Ventilation of the abyssal Southern Ocean during the late Neogene:
A new perspective from the subtantarctic Pacific

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[1] Benthic foraminiferal stable carbon isotope records from the South Atlantic show significant declines toward more “Pacific-like” values at ~7 and ~2.7 Ma, and it has been posited that these shifts may mark steps toward increased CO2 sequestration in the deep Southern Ocean as climate cooled over the late Neogene. We generated new stable isotope records from abyssal subtantarctic Pacific cores MV0502-4JC and ELT 25-11. The record from MV0502-4JC suggests that the Southern Ocean remained well mixed and free of vertical or interbasinal δ13C gradients following the late Miocene carbon shift (LMCS). According to the records from MV0502-4JC and ELT 25-11, however, cold, low δ13C bottom waters developed in the Southern Ocean in the late Pliocene and persisted until ~1.7 Ma. These new data suggest that while conditions in the abyssal Southern Ocean following the LMCS were comparable to the present day, sequestration of respired CO2 may have increased in the deepest parts of the Southern Ocean during the late Pliocene, a critical period for the growth and establishment of the Northern Hemisphere ice sheets.


1. Introduction

[2] In seeking the mechanism behind the glacial-interglacial atmospheric CO2 variations of the past two million years, many researchers have pointed to the potential of the Southern Ocean for storing and releasing significant quantities of CO2 in the form of dissolved inorganic carbon (DIC). Traditionally, changes in Southern Ocean biology have been one of the most frequently invoked mechanisms for explaining low glacial atmospheric CO2 levels, but recent study suggests that changes in the marine biological pump can account for less than half of the observed glacial-interglacial variation [Kohfeld et al., 2005]. In the past decade, many researchers have come to an understanding that the circulation of the Southern Ocean was fundamentally different during the Pleistocene glaciations than at present, and thus many physical mechanisms for sequestering CO2 within the glacial Southern Ocean have been proposed. In the modern ocean, the upwelling of Circumpolar Deepwater at the Antarctic Divergence is the primary mechanism by which waters deeper than 2500 m are exposed to the atmosphere, and with this exposure, CO2 respired at depth can be released. During glacial periods, however, ventilation of these deep waters may have been inhibited by physical changes such as increased surface water stratification [Francois et al., 1997; Sigman et al., 1999, 2004; Jaccard et al., 2005; Brunelle et al., 2007; de Boer et al., 2007; Sigman et al., 2007], increased sea ice cover [Stephens and Keeling, 2000; Adkins et al., 2002], and decreased upwelling [Toggweiler et al., 2006; Watson and Naveira Garabato, 2006].

[3] In the Atlantic sector of the Southern Ocean, glacial intervals since 1.55 Ma have been characterized by benthic δ13C values that are consistently lower than those of the glacial Pacific Ocean [Hodell et al., 2003; Hodell and Venz-Curtis, 2006]. This suggests that the buildup and subsequent release of respired CO2 from the deep Atlantic sector of the Southern Ocean may have influenced atmospheric CO2 on glacial-interglacial timescales. While the low benthic δ13C values attained in the deep South Atlantic during glacial intervals after 1.55 Ma may appear to be a Pleistocene phenomenon, these may actually be part of a larger trend of decreasing δ13C values over the last 9 Ma that occurred in two main steps. The first of these declines coincides with the late Miocene carbon shift (LMCS) at ~7 Ma. Although this decrease in benthic δ13C has been identified in foraminiferal records throughout the world’s oceans [Hag et al., 1980], its magnitude appears greatest in records from the South Atlantic [Hodell and Venz-Curtis, 2006]. The second shift occurred at ~2.7 Ma during the late Pliocene climate transition (LPCT) and has been identified only in benthic δ13C records from >2500 m depth in the Atlantic sector of the Southern Ocean [Hodell and Venz, 1992; Hodell et al., 2002; Hodell and Venz-Curtis, 2006]. Because both the LMCS and the LPCT were associated with shifts in interbasinal δ13C gradients in which carbon isotope values in the South Atlantic became increasingly Pacific-like, it has been posited that these carbon events may mark steps toward increased CO2 sequestration in the deep Southern Ocean as high-latitude climate cooled over the late Neogene [Hodell and Venz-Curtis, 2006].
4] In fact, evidence now suggests that many of the physical mechanisms that likely hindered the release of respired CO$_2$ from the deep Southern Ocean during the glaciations of the late Quaternary were operating by the late Pliocene. While the Northern Hemisphere ice sheets were still in their infancy, Antarctica appears to have been reaching an advanced state of glaciation that was accompanied by changes in the circulation of the Southern Ocean. A strong halocline developed in the Antarctic and subarctic Pacific coincident with the onset of Northern Hemisphere Glaciation at 2.73 Ma [Haug et al., 1999; Sigman et al., 2004], and Antarctic sea ice expanded to the South Orkney microcontinent by 2.5–2.4 Ma [Burckle et al., 1990; Kennett and Barker, 1990]. Most importantly, a decline in atmospheric pCO$_2$ to preindustrial levels may have been a requirement for the initiation of ice sheets in the Northern Hemisphere [Lunt et al., 2008], and the decline in benthic $\delta^{13}$C in the deep South Atlantic (~2500 m) at ~2.7 Ma suggests that a consequence of this late Pliocene expansion of the Antarctic cryosphere may have been increased sequestration of CO$_2$ within the deep Southern Ocean [Hodell and Venz-Curtis, 2006].

5] Unfortunately, our current knowledge of carbon isotope changes in the Southern Ocean during the late Neogene is based almost entirely on stable isotope records from sediment cores recovered from the South Atlantic region. Thus, while Hodell and Venz-Curtis [2006] have shown that the LMCS and LPCT were associated with shifts in interbasinal $\delta^{13}$C gradients between the North Atlantic, South Atlantic, and equatorial Pacific Oceans, the nature, or in the case of the LPCT, even the existence, of these shifts in the Pacific sector of the Southern Ocean has remained largely unknown. Herein we offer new stable isotope records from two piston cores obtained from the depths of approximately 4000 m or greater in the subantarctic Pacific region. These records are significant not only because they provide a circum-Antarctic perspective for the carbon isotope shifts associated with the LMCS and LPCT, but also because they are among the deepest stable isotope records yet available from the late Neogene Southern Ocean.

2. Background

2.1. Using $\delta^{13}$C to Reconstruct Changes in Deepwater Circulation

2.1.1. Controls on the $\delta^{13}$C of Deepwater

6] Carbon isotopes are a valuable water mass tracer in the study of deepwater circulation patterns. In large part because of the role of biologic productivity in the distribution of carbon isotopes in the ocean, deep water masses can acquire distinct $\delta^{13}$C values that can be used to discern their source region and/or age. Prior to sinking, deep waters obtain a preformed $\delta^{13}$C value that is reflective of productivity and air-sea exchange processes in their source region.

7] Deepwater sourced from surface water in which productivity and/or nutrient utilization is high will have a high $\delta^{13}$C value and a low nutrient concentration compared to deepwater sourced in regions of low productivity/nutrient utilization. In the modern ocean, North Atlantic Deepwater (NADW) has $\delta^{13}$C values between 1.0 and 1.5$\%$ because of high nutrient utilization in its source waters, which originate in the subtropics above a strong thermocline, whereas Antarctic Bottom Water (AABW) has an average $\delta^{13}$C value of 0.3$\%$ because of nutrient underutilization near Antarctica [Kroopnick, 1985].

8] The preformed $\delta^{13}$C value of deepwater is also influenced by the isotopic equilibration of atmospheric CO$_2$ with DIC in the surface water mass. Air-sea exchange in the source region acts to increase the preformed $\delta^{13}$C value of the water mass under colder temperatures and lower it under warmer temperatures, but the residence time of the water at the air-sea interface is usually shorter than the time required to reach isotopic equilibrium. Thus, the influence of air-sea exchange is usually highest in areas where wind speeds are high, such as the modern subantarctic, where planktonic foraminifera record a $\delta^{13}$C enrichment of up to 1$\%$ [Charles and Fairbanks, 1990; Broecker and Maier-Reimer, 1992; Lynch-Stieglitz et al., 1995; Ninnemann and Charles, 1997].

9] As deepwater circulates within the ocean, its $\delta^{13}$C value evolves as it mixes with other water masses and “ages.” Aging occurs as the water mass accumulates $^{12}$C from the oxidation of sinking organic matter. The most nutrient-rich water ($\delta^{13}$C ≈ 0) in today’s ocean is found at middepth (~2000 m) in the North Pacific, where nutrients become “trapped” as deepwater upwells at the end of the deepwater conveyor [Matsumoto et al., 2002].

2.1.2. Benthic Foraminifera as a Recorder of Deepwater $\delta^{13}$C

10] The carbon isotopic composition of benthic foraminifera is considered a reliable recorder of the $\delta^{13}$C value of DIC in the surrounding water mass and thus is commonly used in the reconstruction of past deepwater chemistry and circulation. Interspecies differences in microhabitat and vital effects can result in a consistent $\delta^{13}$C offset between many modern species of foraminifera and calcite precipitated in equilibrium with seawater. In general, however, epifaunal foraminifera such as Planulina and Cibicidoides spp., more closely record bottom water $\delta^{13}$C values than infaunal species, which often exhibit lower $\delta^{13}$C values reflective of the decomposition of organic matter in the pore waters [McCorkle et al., 1990].

11] In areas with high surface water productivities, it is possible for the $\delta^{13}$C value of epifaunal benthic foraminifera to show a negative offset of up to 0.6$\%$ from the $\delta^{13}$C of seawater because of the formation of a phytodetritus layer at the sediment surface [Mackensen et al., 1993]. This phenomenon, known as the “Mackensen phytodetritus effect,” has been invoked as a possible explanation for the low $\delta^{13}$C values exhibited by benthic foraminifera in the South Atlantic sector of the Southern Ocean during glacial intervals [Mackensen et al., 2001]. Several South Atlantic sites do show evidence of increased surface water productivity coincident with the onset of Northern Hemisphere Glaciation at 2.75 Ma [Sigman et al., 2004]. However, deep sea sediments in the region record a consistent glacial-interglacial shift in benthic $\delta^{13}$C, regardless of the productivity or sedimentary regime, which largely rules out the existence of a significant surface productivity overprint [Ninnemann and Charles,
2002]. An alternative explanation is that the low $\delta^{13}C$ values reflect reduced ventilation of the deep Southern Ocean resulting from changes in the Antarctic source region during glacial intervals, such as increased sea ice cover, enhanced surface water stratification, decreased Ekman-induced upwelling, and reduced vertical mixing across the thermocline [Hodell and Venz-Curtis, 2006].

2.2. Setting and Oceanography

[12] Two carbonate-rich cores from the subantarctic Pacific region were examined in this study: MV0502-4JC ($50^\circ 20'S$, 148°08'W, 4286 m) and ELT 25-11 ($50^\circ 02'S$, 127°31'W, 3969 m) (Figure 1). These cores were recovered from the southern edge of the Southwest Pacific Basin near the Eltanin Fracture Zone system, a 1000 km offset between the Pacific Antarctic Ridge and the Southern East Pacific Rise [Lonsdale, 1994]. The Subantarctic Zone, which extends north from the Subantarctic Front to the Subtropical Front, is distinguished by the presence of Subantarctic Surface Water and biocalcareous sedimentation. An unusually deep carbonate compensation depth in the region of approximately 4750 m allows for the preservation of carbonate-rich sediments at abyssal depths [Lyle et al., 2007]. To the south of the sites, the Subantarctic Front and the Polar Front are strongly guided by topography to flow though the Elinatn and Udintsev Fracture Zones [Gille et al., 2004]. The close proximity of these fracture zones makes past migrations of the fronts over the sites unlikely.

[13] The deepwater mass bathing the core sites examined in this study is lower Circumpolar Deepwater (CDW). CDW, the deepwater mass of the Antarctic Circumpolar Current (ACC), is divided into three components, upper CDW (1400–2800 m), largely returning Pacific Deepwater (PDW) characterized by low oxygen and high nutrient concentrations, middle CDW (2800–3400 m), a high-salinity layer within the maximum influence of the NADW, and lower CDW (>3800 m), a cold, low-salinity water mass primarily composed of AABW [Hall et al., 2003]. After AABW forms through the sinking of extremely cold shelf waters in regions such as the Weddell Sea, the Ross Sea, and the Adélie Coast, its flow is impeded by sills such as the Drake Passage, and because of its high density, AABW is largely confined to the Southern Ocean basins until entrained upward into the ACC. While AABW manages to enter the Atlantic Ocean through a deep gap in the South Scotia Ridge, AABW is thought to be ponded within the Australian-Antarctic and Southeast Pacific Basins by the ridge systems to the north [Orsi et al., 1999]. Thus, the bottom water that ultimately fills the Southwest Pacific Basin, as well as the entire deep North Pacific, PDW, is water that has been sourced from the lower part of CDW and has been transported northward along the New Zealand platform by the Deep Western Boundary Current (DWBC), ultimately becoming warmer, fresher, oxygen-poorer, and nutrient-richer along its journey to the North Pacific [Whitworth et al., 1999].

3. Methods

3.1. Processing and Analysis of the Sediment

[14] Sediment samples were washed with distilled water over a 63 $\mu$m sieve and oven-dried. Dry sediment samples were weighed both before and after and sieving in order to calculate the weight percent sediment >63 $\mu$m. Ice rafted debris and manganese micronodules were also counted from the >150 $\mu$m size range. For stable isotope analyses, foraminifera of similar size were picked from the >125 $\mu$m fraction, cleaned in methanol, and roasted under vacuum at 200°C for 1 h. Analyses were then conducted in the University of Michigan Stable Isotope Laboratory, where samples were
reacted at 75°C with phosphoric acid in a Kiel automatic carbonate preparation device linked to a Finnigan MAT 251 mass spectrometer. Stable isotope data are reported in standard $\delta$ notation relative to the Vienna Peedee belemnite (VPDB) standard. Analytical precision, which was monitored through the regular analysis of the standard reference carbonate NBS 19, was ±0.03‰ for $\delta^{13}$C and ±0.08‰ for $\delta^{18}$O (1σ, N = 153). Planktonic samples generally consisted of six specimens of *Globigerina bulloides*, and benthic samples consisted of three specimens of either *Cibicidoides mundulus* (*Cibicidoides kullenbergi*), *Planulina wuellerstorfi* (*Cibicidoides wuellerstorfi*), or *Cibicidoides robertsonianus*.

A correction factor of +0.64‰ was applied to the benthic $\delta^{18}$O values to correct for the known departures from isotopic equilibrium of *C. mundulus* and *P. wuellerstorfi* [Shackleton and Hall, 1997]. The same correction factor of +0.64‰ was also used for *C. robertsonianus* because comparison of the $\delta^{18}$O values of *C. robertsonianus* and *P. wuellerstorfi* in samples containing specimens of both species demonstrated no significant offset. A correction factor was not applied to the benthic $\delta^{13}$C values in this study because the $\delta^{13}$C values of *C. mundulus* and *P. wuellerstorfi* are known to reflect equilibrium values [Shackleton and Hall, 1997]. The $\delta^{13}$C value of *C. robertsonianus* also showed no significant offset from *P. wuellerstorfi* in multiple analyses carried out over the same sample interval.

### 3.2. Comparison to Existing Stable Isotope Records

The benthic stable isotope record obtained from MV0502-4JC in this study is compared to existing late Neogene benthic stable isotope records from ODP Sites 607 and 982 in the North Atlantic, ODP Sites 704 and 1090 in the South Atlantic, and ODP Site 849 in the equatorial Pacific, as compiled by Hodell and Venz-Curtis [2006]. Pacific Site 849, located on the western flank of the East Pacific Rise, records the characteristics of average PDW from 0 to 9 Ma [Mix et al., 1995]. Site 607, which is located on the western flank of the Mid Atlantic Ridge, monitors changes in lower NADW from 0 to 3.2 Ma [Raymo et al., 1990], and Site 982 on the Rockall Plateau records the properties of upper NADW from 4.6 to 9.0 Ma [Hodell et al., 2001]. The stable isotope records from Site 704 on the Meteor Rise and Site 1090/TN057-6 on the Agulhas Ridge [Müller et al., 1991; Hodell and Venz, 1992; Venz and Hodell, 2002] were combined by Hodell and Venz-Curtis [2006] to create a single continuous record of CDW in the South Atlantic. Additionally, ODP Site 1088, also located on the Agulhas Rise, provides an important record of South Atlantic intermediate water (<2500 m) variation [Billups, 2002; Hodell et al., 2003; Hodell and Venz-Curtis, 2006]. The locations of these sites are depicted in Figure 2, and the location and depth information for the stable isotope records discussed in this study can be found in Table 1.

### 4. Results

#### 4.1. Chronology

A compilation of the results from MV0502-4JC (Figure 1; 50°20'S, 148°08'W, 4286 m) can be seen in Figure 3; raw data are provided in Data Sets S1 and S2. The chronology was developed primarily on the basis of radiolarian and stable isotope stratigraphy (Table 2). To ensure that the core top was intact, $^{13}$C analysis of *G. bulloides* was conducted at the University of Arizona AMS laboratory. Overall, MV0502-4JC was found to extend...
from the Holocene to the Late Miocene with three major hiatuses: an early Pliocene–early late Pliocene hiatus (hiatus A, between ~10.7 and 10.2 meters below seafloor (mbsf)), and two Pleistocene hiatuses from ~1.57–0.7 Ma (hiatus B, ~4 mbsf) and ~0.45–0.25 Ma (hiatus C, ~2.4 mbsf). Hiatus A was poorly constrained because of severe dissolution and reworking within the interval 10.7 to 10.2 mbsf.

In the late Miocene portion of the core below hiatus C, an age model could not be constructed because of the presence of only one age datum, the late Miocene carbon shift (LMCS), a global event that has been dated to 7.7 to 6.6 Ma [Tedford and Kelly, 2004]. Radiolarians in the late Miocene portion of the core (~10.7 to 17.2 mbsf) yield age estimates of 10–13 Ma that are incongruous with the established timing of the LMCS (Table 2). The poor nature of the radiolarian record in this part of the core is likely a manifestation of an exceedingly low sedimentation rate and/or the lack of radiolarian species specific to this age range that would otherwise aid in the recognition of reworking. The LMCS, however, is easily identified by the permanent nature of the negative benthic δ13C shift, a concurrent increase in carbonate dissolution, and the absence of an accompanying change in benthic δ18O. In Figure 4, the carbon shift in MV0502-4JC has been aligned with that of Site 704 in order to facilitate comparison with other deep sea records.

In the late Pliocene–early Pleistocene interval of the core between hiatuses A and B (~10.2–4 mbsf), an approximate age-depth relationship was developed to allow comparison with other deep-sea records (Figure 5). The most distinctive feature of this portion of the core is the late Pliocene climate transition (LPCT) [Hodell and Ciesielski, 1990; Hodell and Venz, 1992]. Because the sedimentation rate appears to increase within this interval, two separate linear age-depth models were used with a break at 7.32 mbsf, the depth at which we identify the MIS 71/72 boundary. Below 7.32 mbsf, we correlate the onset of the δ13C shift with that of Site 704/1090 [Hodell and Venz-Curtis, 2006]. Above 7.32 mbsf, MIS 55–59 (1.585–1.698 Ma) were identified on the basis of their highly distinctive nature and a radiolarian age of 1.63–1.79 Ma at 5.12 mbsf. This allowed for the tentative assignment of MIS 61, 63, 67, and 71. These marine isotope stage assignments were then used to calculate a linear age-depth relation on the basis of the oxygen isotope stack of Lisiecki and Raymo [2005].

The majority of the Pleistocene record after ~1.57 Ma was found to be missing because of hiatuses B and C, and the amplitudes of the few glacial-interglacial cycles represented below hiatus B (MIS 14–16 and MIS 2–6) have likely been reduced because of the low sedimentation rate. MIS 14–16 were identified on the basis of the distinctive nature of MIS 16 and a radiolarian age of 0.425–1.08 Ma at 2.57 mbsf, which distinguishes MIS 16 from MIS 12. Additionally, MIS 2–6 were constrained on the basis of radiocarbon dates taken from the top of the core and by the absence of Stylactatus universus (LO 0.425 Ma).

4.1.2. ELT 25-11

In Figure 6, we present results from the Eltanin piston core ELT 25-11 (Figure 1; 50°02’S, 127°31’W, 3969 m), which was recovered approximately 1000 km to the east of MV0502-4JC on the flank of the East Pacific Rise; raw data are provided in Data Sets S3 and S4. The new radiolarian and stable isotope data acquired from ELT 25-11 have allowed for the improvement of an existing nanofossil chronology developed by Geitzenauer and Huddlestun [1972] and later modified by King [1988] (Table 3). Overall, the ELT 25-11 record extends into the late Pliocene, and the stable isotope record, while coarse, displays the distinctive late Pliocene features present in MV0502-4JC, including the positive benthic δ18O and negative benthic δ13C excursions of the LPCT and large positive planktonic and benthic δ13C shifts of ~1% near the late Pliocene/Pleistocene boundary. In the earlier chronology, a hiatus was placed at ~3.74 mbsf and assigned a maximum age range of ~1.95–0.30 Ma, but we suggest that the hiatus actually spans from 1.55 to 0.30 Ma and is located closer to 1.94 mbsf, synchronous with a significant drop in the CaCO3 content. The original placement of the hiatus was based on the disappearance of P. laconosa above 3.89 mbsf. However, our radiolarian stratigraphy indicates an age of 1.73–1.85 Ma at 2.65 mbsf, and the large positive planktonic and benthic δ13C shifts of ~1‰ that we identify in ELT 25-11 between ~3.24 and 2.54 mbsf clearly correlate to similar shifts that were dated to the early Pleistocene in MV0502-4JC.

4.2. Overview of the Results

4.2.1. Late Miocene

Benthic δ18O values between 17.17 and 12.11 mbsf are the lowest and least variable overall, averaging 3.59‰ (maximum, 3.85‰; minimum, 3.32‰) (Figure 3). Before the prominent negative benthic δ13C shift of ~1‰ at ~15.3 mbsf, identified as the LMCS, δ13C values average 1.13 ± 0.18‰. Following the shift, benthic δ13C values average 0.28 ± 0.16‰. Benthic δ13C values in MV0502-4JC are very similar to those recorded at Site 704 both before and after the LMCS, and benthic δ18O values at the two sites are also comparable (Figure 4).

Table 1. Location and Water Depth of Late Neogene Stable Isotope Records Discussed in This Study

<table>
<thead>
<tr>
<th>Site/Core</th>
<th>Location</th>
<th>Water Depth</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODP 704</td>
<td>46°52’S, 7°5’E</td>
<td>2532 m</td>
<td>Hodell and Venz [1992] and Müller et al. [1991]</td>
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<td>ODP 1090</td>
<td>42°55’S, 8°54’E</td>
<td>3702 m</td>
<td>Venz and Hodell [2002]</td>
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<tr>
<td>ODP 607</td>
<td>41°08’S, 13°34’E</td>
<td>2082 m</td>
<td>Billups [2002], Hodell et al. [2003], and Hodell and Venz-Curtis [2006]</td>
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<tr>
<td>ODP 849</td>
<td>0°11’N, 11°31’W</td>
<td>3850 m</td>
<td>Raymond et al. [1990]</td>
</tr>
<tr>
<td>ODP 982</td>
<td>57°31’N, 15°53’W</td>
<td>1145 m</td>
<td>Mix et al. [1995]</td>
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<tr>
<td>MV0502-4JC</td>
<td>50°20’S, 148°08’W</td>
<td>4286 m</td>
<td>Hodell et al. [2001]</td>
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<td>ELT 25-11</td>
<td>50°02’S, 127°31’W</td>
<td>3969 m</td>
<td>this study</td>
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Figure 3
Table 2. Important Age Datums Identified in MV0502-4JC

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Age or Age Range</th>
<th>Basis for Age Assignment</th>
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<tbody>
<tr>
<td>4–6</td>
<td>9.849 ± 51</td>
<td>radiocarbon dates</td>
</tr>
<tr>
<td>16–18</td>
<td>16,799 ± 96</td>
<td>radiocarbon dates</td>
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<tr>
<td>166–168</td>
<td>&lt;0.425</td>
<td>radiocarbon dates</td>
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<tr>
<td>256–258</td>
<td>0.425–1.08</td>
<td>radiocarbon dates</td>
</tr>
<tr>
<td>391–393</td>
<td>1.08–1.63</td>
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<tr>
<td>511–513</td>
<td>1.63–1.79</td>
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<tr>
<td>806–808</td>
<td>1.85–2.38</td>
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<td>1021–1023</td>
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<tr>
<td>1141–1143c</td>
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<tr>
<td>1701–1703c</td>
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Stable Isotope Stratigraphy

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<td>Late Pliocene δ13C shift</td>
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<td>1.608</td>
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<tr>
<td>387</td>
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<td>MIS 16/17 [Lisiecki and Raymo, 2005]</td>
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<tr>
<td>354.5</td>
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<td>MIS 15/16 [Lisiecki and Raymo, 2005]</td>
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<td>152</td>
<td>0.130</td>
<td>MIS 5/6 [Lisiecki and Raymo, 2005]</td>
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<tr>
<td>82</td>
<td>0.071</td>
<td>MIS 4/5 [Lisiecki and Raymo, 2005]</td>
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</table>

4.2.2. Late Pliocene

Between 10.2 and 9.6 mbsf (~3.0-2.75 Ma), benthic δ18O values average 3.63 ± 0.09% and are briefly comparable to late Miocene values (Figure 3). Benthic δ18O resembles the Site 704 record, but benthic δ13C values, which average 0.31 ± 0.17%, are more Pacific-like than those at Site 704 (Figure 5). Between 9.6 and 7.3 mbsf (~2.75–1.9 Ma), MV0502-4JC displays dramatic changes associated with the late Pliocene climate transition (LPCT), most notably shifts in mean benthic δ18O and δ13C of ~+1.1‰ and ~−1.05‰, respectively. Following these shifts, δ18O values are significantly higher than those recorded at Sites 704 and 1090. Overall, a comparison between the δ18O values recorded by MV0502-4JC and those of deep equatorial Pacific Site 849, North Atlantic Site 607, and subantarctic Atlantic Sites 704/1090 suggests that mean δ18O values were 0.75 to 1‰ higher at the site of MV0502-4JC (~4000 m water depth) than at the other sites toward the end of the late Pliocene (<2.4 Ma). Benthic δ13C values are similar to those of deep equatorial Pacific Site 849 and subantarctic Atlantic Sites 704/1090 following the LPCT, but drift toward lower values by the end of the Pliocene.

[25] Following the benthic δ18O and δ13C shifts of the LPCT, ice rafted debris also becomes significant for the first time at ~8.9 mbsf and manganese micronodules decrease to trace amounts by ~8.4 mbsf (Figure 3). Initially, the benthic δ18O and δ13C shifts are associated with a decrease in the carbonate content between ~8.6 and 8.3 mbsf but are followed by an increase in the quality and quantity of planktonic foraminifera as well as an increase in the sedimentation rate to ~1.1 cm/ky by ~7.3 mbsf. Ash is present in samples throughout this interval and the reworking of radiolarians of Miocene-Oligocene age was noted at 8.07 mbsf.

[26] The record from ELT 25-11, while coarse, also shows significant shifts in benthic δ18O and δ13C during the LPCT (Figure 6). Benthic δ18O shifts by ~+1.1‰ (from 3.6‰ to 4.7‰) between 6.3 and 3.7 mbsf, and benthic δ13C shifts by ~−1.6‰ (from 1.09‰ to −0.5‰) over the same interval. While the δ18O shift in ELT 25-11 is very similar to that of MV0502-4JC, the δ13C shift is larger than that in MV0502-4JC because of significantly higher δ13C values in ELT 25-11 preceding the LPCT.

4.2.3. Pleistocene

[27] Below hiatus B (~4.0 mbsf, ~1.57–0.68 Ma), a distinctive ~1‰ increase in the benthic and planktonic δ13C values occurs between 5.62 and 4.77 mbsf (~1.7–1.65 Ma) (Figures 3 and 5). This ~1‰ increase in benthic and planktonic δ13C is also recorded in ELT 25-11 between ~3.24 and 2.54 mbsf and marks the return of benthic δ13C to values comparable to those recorded prior to the LPCT (Figure 6). Above hiatus B, carbonate contents recover and a strong, distinctive glacial event identified as MIS 16 occurs at ~3.77 mbsf (Figure 3). During MIS 16, both benthic and planktonic foraminifera exhibit the highest δ18O values of the entire record, reaching maximum values of 5.19‰ and 3.95‰, respectively. Following MIS 15 and 14, hiatus C (~2.57 mbsf) is accompanied by two declines in CaCO3 at 2.70 mbsf and 2.30 mbsf. Above hiatus C, we identify isothe
stages 1–6. In this uppermost section of the core, the abundance of planktonic foraminifera reaches a maximum, and sedimentation rates are ~1.2 cm/ka.

5. Discussion
5.1. Late Miocene Carbon Shift

[28] The LMCS is a complicated and poorly understood event that may have consisted of at least two distinct components. First, the LMCS is likely linked to change in global carbon mass balance, as evidenced by the presence of a negative shift in the δ¹³C records of both benthic and planktonic foraminifera [Vincent et al., 1980]. The negative δ¹³C shift could perhaps be explained by enhanced erosion and the addition of δ¹³C-depleted organic soil material to the ocean under the expansion of C4 plants, a hypothesis not inconsistent with a spike in carbonate dissolution or the late Miocene biogenic bloom observed at many sites [Diester-Haass et al., 2006]. Cerling et al. [1997] hypothesized that a drop in atmospheric CO₂ could have driven the expansion of...
C4 grasslands in the late Miocene because C4 photosynthesis is favored over the C3 pathway under low CO$_2$ conditions. This hypothesis has not been supported, however, by large differences in the timing of C4 expansion between continents [Fox and Koch, 2003], or by alkenone-based reconstructions of late Miocene atmospheric CO$_2$ levels [Pagani et al., 1999].

The transfer of carbon between the terrestrial and marine realms can offer only a partial explanation for the LMCS because the size of the $\delta^{13}$C shift varies spatially. Thus, the LMCS likely also reflects a significant reorganization of interbasinal $\delta^{13}$C gradients [Vincent et al., 1980]. Hodell and Venz-Curtis [2006] emphasize the development of a modern interbasinal gradient between North Atlantic Site 982 and South Atlantic Sites 704 and 1088 during the LMCS. While benthic $\delta^{13}$C values at Sites 704 and 982 were similar prior to the LMCS, the magnitude of the carbon shift was greater in the South Atlantic than the North Atlantic, thereby marking the inception of a modern interbasinal gradient in which South Atlantic $\delta^{13}$C values fall about midway between those of the North Atlantic and Pacific (Figure 4).

A longstanding explanation for the interbasinal $\delta^{13}$C changes associated with the LMCS has been increased NADW production. NADW has a high $^{13}$C content that...
would counteract an ocean-wide δ¹³C decline within the North Atlantic region. Ocean-wide changes in carbonate preservation, including a deepening of the CCD [Moore et al., 1984], suggest an increased presence of NADW in the Atlantic basin during the late Miocene. Billups [2002] argues on the basis of the carbon isotope record from Site 1088 that prior to 6.6 Ma, NADW did not extend into the Atlantic sector of the Southern Ocean and that after 6.6 Ma, tectonic changes, including the closure of the Central American Seaway or the subsidence of the Greenland-Scotland Ridge, led to an increased presence of NADW in the Atlantic basin. According to Poore et al. [2006], this increase in NADW strength occurred close to 6 Ma and was largely the result of subsidence of the Greenland-Scotland Ridge.

An alternative explanation for the interbasinal δ¹³C changes associated with the LMCS is a decrease in the preformed δ¹³C value of AABW. Growth of the West

Figure 6. Compilation of the results from ELT 25-11. (a) Benthic δ¹⁸O represented by top line and benthic δ¹³C represented by bottom line. Solid green and open green triangles depict data points obtained from the benthic species *C. mundulus* and *P. wuellerstorfi*, respectively. (b) *G. bulloides* δ¹⁸O represented by top line, and *G. bulloides* δ¹³C represented by bottom line. (c) Weight percent CaCO₃ (top line) and weight percent of the sediment > 63 μm (bottom line). The age constraints shown (dashed lines) are from nannofossil biostratigraphy by King [1988]. The hiatus was assigned an age of ~1.55–0.3 Ma in this study.
Antarctic Ice Sheet (WAIS) has been widely assigned to late Miocene [Ciesielski et al., 1982; Kennett and Barker, 1990] (although most open marine records show no corroborating increase in benthic $\delta^{18}O$), and establishment of the WAIS may have marked the initiation of bottom water formation processes in the Southern Ocean similar to those of the modern day (i.e., under ice shelves) [Hodell and Venz-Curtis, 2006]. Assuming the transfer of carbon from the terrestrial to the oceanic reservoir during the LMCS, a decrease in the preformed $\delta^{13}C$ signature of AABW would have acted to augment a decline in deepwater $\delta^{13}C$ values in the Southern and Pacific Oceans while having little effect on $\delta^{13}C$ values in the North Atlantic.

Interestingly, we find in this study that benthic $\delta^{13}C$ values at the site of MV0502-4JC were similar to those of Site 704 both before and after the LMCS (Figure 4). Thus, the results from MV0502-4JC agree with the interpretation of Hodell and Venz-Curtis [2006] that the LMCS marked the development of modern-like $\delta^{13}C$ gradients between the North Atlantic, Pacific, and Southern Oceans. More importantly, however, these results show that the Southern Ocean remained well mixed following the LMCS, comparable to the present-day state in which it exhibits a relatively uniform $\delta^{13}C$ value of ~0.4‰. Expansion of the WAIS may have forced a decrease in the preformed $\delta^{13}C$ value of AABW during the LMCS, but this expansion was not accompanied by the initiation of a significant horizontal or vertical $\delta^{13}C$ gradient within the Southern Ocean. The formation of a chemocline in the Southern Ocean at ~2500 m would thus accompany a later stage of climatic cooling.

It is important to emphasize that while the benthic $\delta^{13}C$ records from MV0502-4JC and ODP Sites 982, 704, 1088, and 849 are consistent with an increase in the supply of carbon to the oceans as well as the evolution of a modern interbasinal $\delta^{13}C$ gradient between the North Atlantic, Pacific, and Southern Oceans during the LMCS, other marine records do present a more complicated picture of the late Miocene ocean. In particular, following the LMCS benthic $\delta^{13}C$ values at ODP Site 1172 (43°57′57″S, 149°55′70″E, 2620 m) on the East Tasman Plateau stabilize at ~0.5–0.8‰ [Tedford and Kelly, 2004], lower than $\delta^{13}C$ values recorded at North Atlantic ODP Site 982 but higher than those recorded in the subantarctic region (ODP Site 704 and MV0502-4JC). Also, Grant and Dickens [2002] report an ~2 million year temporal offset between the negative $\delta^{13}C$ shift in planktonic foraminifera and bulk carbonate at DSDP Site 590 in the Tasman Sea, challenging the notion that the $\delta^{13}C$ decrease was a globally synchronous datum in all phases of biogenic carbonate. Grant and Dickens [2002] attribute this lag to changes in thermocline structure and nutrient cycling during the LMCS, although a change in the coccolithophorid species assemblage could offer an alternative explanation.

### 5.2. Late Pliocene Climate Transition

Unlike the LMCS, which brought subtle changes to the Southern Ocean, the LPCT marked the onset of a dramatic shift within the abyssal Southern Ocean, particularly at the site of MV0502-4JC. In general, the LPCT is known for a series of $\delta^{18}O$ enrichment events of increasing magnitude at 3.1, 2.7, 2.6, and 2.4 Ma that signal the onset and gradual amplification of Northern Hemisphere Glaciation [Keigwin, 1986]. The magnitude of these late Pliocene glacial-interglacial $\delta^{18}O$ variations is not particularly impressive when compared to the climatic oscillations of the late Pleistocene. At Site 607, for example, $\delta^{18}O$ values oscillate 0.5‰ between 3.1 and 2.95 Ma and 0.9‰ between 2.7 and 2.4 Ma, compared to 1.75‰ during the last glaciation, and it was not until after 2.95 Ma that “glacial” $\delta^{18}O$ values at Site 607 became more positive than those of the present interglacial [Raymo et al., 1992]. Thus, on the basis of the relatively small amplitude of late Pliocene glacial-interglacial $\delta^{18}O$ variations alone, the LPCT has not generally been regarded as a period dramatic oceanic change. However, following the first ODP cruise to the subantarctic Atlantic, Hodell and Ciesielski [1990] discovered that Site 704 recorded an interesting feature during the LPCT that deep sea cores from other regions did not: a 0.5‰ decrease in mean benthic $\delta^{13}C$.

Prior to the LPCT, $\delta^{13}C$ values at Site 704 had increased to once again become very similar to those of the North Atlantic, and thus the interbasinal gradient that had developed between the North and South Atlantic during to the LMCS had lessened significantly [Hodell and Venz-Curtis, 2006]. However, after ~2.75 Ma, $\delta^{13}C$ values at Site 704 underwent a sharp decline [Hodell and Venz, 1992; Hodell et al., 2002]. Hodell and Venz [1992] explained the decrease in $\delta^{13}C$ in the South Atlantic as a decline in NADW formation after 2.7 Ma. In support of this interpretation, data from equatorial Atlantic ODP Sites 925 and 929 reveal that the NADW/AABW boundary in the Atlantic was at reduced depth during the late Pliocene (~2.6–2.1 Ma), suggesting a greater influence of southern source water during that period. However, Hodell and Venz-Curtis [2006] also noticed that while mean benthic $\delta^{13}C$ values at Site 704 declined during the LPCT, $\delta^{13}C$ values at Site 1088 remained the same, marking the development of a chemical divide in the South Atlantic basin at ~2500 m depth. Thus, the $\delta^{13}C$ shift recorded at Site 704 appears to be the reflection of not only a decline in NADW during the LPCT, but also a significant reduction in the ventilation of the deep Southern Ocean, as first proposed by Hodell and Ciesielski [1990].

Hodell and Venz-Curtis [2006] suggest that increased sea ice and enhanced surface water stratification impeded air-sea gas exchange and contributed to lower preformed $\delta^{13}C$. 

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**Table 3. Important Age Datums Identified in ELT 25-11**

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Age or Age Range (Ma)</th>
<th>Basis for Age Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>74</td>
<td>0.26</td>
<td>CN14b/CN15 boundary [King, 1988]</td>
</tr>
<tr>
<td>404</td>
<td>1.95</td>
<td>CN12d/CN13a boundary [King, 1988]</td>
</tr>
<tr>
<td>153–154</td>
<td>&lt;0.425</td>
<td>LO Stylactatus universus</td>
</tr>
<tr>
<td>264–266</td>
<td>1.73–1.85</td>
<td>LO Cycladophora pliocenica and FO Triceraspyris antarctica</td>
</tr>
<tr>
<td>334–336</td>
<td>1.73–1.85</td>
<td>LO Cycladophora pliocenica and FO Triceraspyris antarctica</td>
</tr>
<tr>
<td>647</td>
<td>~2.75</td>
<td>Late Pliocene $\delta^{13}C$ shift [Hodell and Venz-Curtis, 2006]</td>
</tr>
</tbody>
</table>
values in AABW during glacial periods after 2.75 Ma. The LPCT definitely brought significant changes to the Antarctic cryosphere, including the first significant ice rafting to MV0502-4JC and Sites 704 and 1092 [Warnke et al., 1992; Murphy et al., 2002], the development of a strong halocline at 2.73 Ma [Haug et al., 1999; Sigman et al., 2004], and significant sea ice expansion by ~2.5–2.4 Ma [Burek et al., 1990; Kennett and Barker, 1990]. Moreover, because these changes coincide with the onset of Northern Hemisphere Glaciation, the Southern Ocean has been suggested as a possible player in the growth of the Northern Hemisphere ice sheets [Hodell and Ciesielski, 1990; Sigman et al., 2004; Hodell and Venz-Curtis, 2006]. As discussed below, the new stable isotope records from MV0502-4JC and ELT 25-11 lend additional weight to this idea.

[37] Like Site 704, the benthic stable isotope records from MV0502-4JC and ELT 25-11 also record a significant decline in $\delta^{13}C$ around the LPCT. However, while the LPCT at Site 704 appears to record the onset of a glacial-interglacial pattern of deep water ventilation in the Southern Ocean, with consistently poorer ventilation during glacialss than interglacials, combined with a significant episode of $\delta^{18}O$ enrichment, the transition in MV0502-4JC and ELT 25-11 appears to signal a far more dramatic shift in conditions in the abyssal Southern Ocean. First, the benthic $\delta^{13}C$ shift is more extensive and prolonged in these deep subantarctic Pacific records than in the preexisting records from the South Atlantic, and second, the $\delta^{13}C$ decrease was matched by an equally dramatic increase in benthic $\delta^{18}O$ that stands out among other deep sea records from that period. Particularly unusual is the length of time that the low $\delta^{13}C$ values, and hence poorly ventilated conditions, persisted in MV0502-4JC and ELT 25-11, as well as the dramatic return of the $\delta^{13}C$ values to pre-LPCT values after ~1.7 Ma, which is recorded as a 1% increase in both the benthic and planktonic records.

[38] We interpret these benthic $\delta^{13}C$ and $\delta^{18}O$ shifts, which in MV0502-4JC amount to −1.05‰ and +1.1‰, respectively, over the period 2.7 to 1.9 Ma (9.6–7.3 mbsf), as an indication that the abyssal Southern Ocean was filled with very cold, poorly ventilated waters following the LPCT. Whereas we have found that benthic $\delta^{18}O$ values > 4.5‰ were attained in the abyssal (>4000 m water depth) subantarctic Pacific during the latest Pliocene, $\delta^{18}O$ values that high were not recorded at Sites 607, 849, and 704 until the glaciations of the late Pleistocene, at which time the temperature of the deep Atlantic, Pacific, and Southern Oceans is thought to have been within error of freezing point of seawater [Adkins et al., 2002]. The cold, salty bottom waters that filled the deep ocean during the LGM were likely supplied through increased brine rejection [Adkins et al., 2002], and sea ice expansion may have had a similar effect on the deepest waters of the Southern Ocean during the late Pliocene. Further support for a dramatic cooling of Antarctic bottom waters during the LPCT comes from the results of Hayward et al. [2007], who found that a succession of pulsed declines and extinctions of benthic foraminifera with unusual aperture types originated in southern sourced deep waters (AABW and CDW) during the late Pliocene, later extending into NADW and Antarctic Intermediate Water (AAIW) during the mid-Pleistocene climate transition (MPT, 1.2–0.55 Ma). Thus, by 2.4 Ma, as the Northern Hemisphere was beginning to grow ice sheets and the magnitude of the benthic $\delta^{18}O$ oscillations was just more than half that of the last glacial-interglacial cycle, it appears that sea ice expansion around Antarctica may have forced the abyssal Southern Ocean into a state not significantly unlike that of the LGM.

[39] These new stable isotope records from the abyssal subantarctic Pacific call for further examination of the role of the Southern Ocean in the LPCT. The progressive nature of the $\delta^{18}O$ and $\delta^{13}C$ shifts between 2.7 and 1.9 Ma suggests that an ever larger percentage of cold, poorly ventilated AABW accumulated in the abyssal Southern Ocean over this period as a result of increasingly pervasive sea ice cover. Intense sea ice formation would have increased the density of the deepest waters in the Southern Ocean and likely would have decreased the upwelling of these waters, allowing for the build up of biologically fixed carbon in the abyssal Southern Ocean [Watson and Naveira Garibato, 2006]. Because the core sites of MV0502-4JC and ELT 25-11 are located just outside of the Southern Ocean basin, and thus record the signature of lower CDW rather than AABW itself, we infer that, at a minimum, the pool of cold, poorly ventilated water was sizable enough to fill the Pacific sector of the Southern Ocean below a depth of 4000 m. The existence of such a large, isolated water mass in the abyssal Southern Ocean during the late Pliocene is not only a surprising finding but also has significant implications for the amplification of Northern Hemisphere Glaciation during that period.

[40] This pool of poorly ventilated water appears to have persisted until 1.7 Ma, at which time the $\delta^{13}C$ values in MV0502-4JC and ELT 25-11 show a return to pre-LPCT values and the initiation of a more “typical” pattern of glacial-interglacial variation. Planktonic $\delta^{13}C$ values, which were also unusually low during the latest Pliocene and earliest Pleistocene, also increase at 1.7 Ma. This increase in benthic and planktonic $\delta^{13}C$ is consistent with global $\delta^{13}C$ maximum IV (MIS 53–57) identified by Wang et al. [2004] in several deep sea records. Other $\delta^{13}C$ maxima occur at MIS 13 and MIS 27–29 and precede the significant climatic transitions of the mid-Brunhes event and the mid-Pleistocene revolution [Wang et al., 2004]. These $\delta^{13}C$ maxima have been associated with profound reorganizations of the global carbon reservoir and have been linked to changes in productivity, the oceanic “rain ratio,” and increased carbonate dissolution in the Indo-Pacific [Wang et al., 2004]. Thus, the increase in benthic $\delta^{13}C$ in MV0502-4JC and ELT 25-11 after 1.7 Ma likely reflects in part a whole-ocean shift in the $\delta^{13}C$ of DIC, but the shift is unusually large relative to the other deep sea sites examined in this study and thus raises the question of whether these cores might also record the first significant trend toward well-mixed, well-ventilated conditions in the abyssal Southern Ocean following the LPCT.

6. Conclusion

[41] The new abyssal subantarctic Pacific stable isotope record from MV0502-4JC presented in this study supports the finding of Hodell and Venz-Curtis [2006] that the LMCS
marked an important step in the evolution of the modern δ13C gradient between the North Atlantic, Pacific, and Southern Ocean basins. While benthic δ13C values at South Atlantic Site 704 and North Atlantic Site 982 were similar prior to the LMCS, the magnitude of the carbon shift was greater in the South Atlantic than the North Atlantic, thus marking the inception of the modern interbasinal δ13C gradient in which South Atlantic δ13C values fall midway between those of the North Atlantic and Pacific. New results from MV0502-4JC indicate that benthic δ13C and δ18O values in the abyssal subantarctic Pacific were nearly identical to those at South Atlantic Site 704 both before and after the LMCS. Thus, the South Atlantic and South Pacific sectors of the Southern Ocean responded similarly to the LMCS, and despite potential cryospheric changes, the LMCS did not mark the initiation of any interbasinal or vertical stable isolate gradients within the Southern Ocean. Instead, communication between the Atlantic and Pacific sectors of the Southern Ocean remained strong, and the water column appears to have been well mixed and homogenous during the late Miocene, similar to the Southern Ocean today.

The late Pliocene climate transition (LPCT), in sharp contrast to the LMCS, did mark the development of significant vertical δ13C and δ18O gradients in the deep Southern Ocean. From the results of Hodell and Ciesielski [1990] and Hodell and Venz-Curtis [2006], we know that δ13C values at Site 704 declined by 0.5‰ at 2.7 Ma while δ13C values at intermediate Site 1088 remained unchanged, marking the development of a chemical divide in the South Atlantic basin at ~2500 m depth. However, the results of our study of the abyssal subantarctic Pacific cores MV0502-4JC and ELT 25-11 reveals that the abyssal Southern Ocean experienced changes during the LPCT that were far greater than those at Site 704. MV0502-4JC records benthic δ13C and δ18O shifts of −1.05‰ and +1.1‰, respectively, over the period 2.7 to 1.9 Ma (9.6–7.3 mbsf), which indicates that the abyssal Southern Ocean was filled with very cold, poorly ventilated waters consistent with extensive sea ice expansion during the late Pliocene [Burckle et al., 1990; Kennett and Barker, 1990]. Increased sea ice cover and enhanced surface water stratification likely reduced air-sea gas exchange and contributed to lower preformed δ13C values in AABW after ~2.7 Ma [Hodell and Venz-Curtis, 2006], but the low δ13C values recorded in the abyssal subantarctic Pacific may also reflect the accumulation of respired CO2 in the abyssal ocean as these cold, salty bottom waters resisted upwelling [Watson and Naveira Garabato, 2006]. The sea ice and the cold, poorly ventilated bottom waters appear to have persisted in the Southern Ocean until ~1.7 Ma at which time the reventilation of the Southern Ocean is recorded in both the benthic and planktonic δ13C records as an increase of ~+1‰. Thus, while this study cannot identify the cause of the LPCT itself, we have found that the LPCT led to the development of an isolated, poorly ventilated water mass in the abyssal Southern Ocean, the existence of which may have important implications for the expansion of the Northern Hemisphere ice sheets in the late Pliocene.

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carbon-isotopic shift and synchrony of some


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