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Evolution of South Atlantic density and chemical stratification across the last deglaciation

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Explanations of the glacial-interglacial variations in atmospheric pCO\textsubscript{2} invoke a significant role for the deep ocean in the storage of CO\textsubscript{2}. Deep ocean density stratification has been proposed as a mechanism to promote the storage of CO\textsubscript{2} in the deep ocean during glacial times. A wealth of proxy data supports the presence of a "chemical divide" between intermediate and deep water in the glacial Atlantic Ocean, which indirectly points to an increase in deep ocean density stratification. However, direct observational evidence of changes in the primary controls of ocean density stratification, i.e. temperature and salinity, remain scarce. Here, we use Mg/Ca-derived seawater temperature and salinity estimates determined from temperature-corrected \(\delta^{18}O\) measurements on the benthic foraminifer \textit{Uvigerina} spp. from deep and intermediate water-depth marine sediment cores to reconstruct the changes in density of sub-Antarctic South Atlantic water masses over the last deglaciation (i.e. 22-2 ka before present). We find that a major breakdown in the physical density stratification significantly lags the breakdown of the deep-intermediate chemical divide, as indicated by the chemical tracers of benthic foraminifer \(\delta^{13}C\) and foraminifer/coral \(\delta^{14}C\). Our results indicate that chemical destratification likely resulted in the first rise in atmospheric pCO\textsubscript{2}, whereas the density destratification of the deep South Atlantic lags the second rise in atmospheric pCO\textsubscript{2} during the late deglacial period. Our findings emphasise that the physical and chemical destratification of the ocean are not be as tightly coupled as generally assumed.

The last glacial termination was accompanied by an 80 ppm rise in atmospheric pCO\textsubscript{2} (1, 2), and it is widely believed that this increase in pCO\textsubscript{2} was driven by processes occurring within the Southern Ocean (3–5). These Southern Ocean processes are proposed to have released CO\textsubscript{2} from the deep ocean through a combination of decreased nutrient utilisation (6), increased vertical mixing (7) and increased air-sea gas exchange (8). Geochemical records show evidence for an “old” (9) respired dissolved inorganic carbon pool in the glacial Southern Ocean below 2500m (10, 11) which became better ventilated over the course of the deglaciation (9, 12), supporting the idea that the deep ocean was isolated from the atmosphere during glacialis. Over the deglacial period this chemical stratification between the deep ocean and the overlying intermediate ocean decreased, e.g.(11), implying a change in circulation or ventilation within the Southern Ocean which enabled CO\textsubscript{2} to be upwelled and outgassed to the atmosphere (7). The chemical destratification of the ocean has been attributed either to (i) an increase in air-sea gas exchange, through a decline in the extent of sea ice (8) and/or a decrease in surface ocean stratification (13); or (ii) a breakdown in the density stratification between the poorly-ventilated deep ocean and the better-ventilated water masses above (14). Evidence supporting either scenario remains elusive. Pore-water profiles from deep ocean sediments have provided the first estimates of the density of the deep ocean during the Last Glacial Maximum (LGM) (15). These studies found that the glacial deep ocean was highly saline (~37 psu) and had an \textit{in situ} density that was 2 kg/m\textsuperscript{3} denser than modern deep water. These studies lend support to the hypothesis that CO\textsubscript{2} storage within a highly stratified glacial ocean played a significant role in driving lower glacial atmospheric pCO\textsubscript{2}. However, pore-water profiles only provide a ‘snap-shot’ of the physical properties of the deep ocean at the LGM, and do not provide information about the time-dependent changes in the density of deep water over the deglaciation. Thus, from these studies alone, it is impossible to assess whether the destratification of the deep ocean density gradients drove the atmospheric pCO\textsubscript{2} increase over the deglacial period.

Isotope-enabled intermediate complexity models have been used to suggest a mechanistic link between the physical (density) and chemical (\(\delta^{13}C\)) properties of the ocean over glacial-interglacial timescales (16, 17). These models suggest that deep ocean stratification, generated by the formation of dense brines during sea ice growth, is required to reconcile the spatial distribution of seawater \(\delta^{13}C\). This result implies that a decrease in Antarctic sea ice, and therefore reduced brine formation, over the deglacial period will affect both the density of the deep ocean and its chemical properties synchronously. Testing this hypothesis of a mechanistic link between the physical and chemical properties of the ocean requires observational evidence of the density structure evolution of the Southern Ocean over the entire deglacial period.

**Significance**

The cause of the rise in atmospheric pCO\textsubscript{2} over the last deglaciation has been a puzzle since its discovery in the early 1980s. It is widely believed to be related to changes in carbon storage in the deep ocean, but the exact mechanisms responsible for releasing CO\textsubscript{2} from the deep ocean reservoir, including the role of ocean density stratification remains an open question. Here we reconstruct changes in the intermediate-deep density gradient in the South Atlantic across the last deglaciation and find evidence of an early deglacial chemical destratification and a late deglacial density destratification. These results suggest that other mechanisms, besides deep ocean density destratification, were responsible for the ocean-atmosphere transfer of carbon over the deglacial period.

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Deglacial changes in the physical properties of the South Atlantic

Although the deglacial decrease in *Uvigerina spp.* δ¹⁸O is similar in both sites [Figure 2c], our Mg/Ca-derived temperature reconstructions [Figure 2b] suggest that the intermediate waters (GC528) were in fact cooler than the deep water (MD07-3076Q) for the majority of the glacial termination. This temperature inversion between the intermediate and deep sub-Antarctic reverses during the Early Holocene, from 9 ka onwards. It is physically impossible for cold intermediate water to overlie warmer deep water (even accounting for the effect of adiabatic decompression) and remain dynamically stable unless these differences are compensated by salinity.

We use the Mg/Ca-derived benthic temperatures and global sea level records (19) to deconvolve δ¹⁸O of foraminiferal calcite [Figure 2c] into its principal components (20), i.e. temperature and δw [Methods]. In order to extract the salinity component from δw (21), we express δw as an offset from the contemporaneous ‘global mean’ δw, hereafter referred to as δw-calc [Figure 2d], by subtracting the isotopic effect of melting continental ice using global sea level records (19). The isotopic effect of melting ice will have spatial and temporal variations which are masked in our subtraction of a ‘global mean’ δw, however, without transient tracer models to prescribe a regional ‘ice volume effect’, the offset from the contemporaneous global mean δw remains the best approximation of ice sheet melt-derived δ¹⁸O changes in the South Atlantic. Salinity is calculated from δw-calc assuming that the modern relationship between salinity and δw for the Southern Ocean (21) holds over the deglacial period. Recent isotope-enabled fully coupled GCM experiments have suggested that the salinity-δw relationship in the South Atlantic is more temporally constant than in other ocean basins (22) ruling out significant biases in our inferred salinity estimates due to potential variations in the salinity-δw relationship. However, brine rejection during the formation of sea ice increases salinity without fractionating oxygen isotopes; therefore, we suggest that salinity values derived from δw-calc are minimum estimates.

Here, we determine the deglacial evolution of the intermediate-deep density gradient in the high-latitude South Atlantic Ocean by generating temperature and salinity proxy records over the last 20 ka at the intermediate depth site of sediment core GC528 (598m; 58°02.43′W, 53°00.78′S) and the deep site of core MD07-3076Q (3770m; 14°13.7′W, 44°09.2′S) in the sub-Antarctic Atlantic [Figure 1]. We make the assumption that geochemical changes at a given depth occur synchronously within the South Atlantic (see Supporting Information). Combined Mg/Ca and δ¹⁸O measurements on the benthic foraminifer *Uvigerina spp.* are used to estimate benthic seawater temperature (18) and to calculate the δ¹⁸O of deep and intermediate water masses (hereafter referred to as δw). Temperature and δw (closely related to seawater salinity) are combined to produce a continuous record of the evolution of the density gradient in the South Atlantic over the last deglaciation (Methods). We compare the evolution of the density gradient with benthic δ¹³C and δ³⁴S records from the two sites in order to assess the hypothesis of a causal link between the physical and chemical properties of the deglacial ocean.

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The difference in intermediate water salinity between the LGM and the Holocene is small (Figure 2d) as most of the deglacial $\delta^{18}O$ Uvigerina spp. variation can be accounted for by warming. By contrast, the deep water site (MD07-3076Q) was relatively saline (36-37 psu) during the glacial period and salinity decreased by 3-4 psu during the late deglacial (12-9 ka).

Using the Mg/Ca-derived benthic temperatures and our estimates of minimum salinity we calculate the in-situ density of the intermediate and deep site according to the equation of state (23) (Figure 2e). We find good agreement between our density estimates for the Holocene and modern South Atlantic density measurements (Figure 2e). The deglacial density reconstructions indicate the presence of a strong density gradient between intermediate and deep water for the glacial and much of the deglacial period. This density gradient decreases dramatically from 12 ka, and by 10 ka the deep ocean is 2 kg/m$^3$ less dense than at the LGM. Our Mg/Ca-$\delta^{18}O$ derived deep ocean LGM salinities are broadly consistent with previous porewater based estimates (15) (Figure 3). Although both reconstructions carry substantial uncertainty (24) (Supplementary material), the convergence of two independent methods strengthens our confidence in both approaches. Prior to 12 ka the high salinity of the deep water site implies a strong density gradient, despite the temperature inversion of cool intermediate waters overlying warmer deep water. After 10 ka the salinity stratification has broken down, and a weaker density gradient is maintained by the temperature difference between intermediate and deep water. Provided the assumption of zonal seawater density continuity across the sub-Antarctic Atlantic holds true, our findings signal a significant mode switch in the primary physical parameters that govern ocean density stratification in the southern high-latitudes through the last deglaciation.

**Processes controlling the physical properties of water masses over the deglaciation**

To determine the factors affecting the variability in the physical properties of deep and intermediate water masses over the deglaciation, we compare glacial water mass temperature and $\delta_{\text{w,ic}}$ properties with those of water masses present in the Southern Ocean today (Figure 3). Comparison of intermediate LGM temperature-$\delta_{\text{w,ic}}$ with modern measurements of seawater temperature and $\delta_{\text{w}}$ suggests that LGM intermediate water was analogous to modern Antarctic Surface Water (AASW), which is characterised by near freezing temperatures (Figure 3). Such low temperatures suggest that the source location of intermediate water was strongly influenced by sea ice (which forms from seawater with a temperature of -2°C). Glacial sea ice reconstructions using diatom transfer functions (25, 26) predict that winter sea ice could have extended as far north as 57°S at this longitude. We therefore suggest that glacial intermediate water masses at GC528 reflect the cold and fresh signature of surface waters close to the winter sea ice edge that is influenced by seasonal sea ice meltwater. This is in stark contrast to modern intermediate water at GC528,
which is strongly influenced by a modified component of upwelled Circumpolar Deep Water (27) (Figure 3).

The processes controlling the benthic temperature of the deep site are more complex. Deep water formed close to the sea ice margin can only gain heat in two ways; (i) through mixing with other, warmer water masses, and (ii) through the accumulation of geothermal heat in the deep sea. The most probable warm water masses that can mix with sinking southern-sourced waters during the LGM are Drake Passage through flow waters from the Pacific. Although it has been shown that Pacific deep water was not significantly warmer than freezing (18, 28), it remains to be determined whether Pacific intermediate waters were significantly warmer and had an influence on southern-sourced deep water in the Atlantic. Alternatively, the source of warmth in the deep South Atlantic may be derived from the accumulation of geothermal heat, assuming that the deep ocean is stagnant and cannot lose heat to the surface (29). It has been shown by a conceptual model that it would take 10kyr to heat 2km of seawater by 2°C, based on a heat flux of 500mW/m² (29). Both of these processes may have potentially accounted for the observed warmth of the salty LGM deep water in the South Atlantic. However, an analysis of whether a completely stagnant and isolated deep water pool is physically possible or whether it was significantly influenced by Pacific inflow waters goes beyond the scope of this study.

The deglacial evolution of deep water temperature and δw,ice (Figure 3) can be understood by invoking a combination of (i) changes in the northern versus southern mixing ratio and (ii) changes in the end-member δ18O of Antarctic Bottom Water (AABW). In the modern Atlantic Ocean, saline North Atlantic Deep Water (NADW) overlies fresh AABW (Figure 1). The high δ18O signature of NADW reflects high rates of evaporation at the surface, whereas the δ18O of AABW is comparatively more negative (30). The warming and increase in δw,ice over much of the deglaciation (16-12 ka) may indicate a greater proportion of northern-sourced water at MD07-3076Q. This is supported by benthic foraminifer εNd data that suggests an increasing contribution of northern-sourced water in the South Atlantic throughout the deglaciation (31). The late deglacial change in deep water δw,ice to isotopically lighter values after 12ka is likely driven by a change in the mode of AABW formation. The two different modes of southern-sourced deep water formation, i.e. brine rejection during sea ice formation and super-cooling of Ice Shelf Water (ISW) beneath the Antarctic ice shelves (32), impart very different signals on δw,ice. Brines have a δ18O signature close to surface water values (~0‰ in the Southern Ocean), whereas ISW has a negative δ18O signature reflecting incorporation of overlying ice shelf meltwater. We would argue that the marked decrease in the δw,ice of deep water at 12 ka is related to an increasing contribution of ISW constituting AABW. This change may be associated with a retreat in the grounding line of Weddell Sea ice shelves and an intrusion of relatively warm modified northern-sourced water under the ice shelves, further melting the marine-terminating ice sheets around Antarctica (33). In summary, the modes of intermediate and deep water formation have a profound impact on the density structure of the sub-Antarctic ocean.

The link between the physical and chemical properties of the South Atlantic and atmospheric pCO2

In order to assess the hypothesis of a causal link between the physical and chemical properties of the ocean, we compare the timing of changes in the breakdown of the density gradient with changes in benthic foraminifer δ13C and foraminifer/coral benthic-atmospheric 13C ages at both core locations (Figure 4). Benthic foraminifer δ13C at the intermediate water site (GC528) was more positive than the δ13C of the deep site (MD07-3076Q; (34)) at the LGM (Figure 4b). This large δ13C gradient breaks down over the deglaciation (15-10 ka) resulting in relatively homogeneous δ13C values at both sites during the Holocene. Foraminifer/coral benthic-atmospheric 13C age offsets between intermediate (Burdwood Bank (12), Chile Margin (35)) and deep water (MD07-3076Q (9)) are broadly consistent with the δ13C record (Figure 4c). These two records provide strong support for glacial chemical stratification, which subsequently breaks down relatively early in the deglaciation.

Comparison of the deglacial density records (Figure 4d) and the chemical δ13C and 14C records (Figure 4b-c), shows a marked difference in the timing of the breakdown of density and chemical gradients. In the deep site, both the δ13C and 14C records begin to change in early in the deglaciation (17-15 ka), and in the case of the foraminiferal 14C record, these early decreases in the benthic-atmospheric 14C age have been linked to a synchronous rise in atmospheric CO2 (9). However, there is no concomitant change in the intermediate-depth density gradient at this time (Figure 4d). The onset of the physical destratification occurs during the Early Holocene (~10 ka), and appears to lag the late deglacial rise in atmospheric pCO2. Our proxy records suggest that (i) changes in ocean chemistry in the South Atlantic occur without large-scale reorganisation of the ocean’s density structure, challenging the propositions of a close coupling between physical and chemical ocean stratification as suggested by intermediate complexity models (17), and (ii) the density destratification of the South Atlantic could only have impacted atmospheric pCO2 during the late deglaciation.

CO2 stored in the deep ocean can be impeded from being released back to the atmosphere by two physical processes; (i) via an increased residence time of deep water masses in the ocean interior, through an increase in deep ocean stratification acting as a lid to deep carbon (7); or (ii) reduced efficiency of air-sea gas exchange in the regions of deep mixing and upwelling (8). We suggest that during the LGM, both of these processes will have contributed to lower atmospheric pCO2, owing to increased density stratification in the Southern Ocean and because permanent sea ice (8) and/or shallow stratification (13, 36) acted as a barrier preventing CO2 from escaping the surface of the Southern Ocean. Indeed, it is plausible that the retreat of sea ice during the early deglaciation (26, 37) effectively removed a barrier to air-sea exchange, and thus contributed to the increase in atmospheric pCO2 through enhanced ventilation of the deep overturning cell (9, 31). The hypothesis of an early retreat in the extent of Antarctic sea ice is also supported by the warming trend observed in GC528 at 17-15ka [Figure 2b]. However the retreat of sea ice cover in the South Atlantic might not have had a significant effect on the density difference between the intermediate and deep overturning cells because the mode of deep water formation did not change, which is controlled by the position of the grounded ice sheet relative to the continental shelf break. Although the geological evidence for the position of the grounding line in the Weddell Sea is inconsistent (38), there is indication that, at least around the Antarctic Peninsula, the grounding line retreat occurred late in the deglaciation (39, 40). Thus the glacial brine-dominated mode of southern-sourced deep water formation may have persisted until as late as 10 ka. In summary, we argue that changes in the extent of permanent sea ice may occur earlier than changes in the maximum position of the grounded icesheets, thus it is possible to ventilate the deep ocean without decreasing its density.

Over the deglacial period (17-11ka), increasing deep ocean temperatures [Figure 2b] coupled with a 0.6‰ increase in benthic foraminifer δ13C (34) (Figure 4b) is indicative of a greater proportion of northern-sourced water in the deep South Atlantic.
The impinging of warm modified northern-sourced water on the Antarctic continental shelf has been suggested as a possible mechanism (33) which could melt back the grounded ice sheets in the Weddell Sea, freeing shelf space for the formation of ISW, resulting in the observed decrease in deep ocean density stratification at 10ka. Whilst a decrease in the density of deep water has been invoked to explain the deglacial rise in atmospheric pCO₂, via associated changes in the rate of diapycnal mixing and the vertical position of the isopycnal separating the two overturning branches of circulation (16, 17, 41), we suggest that its impact is relatively minor compared to the impact of changes in the rate of air-sea gas exchange in the Southern Ocean. However, it should be noted that vertical shifts in the position of the main pycnocline (41) cannot be resolved in this study, thus it remains to be determined whether these changes play a more important role in regulating atmospheric CO₂.

Although density destratification of the South Atlantic does not appear to play a leading role in regulating atmospheric pCO₂ we propose that density destratification may have been instead important in ‘locking in’ the incipient transition to an interglacial climate state. Prior to the destratification event, the ocean was able to return to its ‘glacial regime’ following a transient perturbation; but not afterwards. We suggest that the density destratification of the South Atlantic, initiated by a change in mode of formation of deep water, acted as a ‘flip switch’, eliminating the ocean’s ability to re-stock its CO₂ inventory at the expense of the atmosphere, and thus forcing climate to switch to an interglacial state. Longer records of the density gradient within the Southern Ocean are required to test this hypothesis.

Conclusion

This study provides the first deglacial record of density changes in the deep and intermediate South Atlantic spanning the last deglaciation. We find that the intermediate ocean was significantly colder than deep waters at the LGM, and this temperature inversion requires that ocean stability is maintained by salinity gradients. We suggest that the physical properties of the glacial South Atlantic were regulated by an increase in Antarctic sea ice extent, which resulted in colder surface waters in the sub-Antarctic, but also led to deep waters being primarily formed through the creation of brines as opposed to super-cooling of ISW. Over the deglaciation, intermediate water warmed in response to a retreat in the Antarctic sea ice margin, and the deep South Atlantic started to reflect both a greater proportion of northern-sourced water but also isotopically lighter AABW from the incorporation of Antarctic ice sheet meltwater. A rapid change in the dominant mode of deep water formation at the onset of the Holocene, from brines to super-cooled ISW, likely resulted in the density destratification of the intermediate-deep ocean during the late deglacial period.

Our density records also enable us to address the question of whether deglacial changes in ocean chemistry are driven by a breakdown in the deep ocean density stratification. We find that the greatest intermediate-deep change in benthic foraminifer δ¹³C and foraminifer/coral δ¹⁴C occurs prior to the density destratification. We suggest that this chemical destratification was driven by an increase in air-sea gas exchange which ventilates the deep overturning cell without affecting its density. The late deglacial breakdown in the density gradient of the South Atlantic occurs at the onset of the Holocene, suggesting deep ocean density destratification did not play a leading role in driving the deglacial rise in atmospheric pCO₂. The difference in the timing of the breakdown of the intermediate-deep chemical gradient compared to the breakdown of the intermediate-deep physical density gradient suggests that chemical and physical stratification is not be tightly coupled as previously inferred. This also raises the interesting possibility that the density destratification of the South Atlantic, induced by a change in the mode of deep water formation, could act as the ‘flip switch’ resulting in the transition to a full interglacial state.

Methods

Materials

Core GC528 [53.01°S, 58.04°W, 598mbsl] was collected on the cruise JR244 of the RRS James Clark Ross. Located on the Falkland Plateau, this core is situated close to the main inflow of AAIW into the Atlantic basin.

Core MD07-3076Q [44° 09.2'S 14° 13.7'W, 3770mbsl] was retrieved from the eastern flank of the mid-ocean ridge. The age model is based on reservoir-age corrected radiocarbon measurements on monospecific planktonic foraminifera and is described fully in ref. (36).

Age model (GC528)

The age model for GC528 (Supporting Information) was generated using 25 radiocarbon dates of monospecific samples of Uvigerina bifurcata (>125μm size fraction, 2-6mg), which were graphitised in the Godwin Laboratory for Palaeoclimate Research, University of Cambridge (hereafter, GLPR) using the hydrogen and iron catalyst method (42) and subsequently analysed at the 14Chrono Centre at the Université de Byzelf by Accelerator Mass Spectrometry. 5 of the 25 samples were graphitised and analysed by BetaAnalytic, no inter-lab offset between samples was found. Carbon-14 ages were calibrated using Bacon age-modelling software (43) with the Marine13 dataset (44).

Reservoir age constraints were taken from paired U-Th/¹⁴C ages in corals(12) after 16ka, prior to 16ka a constant reservoir age of 1.36±0.4kyr (the age of the oldest U-Th/¹⁴C dated coral analysed by Burke et al. (12)) was applied downcore.

Sample Preparation

In GC528, samples of Uvigerina spp. (212-315μm size fraction) were hand-picked, cleaned using the methodology of ref. (45) and split, with ~100ug used for oxygen and carbon isotope and ~400ug for trace element geochemistry were analysed at the GLPR.

In MD07-3076Q, samples of Uvigerina spp. (212-315μm size fraction) were hand-picked and ~3 whole specimens were used for stable isotope analysis, and 10-15 whole specimens were cleaned for Mg/Ca analysis using the methodology of ref. (45).

Oxygen and stable carbon isotopes

Stable isotopes from GC528 were analysed using a MultiCarb prepara-
tion system coupled to a VG SIRA Mass Spectrometer in the GLPR. Measurements of δ¹⁸O and δ¹³C were determined relative to the Vien-
na Peedee Belemnite (VPDB) standard with an analytical precision of ±0.08‰ for δ¹⁸O and ±0.06‰ for δ¹³C. δ¹⁸O was measured on Uvigeri-
na spp. and δ¹³C was measured on Oriddorsalis umbonatus and correct-
ed to equilibrium calcite by +1.0‰ (46). Although O.umbonatus is a shallow infraunal species, the δ¹³C O.umbonatus correlation with coral ¹⁴C trends from intermediate water (12, 35) suggests that there has been no bias in the overprinting of bottom water δ¹³C by porewaters. Stable isotopes from MD07-3076Q, were analysed at the Laboratoire des Sciences du Climat et de l’Environnement, Gif sur Yvette. The mean external reproducibility of the carbonate standard is ±0.05‰ for δ¹³C and ±0.03‰ for δ¹⁴C. δ¹³C was measured on Uvigerina spp. and δ¹³C was measured on Cibicides kullenbergi (34).

Trace metal analysis

Mg/Ca elemental ratios were determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (47). Long-term instrumental preci-
sion of element ratio data, determined by replicate analyses of a standard solution was ±0.46‰, translating into an uncertainty of 0.06°C.

Bottom water carbonic ion concentration has been previously sug-
gested (48) to affect Mg/Ca values in some benthic foraminifera spe-
cies. Deglacial variation in carbonic ion concentration may exert an effect on Mg/Ca which is unrelated to changes in bottom water tem-
perature, particularly at the deep site (MD07-3076Q) where carbonate ion concentrations are lower. However, recent studies (e.g. 18) show
that *Uvigerina* spp. Mg/Ca (in particular) is very insensitive to changes in the carbonate ion concentration.

**Mg/Ca-derived benthic temperatures**

Mg/Ca values were converted into benthic temperatures using the new calibration curve (Supplementary Information): Mg/Ca = (0.0915 ± 0.005)T + (0.843 ± 0.035) R² = 0.92

10% uncertainty in the temperature estimate of each sample is ±0.7°C (Supplementary Information).

**Seawater δ¹⁸O offset from the contemporaneous ‘global mean’ seawater δ¹⁸O (δ¹⁸Oice)**

Seawater δ¹⁸O (∆w) is calculated from the Mg/Ca-derived benthic temperature and the δ¹⁸O of foraminiferal calcite using the linear form of the palaeo-temperature equation of ref. (20):

T = 16.9 – 4.0(∆w – ∆s)

This calibration produces good agreement between modern measurements of ∆s and the calculated core top δ¹⁸O.

To make a comparison to modern seawater values, the contemporaneous ‘global mean’ seawater δ¹⁸O, sometimes referred to as ‘ice-volume effect’, was removed assuming a linear relationship (21) between sea level (19) and δ¹⁸O of seawater. Site-specific deviations from the global mean that would result in a synchronous breakdown of the physical and chemical gradients in the South Atlantic require changes in ∆s in MD07-3076 5kyr earlier than the global mean, which is not supported by regional δ¹⁸O stacks (49). 1σ uncertainty in ∆s in each sample is ±0.35‰.

**In-situ density of seawater (ρ)**

The modern linear relationship between salinity and ∆s in the Southern Ocean (21) is assumed to hold across the deglacial period (Supporting Information). In-situ density was calculated from salinity and benthic temperature, using the equation of state (23).

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