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Letters

Glacial Southern Ocean freshening at the onset of the Middle Pleistocene Climate Transition

Laura Rodríguez-Sanz [a,*], P. Graham Mortyn [a,b], Alfredo Martínez-Garcia [c], Antoni Rosell-Melé [a,d], Ian R. Hall [e]

[a] Institute of Environmental Science and Technology (ICTA), Universitat Autònoma de Barcelona (UAB), Bellaterra 08193, Catalonia, Spain
[b] Department of Geography, Universitat Autònoma de Barcelona, Spain
[c] Geological Institute, ETH Zürich, Zürich 8092, Switzerland
[d] Institució Catalana de Recera i Estudis Avançats (ICREA), Pg. Lluís Companys 23, 08010 Barcelona, Catalonia, Spain
[e] School of Earth and Ocean Sciences, Cardiff University, Cardiff CF10 3AT, UK

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A B S T R A C T

Changes in Southern Ocean hydrography may have played an important role in the Middle Pleistocene Transition (MPT), particularly through their impact on ocean circulation and atmospheric CO_2 concentrations. Here we present foraminiferal Mg/Ca and $\delta^{18}O$ results for the subsurface dwelling planktonic foraminifer *Neogloboquadrina pachyderma* (sinistral) at the Ocean Drilling Program (ODP) Site 1090. Results are used to reconstruct upper ocean temperatures and derive seawater $\delta^{18}O$ in the Subantarctic Atlantic Ocean during the MPT. The new records indicate that, starting at ~1250 ka, glacial temperatures and local (ice volume corrected) seawater $\delta^{18}O$ in the upper water column of the Subantarctic Atlantic Ocean decreased, pointing to cooler (~2 °C) and fresher (~0.4‰) conditions than in the preceding glacial stages. These upper ocean hydrographic changes broadly coincide with the increase in the power of the 100 ky glacial–interglacial cycle in both records and with a shift towards decreased deep ventilation in the glacial Southern Ocean. Our finding suggests that an increase in Southern Ocean stratification, driven by the observed freshening of the upper water column, may have reduced the exchange of carbon between the deep Southern Ocean and the atmosphere during glacial stages. This process may have contributed, in combination with other mechanisms, to lower glacial atmospheric CO_2 concentrations during the MPT.

1. Introduction

During the Middle Pleistocene Transition (MPT), between 1250 and 700 ka (Clark et al., 2006), the periodicity of the glacial–interglacial cycles changed from 41 ky to a less frequent, more intense and asymmetric 100 ky rhythm (e.g., Park and Maasch, 1993; Mudelsee and Schulz, 1997; Schmieder et al., 2000; Clark et al., 2006). This fundamental climate reorganization apparently occurred in the absence of any considerable change in orbital forcing, leading to the concept that the MPT involved a change of the climate system's internal feedbacks (Clark et al., 2006), which has yet to be conclusively addressed.

Some of the hypotheses to explain the MPT invoke a decrease in atmospheric carbon dioxide concentrations (pCO_2) as the driving mechanism (Raymo et al., 1997; Paillard, 1998; Berger et al., 1999; van de Wal and Bintanja, 2009; Martínez-García et al., 2011). Currently available reconstructions indicate that glacial pCO_2 decreased by ~30 ppmv during the MPT, while interglacial pCO_2 levels remained relatively unchanged (Hönisch et al., 2009). A ~30 ppmv shift to lower glacial pCO_2 levels, likely in combination with other climate feedbacks (Clark et al., 2006), may have played an important role in the climate changes observed across the MPT, given the potentially higher climate sensitivity to pCO_2 for a glacial world compared to the present-day (van de Wal and Bintanja, 2009).

The Southern Ocean has been proposed as one of the key regions of the global ocean in modulating pCO_2 variations on glacial-interglacial timescales (Sigman and Boyle, 2000; Sigman et al., 2010 and references therein). In the modern Southern Ocean the efficiency of the biological pump to sequester carbon is limited by the scarcity of micro-nutrients, e.g., iron (Fe). Accordingly, an increase in Fe supply by eolian dust during glacial intervals would stimulate marine export production and enhance major nutrient consumption, contributing to the storage of respired CO_2 in the deep ocean (Martin, 1990). The increased export production in the Subantarctic Zone during glacials was closely coupled to changes in eolian Fe supply (Kumar et al., 1995; Kohfeld et al., 2005; Martínez-Garcia et al., 2009). However, modeling studies and

* Corresponding author. Tel.: +34 93 581 4554.
E-mail address: Laura.Rodriguez@uab.cat (L. Rodríguez-Sanz).

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paleoceanographic data suggest that Fe fertilization of the Subantarctic Zone can explain only a fraction of the complete glacial-interglacial pCO_2 fluctuations of the Late Pleistocene, and hence other mechanisms are required to explain the full amplitude of pCO_2 (90–100 ppmv) shifts (Watson et al., 2000; Kohfeld et al., 2005; Martínez-Garcia et al., 2009) that are observed in the Antarctic ice cores (e.g., Luthi et al., 2008).

The storage of respired CO_2 at depth in the polar Southern Ocean may be another important mechanism to sequester carbon in the deep ocean during glacial times (Toggweiler, 1999). This process may have been modulated by changes in the position of the westerly wind belt (Toggweiler et al., 2006), in the surface ocean stratification (Francois et al., 1997; Toggweiler, 1999), and in the latitudinal extension and temporal duration of the Antarctic sea-ice cover (Stephens and Keeling, 2000; Keeling and Stephens, 2001; Archer et al., 2003). Indeed, Antarctic sea-ice cover, westerly winds changes, and stratification of the Southern Ocean have been proposed as key factors to reduce the pCO_2, by physically inhibiting the CO_2 outgassing and by decreasing the vertical mixing of the water column in the Southern Ocean (Francois et al., 1997; Toggweiler, 1999; Stephens and Keeling, 2000; Sigman et al., 2004).

Various studies have provided evidence of major changes in deep water circulation roughly coincident with the onset of the MPT (Schmieder et al., 2000; Hall et al., 2001; Venz and Hodell, 2002; Hodell and Venz-Curtis, 2006) that might reflect an increase in water column stratification in the Southern Ocean (Hodell and Venz-Curtis, 2006). The enhanced sensitivity of the ocean density to salinity changes during glacial stages (Adkins et al., 2002; de Boer et al., 2008) implies that reconstructions of this physical property of ocean waters in the Southern Ocean are instrumental to accurately assess the impact of surface ocean hydrographic changes on ocean circulation and carbon storage. Indeed, upper ocean stratification in the Subantarctic Zone is a fundamental feature to be addressed in order to provide a causal mechanism for both deep Southern Ocean ventilation (Hodell and Venz-Curtis, 2006) and pCO_2 decreases (Hönisch et al., 2009) at the onset of the MPT and for the glacial stages across the transition and beyond.

Here we report continuous and highly resolved reconstructions of the upper ocean temperature and ice volume corrected oxygen isotope composition of ocean water ($\delta^{18}O_{SW\text{-}IVC}$) from the South Atlantic sector of the Southern Ocean (ODP Site 1090) spanning the entire MPT (1800–580 ka), based on paired Mg/Ca–$\delta^{18}O_C$ measurements on the polar planktonic foraminifer *Neogloboquadrina pachyderma* (sinistral) (*N. pachyderma* (s.)). These reconstructions provide new insights into the hydrography of the Subantarctic Zone of the Southern Ocean during the MPT, allowing their potential impact on the upper ocean stratification and deep Southern Ocean ventilation to be assessed, with implications for the evolution of the global carbon cycle and atmospheric pCO_2 across the MPT.

2. Material and methods

2.1. Sediment core location and chronology

Site 1090 was drilled during ODP Leg 177 (Gersonde et al., 1999) in the Subantarctic Zone (42°54.8′S, 8°54′E) on the northern flank of the Agulhas Ridge (Fig. 1a and b). At a water depth of 3702 m, the site is located at the interface between North Atlantic Deep Water (NADW) and underlying lower Circumpolar Deep Water (CDW). Due to its location, ODP Site 1090 is ideally suited to monitor past dynamics of the Polar Frontal Zone through the Pleistocene glacial-interglacial cycles (Gersonde et al., 1999). Sedimentation rates at the site are of the order of 3–4 cm ky^{-1} (Venz and Hodell, 2002), which implies that temporal resolution for the paleoceanographic records that we generated at this location is potentially high enough to resolve climate variability on orbital timescales (e.g., Venz and Hodell, 2002; Becquey and Gersonde, 2002; Martínez-Garcia et al., 2009). After inspection with an optical microscope we determined that overall the planktonic foraminifera used for analyses were well preserved and thus discarded dissolution-related artifacts in the interpretation of our records (see below). In this study we use the age model presented in Martínez-García et al. (2010), which was obtained by graphically correlating the benthic $\delta^{18}O$ record of ODP Site 1090 (Venz and Hodell, 2002) to the Lisiecki and Raymo (2005) benthic $\delta^{18}O$ global stack (hereafter LR04, Figs. 2a and 3a).

2.2. Foraminiferal Mg/Ca

We analyzed a total of 227 samples from the interval between 17.46 and 43.79 m composite depth, corresponding to an average temporal resolution of ~5 ky over the interval of 1800–580 ka. A minimum of 60 individuals of *N. pachyderma* (s.) from the 150–250 μm fraction were picked for each sample. *N. pachyderma* (s.) geochemical data most likely provide a reconstruction of the austral summer conditions in the upper 130 m of the water column (Mortyn and Charles, 2003; King and Howard, 2003; Fraile et al., 2009). We consider this species ideally suited for this study because (a) it is continuously abundant throughout the core. (b) the geochemistry and ecological preferences of *N. pachyderma* (s.) in the Southern Ocean are fairly well known (e.g. Mortyn and Charles, 2003; Nürnberg, 1995; Donner and Wefer, 1994; Hendry et al., 2009) and (c) considering the modern depth of the mixed-layer in the Southern Ocean (~100–200 m; e.g. Monterey and Levitus, 1997), *N. pachyderma* (s.) calcification depth is still shallow enough to faithfully record past changes in the upper water column.

In order to break open individual chambers, foraminiferal shells were gently crushed between methanol-cleaned glass microscope slides. Afterwards, samples were treated chemically, modifying slightly the cleaning procedures proposed by Barker et al. (2003). Briefly, foraminiferal samples underwent ultra-purified water (milli-Q water) and methanol rinses to remove clay. Then they were cleaned reductively (using anhydrous hydrazine) to remove Fe–Mn oxide coatings and oxidatively (using H_2O_2) to remove the organic matter. Prior to dissolution, samples were leached once with 0.001 M HNO_3 to remove any adsorbed contaminants (Barker et al., 2003).

Cleaned samples were dissolved in 1% HNO_3. An aliquot of the samples was analyzed using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Agilent model 7500ce) to provide a preliminary calcium [Ca^{2+}] determination. The remaining solutions were diluted to 40 ppm [Ca^{2+}] and then injected into the ICP-MS to obtain [Ca^{2+}], magnesium [Mg^{2+}], and other trace metal concentrations (Yu et al., 2005; de Villiers et al., 2002). Analytical precision was monitored calculating the relative standard deviation of two in-house standard solutions analyzed after every 5 samples containing Mg/Ca = 2.58 and Mg/Ca = 7.73 mmol mol^{-1} at a [Ca^{2+}] of 40 ppm. The relative standard deviation was on average 1.3% (N = 158). A commonly used limestone standard (ECRM752-1) with a specified Mg/Ca of 3.75 mmol mol^{-1} (Greaves et al., 2008) was also analyzed. Samples with Al/Ca and Mn/Ca above the commonly used thresholds (Boyle, 1983; Barker et al., 2003; Ferguson et al., 2008) were repeated. Those replicates that yielded significantly different values were disregarded, while those with consistently high (15 out of 227 samples) values were retained as they do not affect any of those features of the records upon which our conclusions are based.

The calibration equation proposed by Elderfield and Ganssen (2000) was selected for converting the *N. pachyderma* (s.) Mg/Ca values for Site 1090 into calcification temperatures. Although this calibration was obtained in the North Atlantic, it gives reasonable temperature values that agree best with both the modern