13}$ C oscillated with an amplitude of ~1.0‰ before returning to values slightly higher than LGM/HS1 values.  $\delta^{13}$ C in *G. menardii* and *N. dutertrei* generally decreased across the deglaciation, with the exception of an increase at the start of HS1 and a slight increase during the YD. As we observed in the Arabian Sea records, there is also some high frequency variability in the *G. menardii* and *N. dutertrei* records, which appears to be greater during the LGM and HS1. However, as in the Arabian Sea records, the high frequency variability is poorly constrained.

In Figure 4.11, the  $\delta^{18}$ O and  $\delta^{13}$ C records have been normalized to *G. ruber*  $\delta^{18}$ O and  $\delta^{13}$ C<sub>DIC</sub>, respectively. The normalized records are generally consistent with the expected depth habitat of each species. *G. ruber* has low  $\delta^{18}$ O and high  $\delta^{13}$ C values relative to the other species, consistent with an oligotrophic mixed layer habitat. *N. dutertrei* has high  $\delta^{18}$ O and low  $\delta^{13}$ C values, indicating a deeper, thermocline habitat. *G. sacculifer*  $\delta^{18}$ O is similar to *G. ruber* values, however *G. sacculifer*  $\delta^{13}$ C is more similar to *N. dutertrei* values, suggesting a deep mixed layer or upwelling seasonal habitat. *G. menardii*  $\delta^{18}$ O oscillated between values similar to *G. ruber* and values more similar to *N. dutertrei*. The record of *G. menardii*  $\delta^{13}$ C is more puzzling; during the LGM and HS1, *G. menardii*  $\delta^{13}$ C was higher than *G. ruber*  $\delta^{13}$ C. *G. menardii*  $\delta^{13}$ C then decreased towards the *N. dutertrei* values after the start of the B-A. It appears that, at times, *G. menardii*  $\delta^{13}$ C was elevated relative to equilibrium values; it is possible that  $\delta^{13}$ C in *G. menardii* has a greater sensitivity to temperature/carbonate ion changes than other species.



**Figure 4.9**: Planktic foraminiferal  $\delta^{18}$ O from Baja California margin core MV99-GC31/PC08 during the last deglaciation for (a) *G. ruber*, (b) *G. sacculifer*, (c) *G. menardii*, and (d) *N. dutertrei*. Thick lines are three point moving averages connected by Microsoft Excel's smoothing function. All values are referenced to the VPDB standard. HS1, B-A, ACR and YD correspond to the Heinrich Stadial 1, Bølling-Allerød, Antarctic Cold Reversal and Younger Dryas intervals, respectively.


**Figure 4.10**: Planktic foraminiferal  $\delta^{13}$ C from Baja California margin core MV99-GC31/PC08 during the last deglaciation for (a) *G. ruber*, (b) *G. sacculifer*, (c) *G. menardii*, and (d) *N. dutertrei*. Thick lines are three point moving averages connected by Microsoft Excel's smoothing function. All values are referenced to the VPDB standard. HS1, B-A, ACR and YD correspond to the Heinrich Stadial 1, Bølling-Allerød, Antarctic Cold Reversal and Younger Dryas intervals, respectively.



**Figure 4.11**: MV99-GC31/PC08 normalized planktic foraminiferal  $\delta^{18}$ O (a) and  $\delta^{13}$ C (b) data. *G. ruber* data are indicated by blue diamonds; *G. sacculifer* data are green squares; *G. menardii* data are black triangles, and *N. dutertrei* data are red circles. Thick lines represent three point moving averages connected by Microsoft Excel's smoothing function, which uses Bezier curves.  $\delta^{18}$ O data have been normalized to *G. ruber* values and  $\delta^{13}$ C have been normalized to  $\delta^{13}$ C<sub>DIC</sub> following the methods of Spero et al. (2003). All values are referenced to the VPDB standard. HS1, B-A, ACR and YD correspond to the Heinrich Stadial 1, Bølling-Allerød, Antarctic Cold Reversal and Younger Dryas intervals, respectively.

In MV99-GC31/PC08, we can directly compare  $\delta^{13}$ C to  $\Delta^{14}$ C in *G. ruber* and *G.* sacculifer (Figure 4.12) (S. J. Lehman and T. M. Marchitto, unpublished data).  $\Delta^{14}$ C in G. sacculifer decreased by ~45-90‰ relative to the Intcal09 atmosphere during HS1. G. ruber  $\Delta^{14}$ C decreased by ~110-145‰ during HS1. While  $\Delta^{14}$ C recorded by G. ruber decreased more than that from G. sacculifer during HS1,  $\delta^{13}$ C in G. sacculifer was lower than that of G. ruber throughout the record, contrary to the expected trend. This difference is likely due to the variability in depth habitat of the different size fractions of G. sacculifer (Spero et al., 2003). As we previously noted, smaller G. sacculifer, which  $\delta^{13}$ C was measured on, appear to live deeper than larger G. sacculifer (Spero and Lea, 1993), which likely dominate the  $\Delta^{14}$ C record. G. *ruber*  $\delta^{13}$ C decreased by ~0.2-0.25‰ during HS1. The decrease in G. *ruber*  $\Delta^{14}$ C is also larger than would be expected from the LGM  $\delta^{13}$ C- $\Delta^{14}$ C relationship shown in Figure 4.3. Assuming the changes were only due to preformed changes, a 0.25% change in  $\delta^{13}$ C would correspond to a  $\Delta^{14}$ C decrease of only ~40‰. This observation suggests that the source of the low  $\delta^{13}$ C and  $\Delta^{14}$ C water had an even steeper relationship than is evident in the compiled LGM data, which is possible given the expected increase in slope with water depth (Figure 4.2), and/or the G. ruber  $\delta^{13}$ C record has been overprinted by other processes.

There were significant changes in local primary productivity along the Baja California margin during the last deglaciation (Ortiz et al., 2004) (Figure 4.12a). Ortiz et al. (2004)

proposed that productivity changes along Baja California were driven by changes in nutricline depth, which is related to El Nino/Southern Oscillation dynamics; i.e., warm intervals corresponded to a more La Nina-like state, with a shallower nutricline in the eastern tropical Pacific and higher productivity. This mechanism is consistent with the  $\delta^{13}$ C records from *N*. *dutertrei* and *G. menardii*, which we interpret to record thermocline conditions. When productivity is high, during the B-A and early Holocene, thermocline  $\delta^{13}$ C is low, indicating higher nutrient concentrations, and vice versa. The trends in *G. ruber*  $\delta^{13}$ C are opposite those of the thermocline species; when productivity is high, *G. ruber*  $\delta^{13}$ C is high and vice versa. The opposing changes between *G. ruber* and the thermocline species are consistent with changes in the  $\delta^{13}$ C gradient caused by productivity. When productivity is high, the export of low  $\delta^{13}$ C organic carbon from the mixed layer to the thermocline increases the  $\delta^{13}$ C gradient. Therefore, while there are minima in  $\delta^{13}$ C record from *G. ruber* at the same times as the minima in intermediate water  $\Delta^{14}$ C, it is unclear whether preformed  $\Delta^{14}$ C<sub>DIC</sub> or local productivity changes are responsible for the  $\delta^{13}$ C minima.

#### 5. Discussion

Using the paired single species  $\delta^{13}$ C and  $\Delta^{14}$ C data from the Arabian Sea and Baja California cores, we can create a deglacial planktic  $\delta^{13}$ C -  $\Delta^{14}$ C crossplot (Figure 4.13), similar to those showing the LGM deep ocean data. As expected, the deglacial planktic data generally plot in the upper right quadrant of the plot, with  $\delta^{13}$ C and  $\Delta^{14}$ C values that are generally higher than the LGM deep ocean values. Most of the deglacial planktic data fall within the modern range of surface/thermocline waters in the upper 200 m, shown by the gray dots in Figure 4.13. However, there are several samples that reach very low  $\Delta^{14}$ C values (large atmosphere to planktic offsets). Within a single species at each core site, the data fall along steep trends, showing large ranges in  $\Delta^{14}$ C with very little change in  $\delta^{13}$ C. This pattern is consistent with the upward mixing of low- $\Delta^{14}$ C intermediate waters, with overprinting of the  $\delta^{13}$ C records by local processes. The planktic  $\delta^{13}$ C -  $\Delta^{14}$ C relationships illustrate the large impact that isotopic fractionation associated with photosynthesis or air-sea gas exchange has on  $\delta^{13}$ C relative to  $\Delta^{14}$ C.

As we noted in Section 1, deglacial planktic  $\delta^{13}$ C minima are widely distributed, observed in the tropical Atlantic Ocean (Curry and Crowley, 1987; Oppo and Fairbanks, 1989; Schneider et al., 1992), tropical Pacific Ocean (Loubere, 1999; Loubere et al., 2007; Pena et al., 2008; Shackleton et al., 1983; Spero and Lea, 2002; Spero et al., 2003; Stott et al., 2009), and Subantarctic Southern Ocean (Loubere and Bennett, 2008; Ninnemann and Charles, 1997; Shackleton and Pisias, 1985). Deglacial  $\delta^{13}$ C minima have also been observed in benthic foraminifera from intermediate depths in the Atlantic Ocean (Oppo and Fairbanks, 1989; Rickaby and Elderfield, 2005) and along the southern margin of Australia (Lynch-Stieglitz and Fairbanks, 1994). Loubere et al. (2007) demonstrated that the evolution of thermocline  $\delta^{13}C_{DIC}$ across the deglaciation in the upwelling regions of the eastern equatorial Pacific (EEP) and eastern equatorial Atlantic (EEA) differed from its evolution in more stratified regions and that the EEP and EEA differed from each other.



**Figure 4.12**: Comparison of MV99-GC31/PC08 planktic foraminiferal  $\delta^{13}$ C to records of surface and intermediate water  $\Delta^{14}$ C and productivity. a. Factor 3 of the diffuse spectral reflectance (DSR) of the MV99-GC31/PC08 core (Ortiz et al., 2004); higher values indicate increased productivity. b. Normalized planktic foraminiferal  $\delta^{13}$ C (as in Figure 9b): *G. ruber* (blue diamonds), *G. sacculifer* (green squares), and *N. dutertrei* (red circles). Thick lines are three point moving averages connected by Microsoft Excel's smoothing function, which uses Bezier curves. c.  $\Delta^{14}$ C gradient between the mixed layer and the Intcal09 atmosphere (*G. ruber* – dark blue triangles, *G. sacculifer* – green squares) (T. M. Marchitto and S. J. Lehman, unpublished data) and the  $\Delta^{14}$ C gradient between intermediate waters from 705 m water depth (black circles) (Marchitto et al., 2007) and the Intcal09 atmosphere. Higher values indicate greater <sup>14</sup>C depletion in the surface or intermediate waters. HS1, B-A, ACR and YD correspond to the Heinrich Stadial 1, Bølling-Allerød, Antarctic Cold Reversal and Younger Dryas intervals, respectively.

While it appears that there was a decrease in preformed  $\delta^{13}C_{DIC}$  that was incorporated into SAMW and AAIW in the Subantarctic Southern Ocean and spread northward into the low latitude thermocline (Ninnemann and Charles, 1997; Oppo and Fairbanks, 1989), the results of Loubere et al. (2007) and the new data presented here, indicate that not all planktic foraminiferal  $\delta^{13}C$  records reflect a preformed  $\delta^{13}C_{DIC}$  change. It may, therefore, be informative to compare the intermediate water  $\Delta^{14}C$  records to the  $\delta^{13}C$  records from more stratified regions of the ocean (Figure 4.14) where it is thought that the preformed  $\delta^{13}C_{DIC}$  signal dominates the records. In many of these records the minima appear as broad low values across the entire deglaciation, lacking the millennial-scale structure evident in the intermediate water  $\Delta^{14}C$  records and in the record of Southern Ocean upwelling (Anderson et al., 2009). There are several possible reasons for the differences in the structure of the records: 1) The  $\Delta^{14}C$  and  $\delta^{13}C_{DIC}$  were overprinted by local changes in hydrography, productivity or nutricline structure. 3) The low resolution of some of the records caused millennial-scale features to be missed or smoothed by bioturbative mixing.



**Figure 4.13**: Deglacial planktic  $\delta^{13}$ C -  $\Delta^{14}$ C crossplot. Normalized  $\delta^{13}$ C and normalized  $\Delta\Delta^{14}$ C values for the Arabian Sea core RC27-23: *G. ruber* (open blue circles), *N. dutertrei* (open red circles), and *G. bulloides* (open purple circles); and Baja California core MV99-GC31/PC08: *G. ruber* (closed blue circles) and *G. sacculifer* (closed green circles).  $\Delta\Delta^{14}$ C values are the  $\Delta^{14}$ C offsets between Intcal09 atmospheric and planktic foraminiferal values, normalized to account for a higher than modern deglacial <sup>14</sup>C inventory. Higher  $\Delta\Delta^{14}$ C values indicate greater <sup>14</sup>C depletion relative to the atmosphere. Also shown are data from the modern ocean for water depths <200 m, excluding the Southern Ocean south of 40°S, (gray dots) (Glodap v1.1 dataset; Key et al., 2004), and the LGM deep Atlantic (black diamonds) Pacific (black squares) and Southern Ocean (black triangle) data as shown in Figure 4.4. The arrows on the right side of the figure indicate the largest atmosphere to intermediate water  $\Delta^{14}$ C offsets that were reconstructed in the Arabian Sea and along the Baja California margin during the deglaciation.



**Figure 4.14**: Compilation of deglacial carbon cycle and climate records. a) *N. pachyderma* (s)  $\delta^{13}$ C from Subantarctic Pacific core E11-2 (Ninnemann and Charles, 1997). b) *G. sacculifer*  $\delta^{13}$ C from Subantarctic Pacific core E11-2 (Ninnemann and Charles, 1997). c) *N. dutertrei*  $\delta^{13}$ C from TR163-19 (orange diamonds) (Spero and Lea, 2002) and *G. sacculifer*  $\delta^{13}$ C from V21-30 (purple open circles) (Koutavas and Lynch-Stieglitz, 2003); both records from the eastern equatorial Pacific. d) *G. ruber*  $\delta^{13}$ C from western equatorial Pacific core MD98-2181 (Stott et al., 2007). e) Atmosphere to intermediate water  $\Delta^{14}$ C gradients reconstructed from Arabian Sea core RC27-23 (blue diamonds) (Bryan et al., 2010) and Baja California core MV99-GC31/PC08 (red circles) (Marchitto et al., 2007). Higher values indicate greater <sup>14</sup>C depletion. f) Atmospheric  $\delta^{13}$ CO<sub>2</sub> from the Epica Dome C (closed circles) (Lourantou et al., 2010) and Taylor Dome (open circles) (Smith et al., 1999) ice cores. Both records are shown on the GICC05 gas age model. h) Atmospheric pCO<sub>2</sub> from the Epica Dome C ice core (Monnin et al., 2007) shown on the GISP2 age model (Marchitto et al., 2007). i) Epica Dome C  $\delta D$  (Jouzel et al., 2007) on the GISP2 age model (Marchitto et al., 2007).

There are some higher-resolution records that do show indications of a W-shaped millennialscale structure (Figure 4.14 c & d) (e.g., Koutavas and Lynch-Stieglitz, 2003; Stott et al., 2007), with low values during HS1 and the YD and higher values during the B-A. For this reason, we suggest that the  $\delta^{13}$ C records lacking millennial-scale structure are either too low resolution to capture the changes or the records are overprinted by local changes. The strongest evidence for a connection between the processes responsible for the release of low- $\delta^{13}$ C and low- $\Delta^{14}$ C CO<sub>2</sub> from the deep ocean is the records of  $\delta^{13}$ CO<sub>2</sub> from Antarctic ice cores (Lourantou et al., 2010; Smith et al., 1999), which yield low values during HS1 and the YD, at the same times as increases in atmospheric CO<sub>2</sub>, increased upwelling in the Southern Ocean, declines in atmospheric  $\Delta^{14}$ C, and minima in intermediate water  $\Delta^{14}$ C.

Returning to our examination of the relationship between  $\delta^{13}C$  and  $\Delta^{14}C$  in the modern ocean, we observed that the most of the remineralization of organic carbon occurs in the middepth ocean; whereas most of aging occurs at greater depths. The deepening of the  $\delta^{13}C$  minima in the LGM ocean suggests a greater residence time of waters in the deep ocean, relative to the modern ocean. However, we note that while we expect regions in the LGM deep ocean with very low  $\delta^{13}$ C to have also had low  $\Delta^{14}$ C, the opposite is not necessary the case. Due to the depth dependence of the remineralization of organic carbon, these tracers could have become decoupled. If much of the deep water aging took place in deepest portions of the LGM ocean, these waters could have become very depleted in <sup>14</sup>C, with only a small decrease in <sup>13</sup>C. This observation leaves open the possibility that the deepest portions of the LGM Pacific Ocean had very low  $\Delta^{14}$ C.

## 6. Conclusion

We have investigated the relationship between minima in planktic foraminiferal  $\delta^{13}$ C and intermediate water  $\Delta^{14}$ C that have been observed during the last deglaciation, presenting new records of planktic foraminiferal  $\delta^{13}$ C from the same cores along the Baja California margin and in the Arabian Sea in which the intermediate water  $\Delta^{14}$ C minima have been observed. A compilation of deep ocean  $\delta^{13}$ C and  $\Delta^{14}$ C reconstructions indicates that the distribution of these tracers during the last glacial maximum (LGM) was significantly different from the modern distribution. This compilation indicates that lowest  $\delta^{13}$ C and  $\Delta^{14}$ C values in the LGM ocean shifted from the mid-depth North Pacific to the deep Atlantic sector of the Southern Ocean. The general correlation between  $\delta^{13}$ C and  $\Delta^{14}$ C was maintained in the LGM ocean, but the slope of the relationship was steeper in the past, with  $\Delta^{14}$ C decreasing proportionally more than  $\delta^{13}$ C. These observations suggest that the deep Southern Ocean could have provided a source of low- $\delta^{13}$ C and  $\Delta^{14}$ C carbon to the upper ocean and atmosphere during the last deglaciation.

The planktic foraminiferal records from the Arabian Sea and the Baja California margin do show declines in  $\delta^{13}$ C at the same times as the declines in intermediate water  $\Delta^{14}$ C. However, it is difficult to isolate possible changes in the preformed  $\delta^{13}$ C<sub>DIC</sub> from local changes in productivity, upwelling and nutricline structure that occurred during the deglaciation. The ambiguity of the source of  $\delta^{13}$ C changes in these records prevent us from directly comparing the  $\delta^{13}$ C and  $\Delta^{14}$ C changes. However, some high-resolution planktic foraminiferal  $\delta^{13}$ C records do show minima with similar timing to the minima in intermediate water  $\Delta^{14}$ C, and records of  $\delta^{13}$ CO<sub>2</sub> from the Antarctic ice cores are consistent with the release of  $^{13}$ C-depleted carbon from the ocean during Heinrich Stadial 1 and the Younger Dryas (Lourantou et al., 2010).

We conclude that the association of  $\delta^{13}$ C and  $\Delta^{14}$ C in the deep glacial ocean as well as the similarity in the timing of deglacial minima are consistent with an association between  $\delta^{13}$ C and  $\Delta^{14}$ C in the deglacial ocean. This association suggests that both of these tracers are recording the redistribution of carbon from a poorly-ventilated deep ocean into the upper ocean and atmosphere. The concurrent timing of deglacial  $\delta^{13}$ C and  $\Delta^{14}$ C minima with Antarctic and Southern Ocean changes suggest that Southern Ocean processes are responsible for the carbon redistribution. This interpretation is consistent with models explaining the glacial/interglacial CO<sub>2</sub> changes through changes in Southern Ocean circulation and biogeochemistry (e.g., Sigman et al., 2010).

## **Chapter V: Summary**

In this dissertation I have investigated the mechanisms behind the atmospheric CO<sub>2</sub> rise and atmospheric  $\Delta^{14}$ C decline that occurred during the last deglaciation. I have attempted to track the redistribution of the hypothesized <sup>14</sup>C- and <sup>13</sup>C-depleted carbon from the deep ocean to the upper ocean and atmosphere during the last deglaciation. Chapter II presented records of intermediate water  $\Delta^{14}$ C during the deglaciation reconstructed using two sediment cores from the northwestern Arabian Sea. These records reveal intervals in which the intermediate waters became extremely depleted in <sup>14</sup>C. The timing and magnitude of the <sup>14</sup>C-depletion the start of the deglaciation is very similar to that previously recorded in the eastern North Pacific near Baja California, and occurs at the same time as the rise in atmospheric CO<sub>2</sub> and decline in atmospheric  $\Delta^{14}$ C. The intermediate water  $\Delta^{14}$ C records in the Arabian Sea and near Baja California are most readily consistent with the upwelling of <sup>14</sup>C-depleted deep water up to the surface of the Southern Ocean as this ocean warmed and destratified during the deglaciation. These <sup>14</sup>C-depleted waters must have spent enough time near the surface of the Southern Ocean to gain buoyancy and renew oxygen concentrations, but not enough time to significantly alter  $\Delta^{14}$ C, before being incorporated into thermocline or intermediate waters such as Subantarctic Mode Water or Antarctic Intermediate Water.

In Chapter III, I present a record of intermediate water  $\Delta^{14}$ C reconstructed using a sediment core from the margin of southern Chile. In the modern ocean, this core site is located near the base of Antarctic Intermediate Water, the water mass that was proposed to have carried a low- $\Delta^{14}$ C signal to the Arabian Sea and Baja California. The  $\Delta^{14}$ C gradient between the atmosphere and intermediate waters was significantly larger than the modern gradient during the last glacial maximum and during the second half of the Antarctic Cold Reversal, suggesting a

greater influence from Circumpolar Deep Water at the core site during these times. Contrary to expectations, this record indicates that the intermediate waters along the Chile margin were relatively well ventilated during Heinrich Stadial 1, the time of the largest <sup>14</sup>C depletion in the Arabian Sea and Baja California records. While these results are consistent with recent intermediate water  $\Delta^{14}$ C records from farther north along the Chile margin, in the Drake Passage and near New Zealand, they are seemingly inconsistent with our interpretations of the Arabian Sea and Baja California records. I suggest that there were multiple modes of intermediate water formation in the Southern Ocean during the deglaciation, with relatively dense, very low- $\Delta^{14}$ C intermediate waters formed by subduction at the Polar Front and less dense, higher- $\Delta^{14}$ C

In Chapter IV, I examined the relationship between the deglacial minima in intermediate water  $\Delta^{14}$ C and minima in planktic foraminiferal  $\delta^{13}$ C, which have been widely recorded during deglaciations. A compilation of  $\Delta^{14}$ C and  $\delta^{13}$ C data from the deep ocean during the last glacial maximum suggests that the deep Southern Ocean could have supplied carbon to the upper ocean and atmosphere that was depleted in both <sup>13</sup>C and <sup>14</sup>C. I presented new planktic foraminiferal stable isotopic measurements from the Arabian Sea and Baja California sediment cores, in which the  $\Delta^{14}$ C minima were documented. These records document declines in  $\delta^{13}$ C at the same times as declines in intermediate water  $\Delta^{14}$ C; however the records are complicated by local changes in upwelling and nutricline structure during the deglaciation. Overall, these results are consistent with an association between  $\Delta^{14}$ C and  $\delta^{13}$ C in the redistribution of carbon during the deglaciation. However, the scaling between the  $\Delta^{14}$ C and  $\delta^{13}$ C minima remain unclear. It is also unclear how the  $\delta^{13}$ C minima relate to the two modes of Southern Ocean intermediate water formation proposed in Chapter III. Based on the processes of nutrient transport from the

Southern Ocean to low latitudes in the modern ocean, I expect that the  $\delta^{13}$ C signal would have been carried by relatively shallow intermediate waters formed through deep wintertime mixing in a process analogous to modern Subantarctic Mode Water. Whereas, in Chapter III, I argued that the low- $\Delta^{14}$ C signal was eroded by mixing and air-sea gas exchange in the intermediate waters formed in this manner. It is, therefore, possible that while low  $\Delta^{14}$ C and  $\delta^{13}$ C deep waters upwelled within the Southern Ocean, the  $\Delta^{14}$ C and  $\delta^{13}$ C minima were spread to low latitudes via different processes.

Based on these findings there are several main conclusions that can be drawn. It is very likely that there was a reservoir of carbon in the ocean that was very depleted in <sup>14</sup>C during the last glacial maximum and deglaciation. It is likely that this carbon reservoir resided in the deep ocean. This result requires that some portion of the glacial deep ocean was isolated from the atmosphere as a result of a long residence time in the deep ocean and/or poor air-sea equilibration during deep water formation. These results provide support for hypotheses explaining the glacial/interglacial atmospheric  $CO_2$  changes that involve these mechanisms. The <sup>14</sup>C-depleted carbon was not incorporated into the intermediate waters that formed in the vicinity of the Drake Passage and flowed along the Chile margin at ~1000 m water depth. There also appears to be an association between <sup>14</sup>C and <sup>13</sup>C in the glacial and deglacial ocean. This association indicates that the poorly ventilated deep ocean reservoir accumulated low  $\delta^{13}C$  carbon.

There are many unanswered questions related to the redistribution of carbon from the deep ocean to the upper ocean and atmosphere during the last deglaciation. While the very similar  $\Delta^{14}$ C signals observed in the Arabian Sea and near Baja California are most readily explained by the upwelling of low- $\Delta^{14}$ C waters in the Southern Ocean, large <sup>14</sup>C depletions have

yet to be found in intermediate waters closer to the Southern Ocean. It remains unclear how the low- $\Delta^{14}$ C signal was transported to the low latitude intermediate waters. Unraveling of this puzzle requires additional intermediate water  $\Delta^{14}$ C records. I suggest that relatively deep, intermediate water sites, in the 1500 to 2000 m depth range, may be particularly informative. Additionally, finding the  $\Delta^{14}$ C minima at a site outside of highly productive, upwelling regions would allow the unambiguous analysis of the relationship between  $\Delta^{14}$ C and  $\delta^{13}$ C through measurements of  $\delta^{13}$ C on benthic foraminifera. Mapping of the poorly ventilated glacial deep water mass remains an important priority. The magnitude of <sup>14</sup>C depletion and the spatial extent of this water mass will determine its importance in the glacial to interglacial carbon cycle changes. Our knowledge of Southern Ocean  $\Delta^{14}$ C during glacial times and accordingly, several of the conclusions in this dissertation draw largely on one record from the northern edge of the Atlantic sector Southern Ocean. This record is not without significant uncertainties; much of the deep water  $\Delta^{14}$ C decrease during the last glacial maximum is accomplished through a large increase in surface reservoir ages. Additional records of glacial deep water  $\Delta^{14}$ C from the Southern Ocean are badly needed.

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# **Appendix A: Estimation of Error in Calendar Ages**

The uncertainty in the calendar age models constructed for the three sediment cores used in Chapters II & III was estimated using a Monte Carlo simulation. The simulation was based on an estimated uncertainty in the placement of tie points and an uncertainty in sedimentation rates in between tie points. In this process I generated two sets of normally distributed random numbers: one for the tie points, and one for the sedimentation rates. These two sets of numbers were used to calculate a set of calendar ages for each sample depth. The standard deviation of the calendar age set was reported as the calendar age error for each sample depth. These calculations were performed using the statistical software R (www.r-project.org). The R code used is shown below with annotations.

## R code for estimating error on calendar ages.

### RC27-23

#Tie Points p=c(8200, 11600, 14600, 21300, 23600) # calendar age of tie points d=c(106.5, 150.5, 186.5, 252.5, 275.5) # depth in core

#Sample Depths x=c(112, 122, 127, 132, 137, 142, 147, 152, 157, 162, 167, 172, 177, 182, 187, 192, 197, 202, 207, 212, 217, 222, 227, 232, 237, 242, 262)

#Create a set of normally distributed random numbers with a mean equal to the calendar age of each tie point and a standard deviation equal to the estimated uncertainty in the placement of each tie point.

z=matrix(ncol=5,nrow=1000) z[,1]=rnorm(1000,p[1],500) z[,2]=rnorm(1000,p[2],200) z[,3]=rnorm(1000,p[3],200) z[,4]=rnorm(1000,p[4],300) z[,5]=rnorm(1000,p[5],200) #Create another set of normally distributed random numbers with a mean equal to the sedimentation rate between each set of tie points and a standard deviation equal to the uncertainty in sedimentation rate.

s=matrix(ncol=4, nrow=1000) r=rnorm(1000,1,0.1) #10% uncertainty in sedimentation rate s[,1]=(d[2]-d[1])/(p[2]-p[1])\*r s[,2]=(d[3]-d[2])/(p[3]-p[2])\*r s[,3]=(d[4]-d[3])/(p[4]-p[3])\*r s[,4]=(d[5]-d[4])/(p[5]-p[4])\*r

#Use the sets of randomly generated tie points and sedimentation rates to derive a set of calendar ages for each sample.

t=matrix(ncol=1000,nrow=27) t[1,]=(x[1]-d[1])/s[,1]+z[,1]t[2,]=(x[2]-d[1])/s[,1]+z[,1]t[3] = (x[3] - d[1])/s[1] + z[1]t[4,]=(x[4]-d[2])/s[,1]+z[,2]t[5] = (x[5] - d[2])/s[1] + z[2]t[6] = (x[6] - d[2])/s[1] + z[2]t[7,]=(x[7]-d[2])/s[,1]+z[,2]t[8,]=(x[8]-d[2])/s[,2]+z[,2]t[9,]=(x[9]-d[2])/s[,2]+z[,2]t[10] = (x[10] - d[2])/s[2] + z[2]t[11,]=(x[11]-d[2])/s[,2]+z[,2]t[12] = (x[12] - d[3])/s[2] + z[3]t[13] = (x[13] - d[3])/s[2] + z[3]t[14] = (x[14] - d[3])/s[2] + z[3]t[15] = (x[15] - d[3])/s[3] + z[3]t[16] = (x[16] - d[3])/s[3] + z[3]t[17,]=(x[17]-d[3])/s[,3]+z[,3]t[18] = (x[18] - d[3])/s[3] + z[3]t[19] = (x[19] - d[3])/s[3] + z[3]t[20,]=(x[20]-d[3])/s[,3]+z[,3]t[21,]=(x[21]-d[3])/s[,3]+z[,3]t[22] = (x[22] - d[4])/s[3] + z[4]t[23] = (x[23] - d[4])/s[3] + z[4]t[24] = (x[24] - d[4])/s[3] + z[4]t[25] = (x[25] - d[4])/s[3] + z[4]t[26] = (x[26] - d[4])/s[3] + z[4]t[27,]=(x[27]-d[4])/s[,4]+z[,4]

#Calculate the mean and standard deviation of the set of calendar ages for each sample

m=vector(length=27)
std=vector(length=27)
for (i in 1:27){
 m[i]=mean(t[i,])
std[i]=sd(t[i,])}

## RC27-14

#Tie Points p=c(8200, 11600, 14600, 21300, 23600) d=c(56.5, 108.5, 146.5, 238.5, 273.5)

# calendar age of tie points
# depth in core

#Sample Depths x=c(67, 76, 76.5, 87, 97, 106, 117, 126, 128, 136, 137.5, 147, 152.5, 157, 167, 176, 187, 197, 203, 207, 240, 275, 225)

#Create a set of normally distributed random numbers with a mean equal to the calendar age of each tie point and a standard deviation equal to the estimated uncertainty in the placement of each tie point.

z=matrix(ncol=5,nrow=1000) z[,1]=rnorm(1000,p[1],500) z[,2]=rnorm(1000,p[2],200) z[,3]=rnorm(1000,p[3],200) z[,4]=rnorm(1000,p[4],300) z[,5]=rnorm(1000,p[5],200)

#Create another set of normally distributed random numbers with a mean equal to the sedimentation rate between each set of tie points and a standard deviation equal to the uncertainty in sedimentation rate.

s=matrix(ncol=4, nrow=1000) r=rnorm(1000,1,0.10) s[,1]=(d[2]-d[1])/(p[2]-p[1])\*r s[,2]=(d[3]-d[2])/(p[3]-p[2])\*r s[,3]=(d[4]-d[3])/(p[4]-p[3])\*r s[,4]=(d[5]-d[4])/(p[5]-p[4])\*r

# 10% uncertainty in sedimentation rate

#Use the sets of randomly generated tie points and sedimentation rates to derive a set of calendar ages for each sample.

t=matrix(ncol=1000,nrow=23) t[1,]=(x[1]-d[1])/s[,1]+z[,1]t[2,]=(x[2]-d[1])/s[,1]+z[,1]t[3,]=(x[3]-d[1])/s[,1]+z[,1]t[4,]=(x[4]-d[2])/s[,1]+z[,2]t[5,]=(x[5]-d[2])/s[,1]+z[,2]t[6] = (x[6] - d[2])/s[1] + z[2]t[7,]=(x[7]-d[2])/s[,2]+z[,2]t[8,]=(x[8]-d[2])/s[,2]+z[,2]t[9,]=(x[9]-d[3])/s[,2]+z[,3]t[10,]=(x[10]-d[3])/s[,2]+z[,3]t[11,]=(x[11]-d[3])/s[,2]+z[,3]t[12] = (x[12] - d[3])/s[3] + z[3]t[13] = (x[13] - d[3])/s[3] + z[3]t[14] = (x[14] - d[3])/s[3] + z[3]t[15,]=(x[15]-d[3])/s[,3]+z[,3]t[16] = (x[16] - d[3])/s[3] + z[3]t[17] = (x[17] - d[3])/s[3] + z[3]t[18] = (x[18] - d[4])/s[3] + z[4]t[19] = (x[19] - d[4])/s[3] + z[4]t[20] = (x[20] - d[4])/s[3] + z[4]t[21,]=(x[21]-d[4])/s[,4]+z[,4]t[22] = (x[22] - d[5])/s[4] + z[5]t[23] = (x[23] - d[4])/s[3] + z[4]

#Calculate the mean and standard deviation of the set of calendar ages for each #sample

m=vector(length=23)
std=vector(length=23)
for (i in 1:23){
 m[i]=mean(t[i,])
std[i]=sd(t[i,])}

## MD07-3128

#Tie Points p=c(11900, 12850, 14600, 18500, 19820) d=c(25, 49, 67, 163, 393)

#Calendar age of tie points # Depth in core

#Sample Depths x=c(31, 41, 51, 55, 61, 65, 71, 95, 109, 131, 151, 165, 179, 221, 301) #Create a set of normally distributed random numbers with a mean equal to the calendar age of each tie point and a standard deviation equal to the estimated uncertainty in the placement of each tie point.

z=matrix(ncol=5,nrow=1000) z[,1]=rnorm(1000,p[1],400) z[,2]=rnorm(1000,p[2],400) z[,3]=rnorm(1000,p[3],400) z[,4]=rnorm(1000,p[4],500) z[,5]=rnorm(1000,p[5],500)

#Create another set of normally distributed random numbers with a mean equal to the sedimentation rate between each set of tie points and a standard deviation equal to #he uncertainty in sedimentation rate.

s=matrix(ncol=4, nrow=1000) r=rnorm(1000,1,0.1) #10% uncertainty in sed rates s[,1]=(d[2]-d[1])/(p[2]-p[1])\*r s[,2]=(d[3]-d[2])/(p[3]-p[2])\*r s[,3]=(d[4]-d[3])/(p[4]-p[3])\*r s[,4]=(d[5]-d[4])/(p[5]-p[4])\*r

#Use the sets of randomly generated tie points and sedimentation rates to derive a set of calendar ages for each sample.

```
t=matrix(ncol=1000,nrow=15)
t[1,]=(x[1]-d[1])/s[,1]+z[,1]
t[2,]=(x[2]-d[2])/s[,1]+z[,2]
t[3] = (x[3] - d[2])/s[2] + z[2]
t[4,]=(x[4]-d[2])/s[,2]+z[,2]
t[5] = (x[5] - d[3])/s[2] + z[3]
t[6] = (x[6] - d[3])/s[2] + z[3]
t[7,]=(x[7]-d[3])/s[,3]+z[,3]
t[8,]=(x[8]-d[3])/s[,3]+z[,3]
t[9,]=(x[9]-d[3])/s[,3]+z[,3]
t[10] = (x[10] - d[4])/s[3] + z[4]
t[11,]=(x[11]-d[4])/s[,3]+z[,4]
t[12] = (x[12] - d[4])/s[3] + z[4]
t[13] = (x[13] - d[4])/s[4] + z[4]
t[14] = (x[14] - d[4])/s[4] + z[4]
t[15] = (x[15] - d[5])/s[4] + z[5]
```

#Calculate the mean and standard deviation of the set of calendar ages for each sample

m=vector(length=15)
std=vector(length=15)
for (i in 1:15){
m[i]=mean(t[i,])
std[i]=sd(t[i,])}

# Appendix B: Normalization of $\Delta^{14}$ C Gradients

In the following, I describe the process that was used to normalize  $\Delta^{14}$ C in the past to what they would be under pre-industrial, pre-nuclear atmospheric <sup>14</sup>C activity. Atmospheric  $\Delta^{14}$ C was higher during the last glacial and deglacial periods. Assuming constant physics, the  $\Delta^{14}$ C gradient between the atmosphere and intermediate or deep waters will be larger when atmospheric  $\Delta^{14}$ C is higher. This can be shown using the generic decay equation:

$$N = N_0 * e^{-\lambda t}$$

where N is the <sup>14</sup>C/<sup>12</sup>C at time t, N<sub>0</sub> is the initial <sup>14</sup>C/<sup>12</sup>C and  $\lambda$  is the decay constant. If we assume that an atmosphere to intermediate water difference is simply a function of decay, then N<sub>0</sub> is atmospheric <sup>14</sup>C/<sup>12</sup>C and N is intermediate water <sup>14</sup>C/<sup>12</sup>C.

 $N_0 - N = N_0 - N_0 * e^{-\lambda t}$ 

or  $N_0 - N = N_0 * (1 - e^{-\lambda t})$ 

 $N_0 - N$  is therefore a function of  $N_{0,}$  and  $(1 - e^{-\lambda t})$  is the slope of the function.

The gradient can be normalized by dividing by N<sub>0</sub>:

$$(N_0 - N)/N_0 = 1 - e^{-\lambda t}$$

which will be constant if t is constant.

Using fraction modern (Fm) works well for this purpose. Since Fm of the preindustrial prenuclear atmosphere is 1, dividing by atmospheric Fm normalizes to preindustrial values.

The process I have used for normalization is outlined below:

1) Convert atmospheric and benthic  $\Delta^{14}$ C values to Fm

$$Fm = \Delta^{14}C/1000 - 1$$

2) Subtract benthic Fm from atmospheric Fm to get the absolute Fm gradient

 $\Delta Fm = Fm_{Atm} - Fm_B$ 

3) Divide the absolute Fm gradient by atmospheric Fm to get the normalized Fm gradient

 $\Delta Fm_{norm} = \Delta Fm/Fm_{Atm}$ 

4) Convert the Fm gradient back to a  $\Delta^{14}$ C gradient

 $\Delta \Delta^{14} C_{norm} = \Delta F m_{norm} * 1000$
1. RC27-23 stable isotope measurements <sup>a,b</sup> conducted at the WHOI Mass Spectrometry Facility							y Facility		
Depth	Calendar	G.	<i>G</i> .	<i>G</i> .	<i>G</i> .	G.	G.	Ν.	Ν.
in Core	Age	ruber	ruber	sacculifer	sacculifer	menardii	menardii	dutertrei	dutertrei
(cm)	(kyr BP)	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
122	9398	0.88	-1.63	0.97	-1.02	0.93	0.36	1.21	-0.41
127	9784	0.75	-1.23	0.59	-0.77	0.82	-0.72	1.40	-0.51
132	10170	0.63	-1.50	0.81	-0.86	0.75	-0.49	1.10	-0.58
137	10557	0.27	-1.30	0.81	-1.09	0.73	0.22	0.66	-0.58
142	10943	0.57	-1.06	0.82	-0.86	0.60	0.01	1.01	0.21
147	11330	-0.09	-1.06	0.77	-0.51	0.60	0.36	1.00	0.23
152	11725	0.29	-0.59	0.67	-0.52	0.70	0.30	0.43	0.45
157	12142	0.25	-0.38	0.33	-0.47	0.95	1.12	0.89	-0.06
162	12558	0.38	-1.28	0.66	-0.08	0.80	0.14	0.92	-0.18
167	12975	0.38	-0.90	0.55	-0.28	0.64	0.24	0.61	0.40
172	13392	0.54	-0.83	0.38	-0.28	0.71	0.09	1.09	0.23
177	13808	0.25	-1.12	0.54	-0.53	0.78	0.11	1.34	0.07
182	14225	0.46	-0.94	0.50	-0.67	0.53	0.50	0.85	-0.21
187	14648	0.53	-0.39	0.23	-0.02	0.65	0.38	0.84	0.42
192	15125	0.35	-0.16	0.69	0.25	0.43	0.61	1.23	0.61
197	15602	-0.11	-0.69	0.68	0.23	0.71	0.14	1.12	0.73
202	16080	0.36	-0.31	0.32	-0.18	0.41	0.65	0.91	0.43
207	16557	0.10	-0.45	0.63	0.40	0.88	0.77	1.15	0.37
212	17034	0.30	0.00	0.46	0.37	0.94	0.95	1.26	0.67
217	17511	0.21	-0.24	0.74	0.32	0.94	1.05	1.43	0.79
222	17989	0.49	-0.75	0.64	0.18	1.10	0.98	1.31	-0.71
227	18466	0.07	-0.21	0.74	0.63	1.20	0.84	1.48	0.56
232	18943	0.10	-0.60	0.80	0.10	0.93	1.18	1.39	0.77
237	19420	-0.09	-0.08			0.81	1.11	1.28	0.86
242	19898	0.39	0.24	0.39	0.24	0.73	1.50	0.95	0.53
247	20375	-0.07	0.40	0.59	0.02	0.96	1.20	1.12	0.83
252	20852	0.17	-0.17	0.45	0.20	0.62	1.40	1.27	0.88
257	21409	0.14	0.10			0.91	1.19	0.57	0.75
262	21974	-0.08	0.11			0.56	1.24	0.84	0.65
267	22539	0.14	0.08	0.61	0.47	0.72	1.22	1.05	0.64

## Appendix C: Planktic for aminiferal $\delta^{13}$ C data

a. All measurements are reported relative to the VPDB standard.

b. The analytical precision determined from repeat analysis of the NBS19 calcite standard is  $\pm 0.07$  for  $\delta^{18}$ O and  $\pm 0.03$  for  $\delta^{13}$ C.

Depth in	Calendar Age	$G$ ruber $\delta^{13}C$	$G$ ruber $\delta^{18}$	$N$ dutartrai $\delta^{13}C$	$N$ dutertrei $\delta^{18}$ O	
Core (cm)	(kyr BP)	0. ruber o C	0. ruber 0 0	N. uniertrei 0 C	N. dulertrei 0 0	
127	9784	0.89	-1.75	1.04	-0.94	
132	10170	0.59	-1.61	0.88	-0.74	
137	10557	0.68	-1.51	0.80	-0.67	
142	10943	0.53	-1.40	0.94	-0.73	
147	11330	0.55	-1.22	0.59	-0.49	
152	11725	0.71	-1.23	1.07	-0.91	
157	12142	0.25	-0.93	0.71	0.08	
162	12558	0.63	-1.17	0.98	-0.32	
167	12975	0.37	-0.80	0.82	-0.02	
172	13392	0.34	-1.07	0.81	0.00	
177	13808	0.35	-0.94	0.89	-0.07	
182	14225	0.49	-1.07	0.97	-0.31	
187	14648	0.38	-0.37	0.61	0.41	
197	15602			0.57	0.35	
202	16080			0.79	0.65	
207	16557	-0.06	-0.44	1.09	0.37	
217	17511	0.26	-0.83	0.66	0.88	
222	17989			0.73	-0.20	
227	18466			1.41	0.75	
232	18943	0.27	-0.16			
237	19420			1.06	0.83	
242	19898	0.18	-0.11	0.85	0.54	
247	20375	0.47	-0.08	1.25	0.84	
252	20852	0.39	-0.07	1.40	0.59	

2. RC27-23 stable isotope measurements<sup>a,b</sup> conducted at the University of California, Davis Stable Isotope Laboratory

a. All measurements are reported relative to the VPDB standard.

b. The analytical precision determined from repeat analysis of the NBS19 calcite standard is  $\pm 0.05\%$  for  $\delta^{18}$ O and  $\pm 0.04\%$   $\delta^{13}$ C.

	Calendar	<u> </u>	G.	G.	G.	G.	G.	<i>N</i> .	<i>N</i> .
Composite	Age	ruber	ruber	sacculifer	sacculifer	menardii	menardii	dutertrei	dutertrei
Depth (m)	(kyr BP)	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}$ C	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
3.26	10810			1.65	-1.48	0.80	0.22	1.83	0.34
3.41	11321							1.66	0.59
3.56	11809	1.25	-0.81	1.59	-0.81	1.21	0.88	2.10	0.66
3.66	12115	0.63	-0.65			2.02	-0.23	2.43	0.46
3.91	12884	0.90	-0.36	1.72	-0.87	1.64	0.19	1.88	0.77
4.11	13566	1.27	-0.26	0.99	-0.54	1.80	0.21	1.85	0.77
4.22	13942	0.90	-0.63	1.38	-0.33	1.67	0.55	1.63	0.45
4.31	14199	1.27	-1.03	1.92	-0.72	1.56	0.22	1.82	0.27
4.375	14374	1.26	-0.59	1.60	-0.60	1.69	0.01	1.94	0.57
4.475	14648	0.85	-0.19	1.52	-0.53	2.36	0.18	2.18	0.52
4.565	14965	1.10	-0.37	1.52	-0.74	2.11	0.18	2.23	0.64
4.66	15299	0.97	-0.48			1.77	0.18	1.87	0.61
4.765	15669	1.14	-0.57	1.43	-0.07	2.49	0.23	1.92	0.89
4.865	16021	1.00	-0.51			1.72	0.11	2.04	0.49
4.965	16374	1.14	-0.65			2.48	0.49	1.98	0.62
5.065	16726	1.12	-0.21	1.49	-0.52	2.32	0.63	1.95	0.51
5.165	17078	1.04	-0.38	1.29	-0.41	2.10	-0.34	1.97	1.22
5.265	17430	1.09	-0.28	1.38	-0.31	2.74	-0.25	2.20	0.83
5.365	17782	0.98	-0.62	1.43	-0.40	2.38	0.03	2.16	1.13
5.47	18120	1.05	-0.33	1.33	-0.07	2.33	0.21	2.38	1.00
5.56	18407	1.16	-0.80			2.17	0.14	2.61	1.75
5.72	18919	1.49	-0.80	1.46	-0.34	2.04	0.28	1.47	1.40
5.88	19430	0.99	-0.87	1.15	-0.37	2.03	0.45	1.60	1.10
6.04	19941	0.83	-0.16	1.59	-0.26	2.46	0.13	1.79	1.35
6.22	20516	1.15	-0.65	1.50	-0.29	2.34	-0.09	2.24	0.70
6.415	21138	1.22	-0.54	1.66	-0.46	2.45	-0.11	2.73	0.75
6.615	21774	1.03	0.04	1.42	-0.33	2.61	-0.09	2.15	0.99
7.135	23429	1.04	-0.89	1.80	-0.49	2.31	0.10	2.29	0.61
7.585	25146			1.33	-0.46	2.20	-0.33	2.29	0.56

3. MV99-GC31/PC08 stable isotope measurements<sup>a,b</sup> conducted at the WHOI Mass Spectrometry Facility

a. All measurements are reported relative to the VPDB standard. b. The analytical precision determined from repeat analysis of the NBS19 calcite standard is  $\pm 0.07$  for  $\delta^{18}$ O and  $\pm 0.03$  for  $\delta^{13}$ C.

Composite	Calendar Age	G. ruber $\delta^{13}$ C	G. ruber $\delta^{18}$ O	<i>N. dutertrei</i> δ <sup>13</sup> C	N. dutertrei $\delta^{18}$ O	
Depth (m)	(kyr BP)					
2.55	8272	1.26	-1.64	1.49	0.06	
2.755	9015			1.19	0.36	
2.93	9648			1.44	0.38	
3.07	10155			1.69	0.33	
3.26	10810			1.74	0.31	
3.41	11321			1.68	0.47	
3.56	11809	1.23	-0.61	1.62	0.65	
3.63	12023	1.15	-0.54	1.96	0.38	
3.66	12115			1.81	0.36	
3.91	12884			1.96	0.71	
3.98	13123	1.24	-0.60	1.67	0.52	
4.04	13328	1.26	-0.66	1.96	0.67	
4.11	13566			1.84	0.50	
4.22	13942	1.00	-0.82	2.05	0.59	
4.31	14199			1.54	0.72	
4.34	14280	1.43	-0.57	2.01	0.53	
4.375	14374	1.32	-0.78	1.70	0.62	
4.43	14522	1.26	-0.84	1.86	0.61	
4.475	14648	1.14	-0.53	1.95	0.68	
4.565	14965	1.15	-0.09	2.24	0.40	
4.66	15299			1.92	0.96	
4.765	15669	1.15	-0.51	2.04	0.54	
4.865	16021			2.20	0.92	
4.965	16374	1.14	-0.24	2.38	0.44	
5.065	16726	1.38	-0.33	2.02	0.83	
5.165	17078			1.92	0.80	
5.265	17430			2.00	1.18	
5.365	17782			2.88	0.61	
5.47	18120			2.15	0.67	
5.56	18407			1.91	0.95	
5.72	18919	1.26	-0.68	2.06	0.67	
5.88	19430	1.39	-0.76	1.84	1.22	
6.04	19941	1.39	-0.55	2.04	1.14	
6.22	20516	1.27	-0.73	2.18	0.94	
6.415	21138	1.14	-0.57	2.35	0.71	
6.615	21774	1.30	-0.66	1.90	0.98	

4. MV99-GC31/PC08 stable isotope measurements<sup>a,b</sup> conducted at the University of California, Davis Stable Isotope Laboratory

a. All measurements are reported relative to the VPDB standard. b. The analytical precision determined from repeat analysis of the NBS19 calcite standard is  $\pm 0.05\%$  for  $\delta^{18}$ O and  $\pm 0.04\%$   $\delta^{13}$ C.