

# Breathing more deeply: Deep ocean carbon storage during the mid-Pleistocene climate transition

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## ABSTRACT

**The ~100 k.y. cyclicality of the late Pleistocene ice ages started during the mid-Pleistocene transition (MPT), as ice sheets became larger and persisted for longer. The climate system feedbacks responsible for introducing this nonlinear ice sheet response to orbital variations in insolation remain uncertain. Here we present benthic foraminiferal stable isotope ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ) and trace metal records (Cd/Ca, B/Ca, U/Ca) from Deep Sea Drilling Project Site 607 in the North Atlantic. During the onset of the MPT, glacial-interglacial changes in  $\delta^{13}\text{C}$  values are associated with changes in nutrient content and carbonate saturation state, consistent with a change in water mass at our site from a nutrient-poor northern source during interglacial intervals to a nutrient-rich, corrosive southern source during glacial intervals. The respired carbon content of glacial Atlantic deep water increased across the MPT. Increased dominance of corrosive bottom waters during glacial intervals would have raised mean ocean alkalinity and lowered atmospheric  $p\text{CO}_2$ . The amplitude of glacial-interglacial changes in  $\delta^{13}\text{C}$  increased across the MPT, but this was not mirrored by changes in nutrient content. We interpret this in terms of air-sea  $\text{CO}_2$  exchange effects, which changed the  $\delta^{13}\text{C}$  signature of dissolved inorganic carbon in the deep water mass source regions. Increased sea ice cover or ocean stratification during glacial times may have reduced  $\text{CO}_2$  outgassing in the Southern Ocean, providing an additional mechanism for reducing glacial atmospheric  $p\text{CO}_2$ . Conversely, following the establishment of the ~100 k.y. glacial cycles,  $\delta^{13}\text{C}$  of interglacial northern-sourced waters increased, perhaps reflecting reduced invasion of  $\text{CO}_2$  into the North Atlantic following the MPT.**

## INTRODUCTION

Prior to the mid-Pleistocene transition (MPT), the growth and decay of Northern Hemisphere ice sheets responded to orbitally induced changes in insolation primarily on obliquity (~41 k.y.) time scales. After the MPT, the waxing and waning of these ice sheets was characterized by a generally slow buildup of continental ice followed by rapid glacial termination, defining a quasi-periodicity of ~100 k.y. (Hays et al., 1976; Maslin and Ridgwell, 2005). The underlying mechanisms for this change in ice sheet response remain unknown, although several possibilities have been proposed, including ice sheet dynamics (Clark and Pollard, 1998), deep ocean cooling (Tziperman and Gildor, 2003), and large-scale changes in thermohaline overturning circulation (Raymo et al., 1990; Pena and Goldstein, 2014). Ocean circulation affects heat and salt transport, but also ocean carbon storage, which in turn affects atmospheric  $p\text{CO}_2$  levels and hence climate (e.g., Boyle, 1988a; Toggweiler, 1999; Hodell et al., 2003). Unfortunately, ice core  $p\text{CO}_2$  records do not capture

the entire transition and only demonstrate that the amplitude of glacial to interglacial  $\text{CO}_2$  variations during the latter half of the MPT (ca. 800–600 ka) was smaller than during the late Pleistocene (Lüthi et al., 2008). Geochemical evidence suggests there was no particularly pronounced long-term decrease in atmospheric  $\text{CO}_2$  across the MPT (Hönisch et al., 2009), although analysis of blue ice from Antarctica suggests that glacial  $p\text{CO}_2$  ca. 1 Ma may have been ~30 ppm higher than in any glacial interval following 800 ka (Higgins et al., 2015). Inter-site gradients in neodymium isotopes ( $\epsilon_{\text{Nd}}$ ) and benthic foraminiferal carbon isotopes suggest increased influence of glacial southern-sourced deep waters through the MPT (Pena and Goldstein, 2014; Elderfield et al., 2012; Raymo et al., 1997). However, benthic foraminiferal carbon isotopes reflect a combination of biochemical and physical processes, including air-sea gas exchange in source water regions (Raymo et al., 1997; Lynch-Stieglitz et al., 1995), and  $\epsilon_{\text{Nd}}$  only acts as a proxy for source-water region and water mass mixing (e.g., Thomas and Via, 2007). Therefore, the

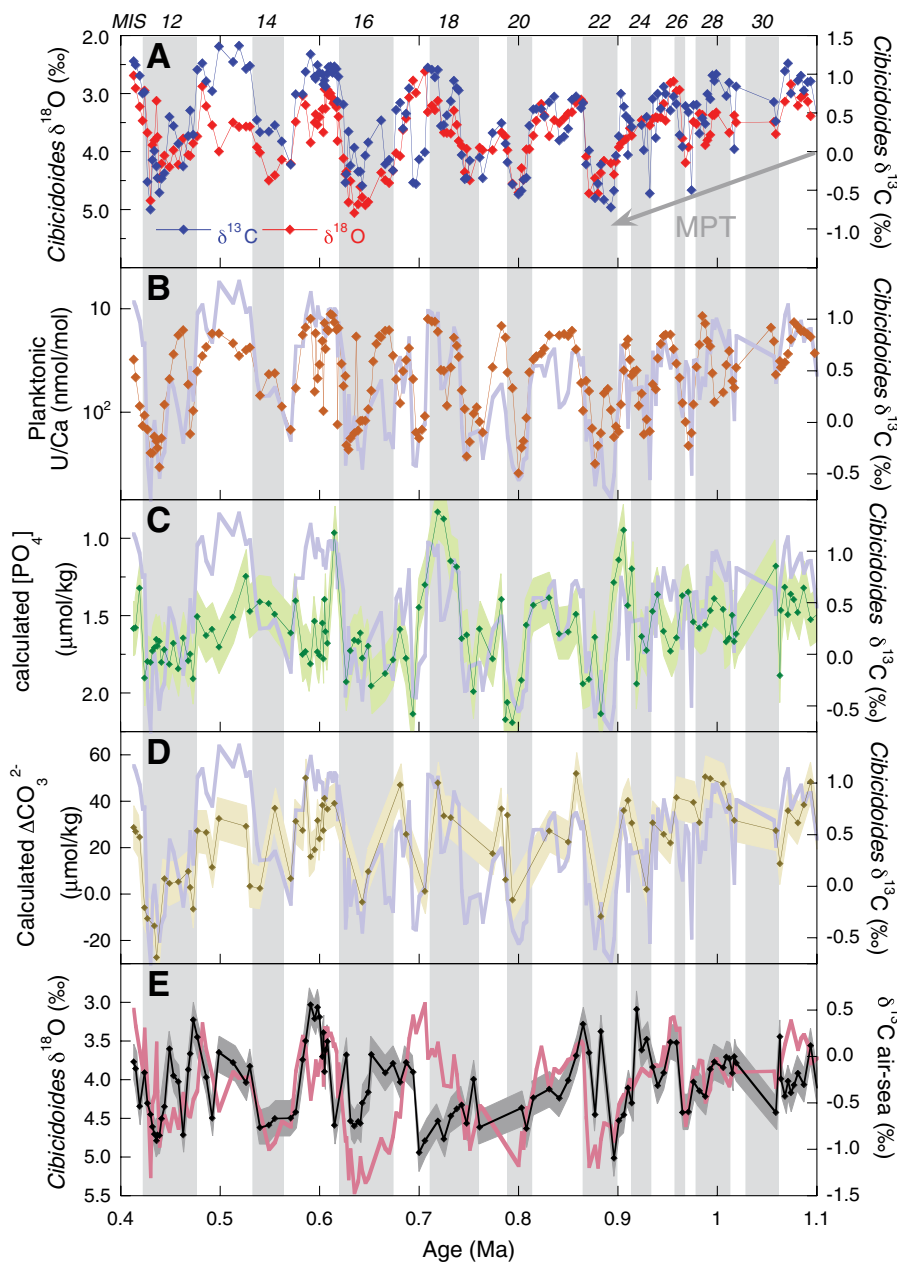
implications of reconstructed ocean circulation for deep ocean carbon storage are not clear.

Deep ocean carbon storage as expressed by nutrient concentrations and carbon chemistry is important, however, to fully understand climate dynamics and the carbon cycle, and it can be quantified using benthic foraminiferal metal/Ca ratios. Here we present paired benthic foraminiferal stable isotope and trace metal records (B/Ca, Cd/Ca) and planktonic foraminiferal U/Ca ratios through the MPT from Deep Sea Drilling Project (DSDP) Site 607, which today sits in the core of North Atlantic Deep Water (NADW) (see the methods section of the GSA Data Repository<sup>1</sup>). The similarity between the benthic foraminiferal  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  trends in our downcore records (Fig. 1A) indicates a close relationship between these “climate” and “carbon cycle” signals, which has been described previously (e.g., Raymo et al., 1990, 1997; Poirier and Billups, 2014). We use our metal/Ca records to explore potential mechanisms behind this tight coupling. The Cd/Ca and B/Ca records constrain the bottom water nutrient content and seafloor carbonate saturation state respectively. Together, our proxies suggest that the benthic  $\delta^{13}\text{C}$  record contains an ocean carbon storage signal and an air-sea  $\text{CO}_2$  exchange signal, both of which can drive significant changes in atmospheric  $p\text{CO}_2$  (Lynch-Stieglitz et al., 1995).

## TRACE METAL PROXIES

Records of U/Ca have been used to reconstruct variations in pore water redox conditions, which are a function of organic matter flux, sedimentation rate, and/or bottom water dissolved oxygen content (e.g., Jaccard et al., 2009). Although there is no calibration for this proxy, it is used to aid interpretation of the other proxies considered here (Fig. 1B). Core-top calibrations have enabled benthic foraminiferal Cd/Ca and

<sup>1</sup>GSA Data Repository item 2016346, Appendix DR1, methodology, site map, and explanation of proxy interpretations, is available online at [www.geosociety.org/pubs/ft2016.htm](http://www.geosociety.org/pubs/ft2016.htm) or on request from [editing@geosociety.org](mailto:editing@geosociety.org).



**Figure 1.** A: Deep Sea Drilling Project (DSDP) Site 607 (North Atlantic) *Cibicidoides* sp.  $\delta^{18}\text{O}$  (red) and  $\delta^{13}\text{C}$  (blue) (MPT—mid-Pleistocene transition). B: DSDP Site 607  $\delta^{13}\text{C}$  record (purple line) and *Globigerina bulloides* U/Ca (brown diamonds); note logarithmic scale. C: DSDP Site 607  $\delta^{13}\text{C}$  record (purple line) and bottom water  $[\text{PO}_4]$  reconstructed using benthic foraminiferal Cd/Ca (green diamonds). Pale green envelope represents  $[\text{PO}_4]$  uncertainty window of  $\pm 0.17 \mu\text{mol/kg}$  (see Data Repository [see footnote 1] for details). D: DSDP Site 607  $\delta^{13}\text{C}$  record (purple line) and bottom water carbonate saturation state ( $\Delta\text{CO}_3^{2-}$ ) reconstructed using *Cibicidoides wuellerstorfi* B/Ca (brown diamonds). Pale brown envelope represents  $\Delta\text{CO}_3^{2-}$  uncertainty window of  $\pm 9 \mu\text{mol/kg}$  (see Data Repository for details). E: DSDP Site 607  $\delta^{18}\text{O}$  record (red line) and  $\delta^{13}\text{C}$  air-sea exchange signal (filled black diamonds).  $\delta^{13}\text{C}$  air-sea exchange signal calculated using the  $[\text{PO}_4]$  record (C) and “corrected  $\delta^{13}\text{C}$  record” (see text for details). Gray vertical bars highlight the timing of marine isotope stages (MIS), after Lisiecki and Raymo (2005).

B/Ca to be used to reconstruct changing nutrient content and carbonate saturation state of ancient water masses, with a particular focus on ocean carbon dynamics of the Last Glacial Maximum and late Pleistocene (e.g., Boyle, 1992; Rickaby et al., 2010; Yu and Elderfield, 2007; Allen et al., 2015). Here we apply these same principles to

our MPT records (see the Data Repository for methods and calibration details).

#### TRACE METAL RECORDS AT DSDP SITE 607

Our trace metal records display distinct variability on glacial to interglacial time scales as

defined by the paired stable isotope records (Fig. 1; Fig. DR1 in the Data Repository). The U/Ca and  $\delta^{13}\text{C}$  records indicate a tight coupling between pore water redox conditions and ocean circulation change (Fig. 1B). This could reflect a switch between different water masses, but because the U/Ca record also displays a striking similarity with both alkenone mass accumulation rates (Lawrence et al., 2013) and radiolaria abundance (Fig. DR2), we interpret the U/Ca record as predominantly reflecting changes in organic matter flux into the sediment caused by local productivity changes. North and South Atlantic productivity apparently changed in parallel with climate on these orbital time scales and has been ascribed to changes in the depth of the nutricline, driven by migration of westerlies in both hemispheres (Lawrence et al., 2013). The lack of a convincing relationship between U/Ca and benthic foraminiferal Cd/Ca after marine isotope stage (MIS) 18 suggests that the Cd/Ca record predominantly reflects the nutrient content of the bottom water mass and has not been significantly overprinted by the local changes in productivity (see the Data Repository; Fig. DR2). We argue therefore that the glacial-interglacial variations in B/Ca also reflect changes in the saturation state of the bottom water mass, with minimal overprinting by local changes in productivity, and we discuss the significance of these below.

#### ATLANTIC OCEAN CARBON STORAGE THROUGH THE MPT

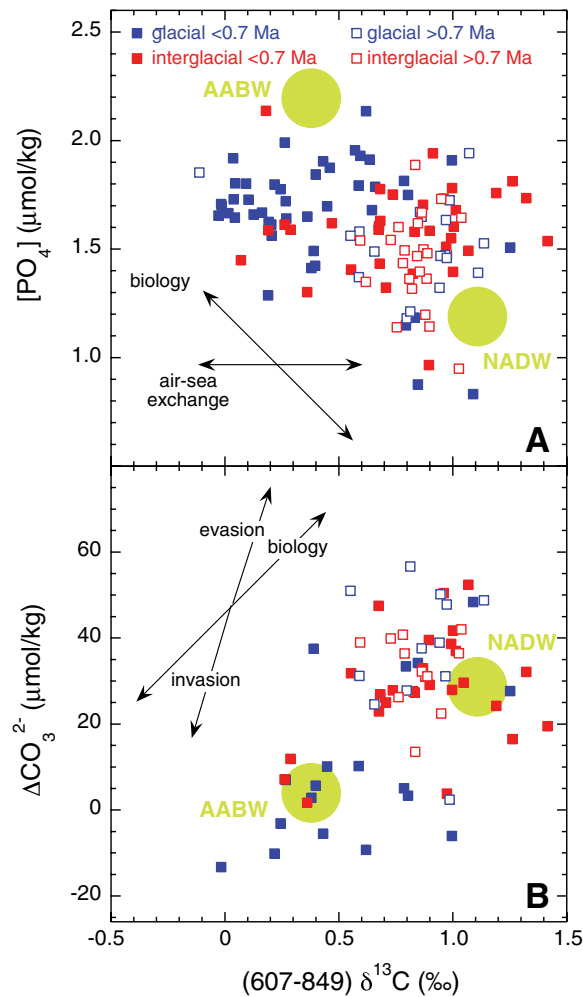
Neodymium isotopes trace the increasing influence of southern-sourced deep waters relative to North Atlantic-sourced waters during glacial intervals through the MPT (Pena and Goldstein, 2014). Today, DSDP Site 607 sits in the core of North Atlantic Deep Water, a well-ventilated water mass. In general, intervals of low benthic foraminiferal  $\delta^{13}\text{C}$  values at Site 607 are associated with low *Cibicidoides wuellerstorfi* B/Ca and high benthic foraminiferal Cd/Ca (Figs. 1C and 1D). The stronger incursions of southern-sourced bottom waters into the deep Atlantic recorded by  $\epsilon_{\text{Nd}}$  (Pena and Goldstein, 2014) are therefore associated with lower bottom water carbonate saturation state ( $\Delta\text{CO}_3^{2-}$ ) and increased nutrient content. Of particular note is the increase in the extent of remineralized organic matter stored in glacial deep waters following the MPT (Figs. 1C and 1D; Fig. DR3). There are two ways to interpret this signal. The first is that the glacial southern-sourced water mass became more corrosive (e.g., more poorly ventilated) across the MPT. Our trace metal records may be recording such an increase in ocean carbon storage directly. The second way to interpret the change in glacial bottom water mass characteristics at Site 607 is primarily through an increased volume of corrosive southern-sourced waters, with Site 607 consequently experiencing a greater proportion of this water mass relative

to northern-sourced waters through the MPT. It has been proposed that an increased volume of poorly ventilated deep waters would effectively increase the deep ocean carbon reservoir, leading to reduced atmospheric  $p\text{CO}_2$  (Skinner, 2006). If corrosive southern-sourced waters bathed a greater proportion of carbonate-bearing seafloor sediments, carbonate dissolution in deep waters would increase, raising whole-ocean alkalinity and hence lowering atmospheric  $p\text{CO}_2$  (Boyle, 1988a). In either case, we argue that a change in ocean circulation resulted in a lowering of glacial  $p\text{CO}_2$  across the MPT.

In the absence of air-sea exchange effects, a  $1 \mu\text{mol/kg}$  increase in  $[\text{PO}_4]$  would be expected to be associated with a 1.1‰ decrease in  $\delta^{13}\text{C}$  (Broecker and Maier-Reimer, 1992). After MIS 18 (ca. 0.7 Ma), the relationship between  $[\text{PO}_4]$  and  $\delta^{13}\text{C}$  appears to change, with larger-amplitude changes in  $\delta^{13}\text{C}$  that are not associated with correspondingly large amplitude changes in  $[\text{PO}_4]$  (Figs. 1C and 2A; Fig. DR4). We suggest three reasons for this observation. The first is that Cd/Ca is not a faithful recorder of bottom water  $\text{PO}_4$  concentrations. Despite the rigorous cleaning technique employed, the foraminifera have variable and in some cases high Mn/Ca, which has been associated with diagenetic incorporation of Cd into foraminiferal coatings (Boyle, 1983). However, despite the large interspecies offsets for Mn/Ca, there are no interspecies offsets for Cd/Ca (Fig. DR5), and there is no correlation between Cd/Ca and Mn/Ca (Fig. DR6). We therefore discard this option. The second possibility is that the slope of the  $[\text{PO}_4]$ - $\delta^{13}\text{C}$  relationship altered due to changing  $\delta^{13}\text{C}$  of organic matter. This option would require lighter  $\delta^{13}\text{C}$  of organic matter after the MPT, which is unlikely for at least the glacial intervals as it would imply increased sea-surface  $[\text{CO}_2]_{\text{aq}}$  (Popp et al., 1999). Our preferred option is that the  $\delta^{13}\text{C}$  record contains a significant signal of air-sea  $\text{CO}_2$  exchange.

### SEA ICE INFLUENCE ON CARBON CYCLING

Benthic carbon isotope records reflect (1) whole-ocean changes in  $\delta^{13}\text{C}$ , (2) regional variations in the amount of respired organic carbon/nutrient content, and (3) air-sea  $\text{CO}_2$  exchange signals that in turn contain both a temperature component and a  $\text{CO}_2$  outgassing or invasion signal (Lynch-Stieglitz et al., 1995). Temperature affects surface water  $\delta^{13}\text{C}$  but not  $\Delta\text{CO}_3^{2-}$  or  $[\text{PO}_4]$ , while  $\text{CO}_2$  outgassing or invasion affects both  $\delta^{13}\text{C}$  and  $\Delta\text{CO}_3^{2-}$  but with minimal influence on  $[\text{PO}_4]$  (Fig. 2). We follow Lynch-Stieglitz et al. (1995) to remove the biological influence and calculate the air-sea exchange signal ( $\delta^{13}\text{C}_{\text{air-sea}}$ ) (Fig. 1E). We do this after correcting for changes in whole-ocean  $\delta^{13}\text{C}$  by subtracting the Ocean Drilling Program Site 849  $\delta^{13}\text{C}$  record from the DSDP Site 607  $\delta^{13}\text{C}$  record (see the Data Repository).



**Figure 2.** Corrected  $\delta^{13}\text{C}$  (Deep Sea Drilling Project [DSDP] Site 607  $\delta^{13}\text{C}$  minus Ocean Drilling Program [ODP] Site 849  $\delta^{13}\text{C}$ ) versus reconstructed bottom water  $[\text{PO}_4]$  (A) and reconstructed carbonate saturation state ( $\Delta\text{CO}_3^{2-}$ ) (B). Blue symbols are from glacial intervals, red symbols are from interglacial intervals, based on marine isotope stages of Lisiecki and Raymo (2005). Open symbols are samples older than 0.7 Ma, closed symbols are samples younger than 0.7 Ma. Uncertainties in reconstructed  $[\text{PO}_4]$  are  $\sim\pm 0.17 \mu\text{mol/kg}$ , and uncertainties in reconstructed  $\Delta\text{CO}_3^{2-}$  are  $\sim\pm 9 \mu\text{mol/kg}$  (see the Data Repository [see footnote 1] for details). “Biology” arrow in A shows expected trendlines caused by changes in concentration of respired organic matter, based on modern Redfield ratios and carbon isotopic composition of organic matter (Lynch-Stieglitz et al., 1995). Horizontal arrow indicates that changes in air-sea  $\text{CO}_2$  exchange will not impact  $[\text{PO}_4]$ . Slopes of corresponding arrows in B are from Yu et al. (2008). Green circles represent composition of modern Antarctic Bottom Water (AABW) and North Atlantic Deep Water (NADW).

Today, isotopically light  $\text{CO}_2$  outgasses from water high in dissolved inorganic carbon (DIC) in the Southern Ocean, and invades low-DIC water in the North Atlantic, raising and lowering the  $\delta^{13}\text{C}$  values of the surface waters in the respective regions (Lynch-Stieglitz et al., 1995). The amount of outgassing or invasion may be controlled by the extent of sea ice, which acts as a barrier between the surface water and atmosphere. Our  $\delta^{13}\text{C}_{\text{air-sea}}$  record is consistent with an increase in glacial Southern Ocean sea ice extent across the MPT (MIS 30–22; 1.1–0.9 Ma), reducing outgassing of  $^{12}\text{C}$ -enriched  $\text{CO}_2$  and lowering the  $\delta^{13}\text{C}$  composition of southern-sourced waters (Fig. 1E). A similar trend of decreasing  $\delta^{13}\text{C}_{\text{air-sea}}$  may be caused by an internal “chemical divide” reducing deep water ventilation (Toggweiler, 1999). In either case, both scenarios would result in increased deep ocean carbon storage and reduced atmospheric  $p\text{CO}_2$ . Models suggest that increased summer sea ice in the Southern Ocean could lead to the observed increased influence of southern-sourced waters in the Atlantic basin during glacial intervals (Watson and Naveira Garabato, 2006; Ferrari et al., 2014). It is therefore possible that Southern Ocean sea ice extent

was a critical feedback mechanism resulting in lower  $p\text{CO}_2$  during glacial intervals through the MPT, via both increased ocean carbon storage and also reduced outgassing of  $\text{CO}_2$ .

After MIS 18, the  $\delta^{13}\text{C}$  changes between glacial and interglacial stages are associated with little change in  $[\text{PO}_4]$  but significant change in  $\Delta\text{CO}_3^{2-}$  (Figs. 1C, 1D, and 2). This indicates that the air-sea gas exchange effects are not simply temperature related; instead they likely reflect changes in  $\text{CO}_2$  invasion into or outgassing from the ocean. Following the establishment of the  $\sim 100$  k.y. glacial-interglacial cycles, the  $\delta^{13}\text{C}$  of the northern-sourced waters that bathe DSDP Site 607 during interglacial intervals increases (Fig. 1A). Our trace metal records (Figs. 1C–1E) suggest that this reflects an increase in interglacial North Atlantic-sourced water  $\delta^{13}\text{C}$  from MIS 15 onward, perhaps caused by reduced invasion of  $\text{CO}_2$  into the North Atlantic.

### CARBON CYCLE INFLUENCE ON 100 K.Y. ICE AGE CYCLES

We propose that carbon cycle feedbacks resulted in lower atmospheric  $p\text{CO}_2$  during glacial intervals across the MPT. Our records capture the increased storage of carbon in the

deep North Atlantic as southern-sourced waters displaced northern-sourced waters during glacial intervals across the MPT. The increased corrosivity of deep waters would have promoted enhanced seafloor dissolution of carbonate sediments, raising whole-ocean alkalinity and drawing down CO<sub>2</sub> (Boyle, 1988a). However, to explain the full amplitude of the glacial-interglacial δ<sup>13</sup>C cycles at DSDP Site 607 seems to require a change in the source water δ<sup>13</sup>C composition perhaps driven by air-sea gas exchange. We propose that an increase in glacial sea ice extent reduced CO<sub>2</sub> outgassing from upwelling waters in the Southern Ocean, lowering glacial pCO<sub>2</sub> further. The oceans “inhale” and “exhale” CO<sub>2</sub> on glacial-interglacial time scales. It seems that the feedback processes described here allowed the oceans to breathe more deeply through the MPT. We suggest that sea ice extent played an integral role in driving a lowering of glacial pCO<sub>2</sub> through the MPT, either directly or indirectly through a deep chemical divide mechanism. This may have allowed increased buildup of Northern Hemisphere ice, which persisted for longer, eventually heralding the onset of the ~100 k.y. ice age cycles.

#### ACKNOWLEDGMENTS

This work was funded by Natural Environment Research Council grant NE/I006427/1 grant to Lear, and a Deutsche Forschungsgemeinschaft grant to Dierker-Haass. We are extremely grateful to Kira Lawrence for providing some samples from DSDP Hole 607A and discussing the Site 607 age model and alkenone record. Anabel Morte-Rodenas provided invaluable laboratory assistance. This manuscript was greatly improved by three careful, anonymous reviewers, and we are grateful for the efficient editorial handling by editor Parrish.

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Manuscript received 13 July 2016

Revised manuscript received 26 September 2016

Manuscript accepted 28 September 2016

Printed in USA