South Atlantic intermediate water mass geometry for the last glacial maximum from foraminiferal Cd/Ca

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[1] Paleoceanographic studies using benthic foraminiferal Cd as a nutrient tracer have provided a robust means of reconstructing glacial Atlantic Ocean water mass geometry, but a paucity of data from the South Atlantic above 1200 m has limited investigation of Antarctic Intermediate Water (AAIW) configuration and formation. A new Cd depth profile from Brazil margin sediments suggests that AAIW penetrated northward at 1100 m to at least 27°S in the glacial Atlantic. It exhibited substantially reduced $\delta^{13}C_{as}$ values, confirming preliminary evidence that this AAIW was unique to the glacial Atlantic and that it formed differently than today, with less atmospheric contact.

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1. Introduction

[2] Decades of paleoceanographic research using benthic foraminiferal nutrient proxies have produced a well-resolved picture of Atlantic Ocean water mass structure during the last glacial maximum (LGM), especially with regard to deep water masses (>2000 m), allowing interpretation of past circulation patterns [e.g., *Curry and Oppo*, 2005; *Marchitto and Broecker*, 2006; *Lynch-Stieglitz et al.*, 2007]. However, a current lack of benthic foraminiferal Cd depth transect studies for the shallow and intermediate South Atlantic (<1250 m) confounds interpretation of altered AAIW circulation and formation. AAIW, which is formed in the Antarctic Polar Frontal Zone and is widely distributed in southern hemisphere oceans [e.g., *Lynch-Stieglitz et al.*, 1994], is an important component of global ocean circulation and serves as an indirect supply for formation of North Atlantic Deep Water (NADW) [*Gordon*, 1986]. It is also considered to have played a strong role in the balance between northern and southern sourced intermediate and deep waters in the Atlantic Ocean over glacial-interglacial time scales [*Zahn and Stüber*, 2002; *Rickaby and Elderfield*, 2005; *Pahnke et al.*, 2008]. Using Brazil margin sediments, we provide the requisite LGM Cd depth profile for constraining the depth and distribution of AAIW, as well as its mechanism of formation, allowing investigation of the upper arm of Atlantic meridional overturning circulation under glacial climate boundary conditions.

[3] Marine sediment cores were collected from the Brazil margin (cruise KNR 159–5) between water depths of 441 and 1627 m and latitudes of 27°42′S and 26°23′S (Table 1). Presently, AAIW, which is a cold, fresh, and nutrient-rich water mass, is centered at about 1000 m in the study area and overlies NADW (Figure 1). Above AAIW in the water column is warm and saline South Atlantic Central Water (SACW), which has a lower nutrient content. Ocean circulation and the water masses overlying the Brazil margin were markedly different at the LGM. The bathymetric extent of NADW was reduced, with the resultant shoaled water mass recharacterized as Glacial North Atlantic Intermediate Water (GNAIW), allowing for deep water of southern origin to penetrate farther northward [e.g., *Boyle and Keigwin*, 1982; *Oppo and Fairbanks*, 1987; *Curry et al.*, 1988; *Marchitto et al.*, 1998]. *Oppo and Horowitz* [2000] used paired benthic foraminiferal Cd and $\delta^{13}C$ results to reconstruct LGM intermediate and deep water mass (1268–2438 m) structure on the Brazil margin, but with sediments that lay below the core of AAIW. Further investigation using $\delta^{13}C$ alone suggested the presence of AAIW at 1000 m [*Curry and Oppo*, 2005], but productivity and air/sea gas exchange effects on seawater carbon isotopic composition merit further study with the Cd nutrient tracer. We provide these results, which when paired with the previously generated $\delta^{13}C$ data allow investigation of the carbon isotopic signature due to air/sea exchange of CO_2 ($\delta^{13}C_{as}$), thus contributing an additional water mass tracer that can be used to infer a change in AAIW formation at the LGM.

2. Nutrient Proxies

[4] Measurements of Cd/Ca in foraminifera tests were used to infer the nutrient content of the seawater in which calcification occurred [e.g., *Boyle*, 1992; *Lynch-Stieglitz et al.*, 1996; *Oppo and Horowitz*, 2000], and sediment samples from different depths across the Brazil margin allowed reconstruction of overlying water masses. Marine photosynthetic activity and remineralization of organic carbon give rise to an inverse relationship between $\delta^{13}C$ of dissolved inorganic carbon and PO_4 in seawater [*Broecker and Peng*, 1982], while a positive correlation is observed between Cd and PO_4, although the

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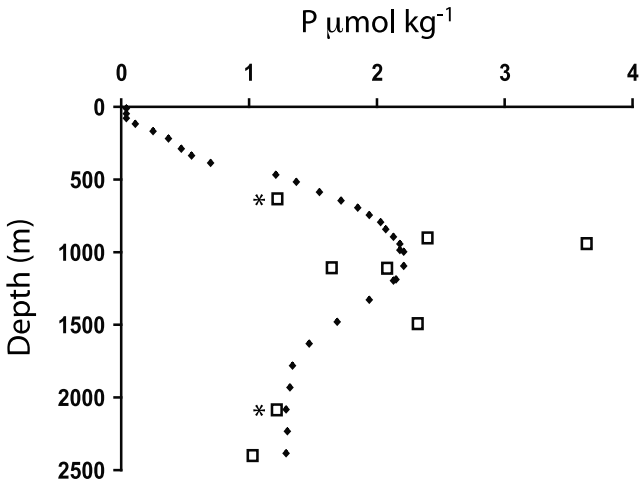

Figure 1. Phosphate abundance estimates from near core top benthic foraminifera (open squares) compared to seawater measurements (black diamonds) from GEOSECS Station 57 [*Bainbridge*, 1981]. AAIW is characterized by its elevated nutrient content. Data with poor reproducibility (RSD > 20%) are marked with an asterisk.

reasons for the latter relationship are not as well understood [e.g., *Boyle*, 1988]. We assume that these relationships were also valid at the LGM and whole ocean inventories of PO_4 and Cd did not vary since [*Boyle*, 1988].

[5] Although the Cd/Ca signal we interpret is entirely due to nutrient cycling, only part of the $\delta^{13}C$ signal is; the rest is due to temperature-dependent isotopic fractionation during air/sea exchange of CO_2 [e.g., *Lynch-Stieglitz et al.*, 1996]. Air/sea exchange at cold temperatures produces ^{13}C enrichment in seawater, while warmer temperatures lead to isotopic depletion and reduced $\delta^{13}C_{as}$ values [*Mook et al.*, 1974]. Additionally, increases in wind strength at the sea surface result in increased $\delta^{13}C_{as}$. Knowing the Cd and $\delta^{13}C$ content of a water mass, and assuming no change in the Redfield ratio of organic material, enables calculation of $\delta^{13}C_{as}$ using the equations of *Lynch-Stieglitz et al.* [1996]: $\delta^{13}C_{as} = \delta^{13}C_{foram} + 2.75*Cd_W - 2.0$ for the Holocene, and $\delta^{13}C_{as} = \delta^{13}C_{foram} + 2.375*Cd_W - 1.46$ for the LGM ($PO_4 > 1.34$ mmol kg^{-1}). *Marchitto and Broecker* [2006] provide the following adjusted equations for $PO_4 < 1.34$ mmol kg^{-1}: $\delta^{13}C_{as} = \delta^{13}C_{foram} + 5.29*Cd_W - 2.7$ (Holocene) and $\delta^{13}C_{as} = \delta^{13}C_{foram} + 4.57*Cd_W - 2.05$ (LGM). The LGM equations reflect a 4% increase in total inorganic carbon, an organic matter $\delta^{13}C$ increase of 2.0‰, and a 0.3‰ whole ocean $\delta^{13}C$ decrease. The $\delta^{13}C_{as}$ signature of water masses is considered to be a conservative property and can be used as a water mass tracer, providing there was no atmospheric contact after formation.

3. Methods

[6] Brazil margin sediments deposited during the LGM were identified using existing benthic foraminiferal $\delta^{18}O$ stratigraphic records, and samples intended for Cd/Ca analysis were selected from the shallowest points in each core with glacially enriched isotopic values and viable foraminifera tests. The $\delta^{18}O$ and $\delta^{13}C$ results of *Oppo and Horowitz* [2000] and *Curry and Oppo* [2005] were used to identify LGM samples and, along with the Cd/Ca results generated here, to calculate $\delta^{13}C_{as}$. Stratigraphic isotopic records for core 95 JPC (Table 1) are not included in *Curry and Oppo* [2005], but a foraminiferal radiocarbon age of 21.8 ka in an overlying sediment sample confirms our selection of glacial age sediments in this core.

[7] Cd/Ca and Mn/Ca were determined in several species of benthic foraminifera. *Hoeglundina elegans* were used when present and apparently unaffected by dissolution. In their absence or when *H. elegans* exhibited dissolution features such as pitting, *Cibicidoides pachyderma* or *Uvigerina* spp. were selected based on availability and condition (Table 1). Each sample consisted of 5–8 specimens, which were crushed to open all chambers and then cleaned according to the procedure of *Boyle and Keigwin* [1985] with the oxidative and reductive steps reversed [*Boyle and Rosenthal*,

Table 1. Brazil Margin Sediment Cores Used in This Study and LGM Sample Analytical Results

Core	Latitude (°S)	Longitude (°W)	Depth[a] (m)	Sample Depth (cm)	Foraminifera	Cd/Ca	Cd_W (nmol kg^{-1})	$\delta^{13}C$[b] (‰)	$\delta^{13}C_{as}$[c] (‰)
14 GGC	26°40.84′	46°26.92′	441	168.5	*Uvigerina* spp.	0.033	0.25	1.03	0.14
14 GGC	26°40.84′	46°26.92′	441	176.5	*Uvigerina* spp.	0.014	0.11	1.07	−0.50
137 JPC	26°41.39′	46°20.65′	462	56.5	*Uvigerina* spp.	0.019	0.15	1.31	−0.06
10 GGC	26°28.86′	45°55.64′	630	100.5	*C. pachyderma*	0.030	0.23	1.03	0.03
99 GGC	27°22.15′	46°50.63′	790	80.0	*C. pachyderma*	0.037	0.29	0.50	−0.27
153 JPC	26°23.47′	45°41.69′	898	40.5	*C. pachyderma*	0.048	0.37	0.46	−0.12
38 JPC	27°15.97′	46°37.90′	936	32.5	*H. elegans*	0.048	0.48	0.54	0.22
38 JPC	27°15.97′	46°37.90′	936	40.5	*H. elegans*	0.053	0.53	0.50	0.30
90 GGC	27°21.00′	46°37.89′	1105	144.5	*H. elegans*	0.061	0.61	0.38	0.38
105 JPC	27°21.00′	46°37.79′	1108	48.0	*C. pachyderma*	0.077	0.59	0.36	0.30
105 JPC	27°21.00′	46°37.79′	1108	40.0	*C. pachyderma*	0.062	0.48	0.26	−0.06
36 GGC	27°15.16′	46°28.22′	1268	148.0	*H. elegans*	0.042	0.42	0.53	0.06
36 GGC	27°15.16′	46°28.22′	1268	152.0	*H. elegans*	0.042	0.42	0.64	0.17
95 JPC	27°31.64′	46°33.15′	1485	24.5	*H. elegans*	0.036	0.36	0.86	0.24
17 JPC	27°41.83′	46°29.64′	1627	64.0	*H. elegans*	0.020	0.20	0.92	−0.22

[a]Not corrected for reduced LGM sea level.
[b]From *Oppo and Horowitz* [2000] and *Curry and Oppo* [2005].
[c]Determined using the LGM equations of *Lynch-Stieglitz et al.* [1996] and *Marchitto and Broecker* [2006], which include whole-ocean $\delta^{13}C$ corrections.

Table 2. Brazil Margin Holocene Sediment Analytical Results

Core	Depth (m)	Sample Depth (cm)	Foraminifera	Cd/Ca	Cd_W (nmol kg^{-1})	$\delta^{13}C$[a] (‰)	$\delta^{13}C_{as}$[b] (‰)
10 GGC	630	0.5	*C. pachyderma*	0.031	0.24[c]	1.56	0.12[c]
152 GGC	899	0.5	*C. pachyderma*	0.092	0.71	1.39	1.34
37 GGC	938	0.5	*C. pachyderma*	0.157	1.21	1.39	2.70
90 GGC	1105	0.5	*C. pachyderma*	0.053	0.41	1.27	0.39
105 JPC	1108	0.0	*Uvigerina* spp.	0.076	0.58	1.11	0.71
94 GGC	1490	0.0	*C. pachyderma*	0.108	0.68	1.10	0.96
33 GGC	2082	8.5	*C. pachyderma*	0.050	0.24[c]	1.11	−0.34[c]
73 GGC	2397	0.0	*C. pachyderma*	0.038	0.16	1.08	−0.77

[a]Holocene results from *Oppo and Horowitz* [2000] and *Curry and Oppo* [2005]. $\delta^{13}C$ results are not from the same samples in which Cd was measured (and in some cases are from different cores within 77 m water depth).

[b]Determined using the modern seawater equations of *Lynch-Stieglitz et al.* [1996] and *Marchitto and Broecker* [2006]. Holocene $\delta^{13}C_{as}$ values are considered estimates because $\delta^{13}C$ results are not from the same samples in which Cd was measured.

[c]These Cd results exhibited RSDs > 20% and are thus likely erroneous. $\delta^{13}C_{as}$ values calculated from these results are similarly considered invalid.

1996]. Cd, Mn, and Ca abundance analyses were performed on a Hitachi Z8200 atomic absorption spectrophotometer (AAS) with tandem flame and graphite furnace. Mn/Ca was measured to assess the presence of manganese carbonate overgrowths, which may contain contaminating Cd [*Boyle*, 1988]. No samples were rejected on this basis because the greatest Mn/Ca ratio observed was 74.1, which is within the chosen acceptable limit of 100.

[8] Three consistency standards with different Cd/Ca values were also analyzed (n = 2) in order to assess the precision of the AAS graphite furnace measurements. For decreasing Cd/Ca values, relative standard deviations (RSDs) of 8.38, 4.93, and 1.89% were obtained for these standards, although these external precision estimates may not be meaningful because all of the LGM data resulted from a single AAS run. Consistency standard results are specific to this investigation but are comparable to prior laboratory values. Two Cd/Ca measurements were performed for each dissolved foraminifera sample and the results were averaged. Duplicate samples with an RSD > 20% were rejected. The Cd content of the seawater in which the foraminifera grew (Cd_W) was calculated from the Cd/Ca results by applying a depth-dependent Cd distribution coefficient for calcitic foraminifera (*C. pachyderma* and *Uvigerina* spp.) according to the procedure of *Boyle* [1992]. No depth correction was necessary for *H. elegans*, which is aragonitic and exhibits a distribution coefficient of 1 [*Boyle et al.*, 1995]. For consistency, none of the LGM data from this investigation and others that we present here has been depth-corrected for sea level change.

4. Results and Discussion

4.1. Core Top Calibration

[9] Benthic foraminiferal Cd/Ca was determined for near core top sediment samples from most of the coring sites used in this study (Table 2) in order to ensure that estimates of seawater Cd abundance derived from our approach accurately reflect water column nutrient composition. Resultant Cd_W values were converted to estimates of phosphate abundance using the relationship determined by *Boyle* [1988] for P > 1.3 mmol/kg, and were compared to seawater PO_4 (Figure 1) measured at nearby (23°S, 35°W) GEOSECS Station 57 [*Bainbridge*, 1981]. Foraminiferal results are generally in good agreement with the seawater nutrient measurements, with the exception of elevated P abundance in the 938 m core, which may have been caused by localized sedimentary processes related to organic matter remineralization. This outlier did not impact identification of high versus low nutrient Holocene water masses, which were unambiguously discerned using the foraminiferal Cd nutrient proxy (Figure 1). The core top results demonstrate that no Cd proxy calibration correction is needed in this study. Although *Oppo and Horowitz* [2000] applied a $\delta^{13}C$ correction of −0.4‰ to Brazil margin benthic foraminiferal data based on a core top calibration, we did not apply this correction to any of the $\delta^{13}C$ data presented here, in keeping with the approach of *Curry and Oppo* [2005]. As a result, the Brazil margin $\delta^{13}C$ values we present may represent minor overestimates of water column isotopic composition.

4.2. Water Mass Structure

[10] The LGM Cd_W depth profile (Figures 2 and 3) suggests the presence of three distinct water masses between 441 and 1627 m. A high-nutrient water mass was centered at about 1100 m and was bordered above and below by water masses with lower nutrient contents. This geometry was suggested by a study of Brazil margin benthic foraminiferal $\delta^{13}C$ [*Curry and Oppo*, 2005], but until now was not resolved in the south Atlantic with the Cd nutrient tracer. The glacial high-nutrient water mass we observe was likely AAIW, as it exhibited a Cd_W signature comparable to its modern counterpart (Figure 2b). Cd_W ranges from 0.48 to 0.61 nmol/kg in the core of LGM AAIW at 1100 m (sediment cores at 1105 and 1108 m), and near core top values at this depth are similar (0.41 and 0.58 nmol/kg). However, elevated Cd_W values (0.68–1.21 nmol/kg) in shallower (899–938 m) and deeper (1490 m) core top sediments suggest that LGM AAIW had a lower overall nutrient content and occupied a narrower depth range than modern AAIW (Figure 2b). Glacial Cd_W values of 0.6–0.7 nmol/kg determined for AAIW on the southern Australian continental shelf [*Lynch-Stieglitz et al.*, 1996] support the assignment of AAIW in the Brazil margin LGM water mass structure.

[11] The low-nutrient water mass beneath AAIW at the LGM (Figure 2) was most likely GNAIW, which was also identified at 1567 m on the Brazil margin with a similar

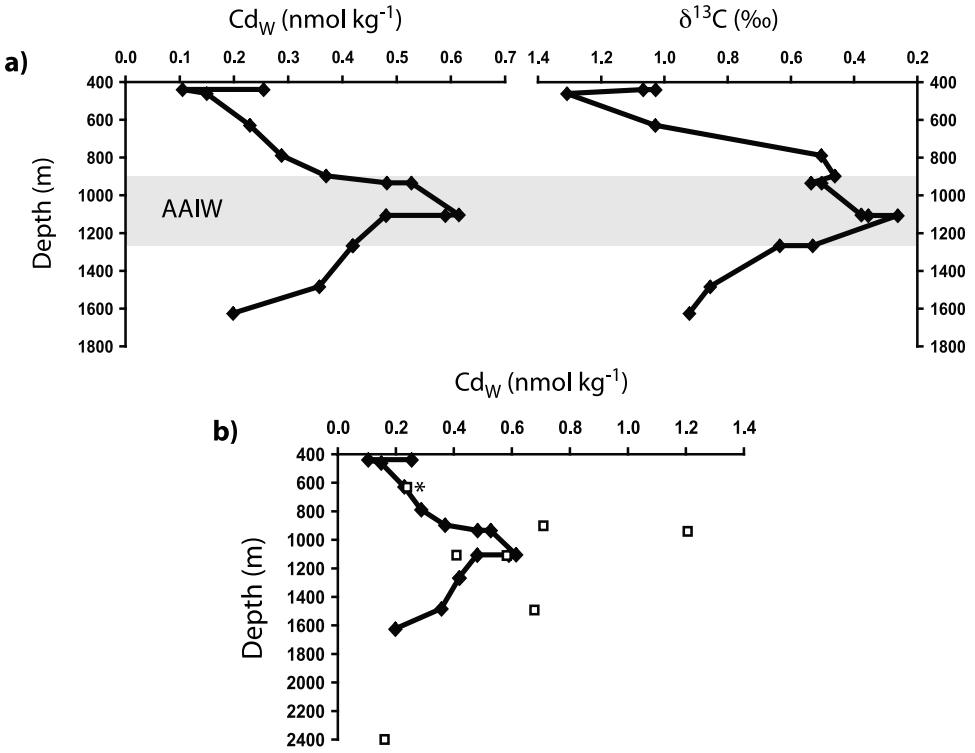

Figure 2. (a) Brazil margin LGM Cd_W (this study) and $\delta^{13}C$ [*Oppo and Horowitz*, 2000; *Curry and Oppo*, 2005] depth profiles. $\delta^{13}C$ values are reversed on the *x* axis to show increased nutrient conditions to the right in both plots. The inferred position of Antarctic Intermediate Water (AAIW) is indicated with gray shading. (b) Cd_W depth profiles for the LGM (black diamonds) and from near core top sediments (open squares). Data with poor reproducibility (RSD > 20%) are not shown, except for the 630 m Holocene datum (RSD = 56.17%), which is marked with an asterisk and is provided as an estimate of modern upper water mass nutrient composition.

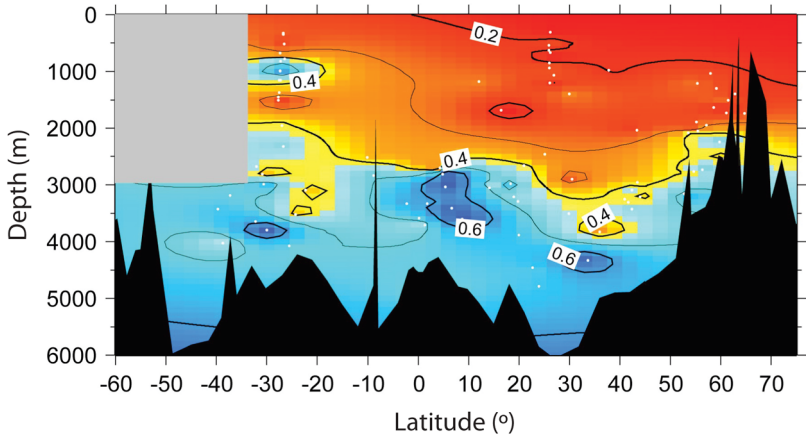

Figure 3. LGM longitudinal Cd_W transect for the Atlantic Ocean, composed of data generated for this study and that compiled by *Marchitto and Broecker* [2006] from the following sources: *Boyle and Keigwin* [1987], *Boyle* [1992], *Oppo and Rosenthal* [1994], *Bertram et al.* [1995], *Beveridge et al.* [1995], *Lea* [1995], *Rosenthal et al.* [1997], *Marchitto et al.* [1998], *Martin and Lea* [1998], *Oppo and Horowitz* [2000], *Rickaby et al.* [2000], *Willamowski and Zahn* [2000], *Marchitto et al.* [2002], *Zahn and Stüber* [2002], *Came et al.* [2003], *Rickaby and Elderfield* [2005], and *Marchitto and Broecker* [2006].

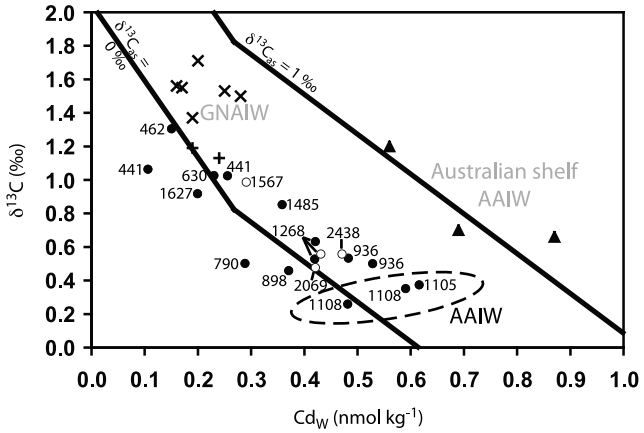

Figure 4. Benthic foraminiferal Cd_W plotted against $\delta^{13}C$ for LGM Atlantic and subantarctic intermediate water masses, depicting differences in nutrient composition and $\delta^{13}C_{as}$ (lines of constant $\delta^{13}C_{as}$ are shown). Brazil margin data from this study (black circles) are compared to those of *Oppo and Horowitz* [2000] from the same location (open circles), GNAIW data from the Bahama banks [*Marchitto et al.*, 1998; *Marchitto and Broecker*, 2006] (cross symbols) and North Atlantic [*Boyle*, 1992] (plus symbols), and intermediate water data from the south Australian shelf [*Lynch-Stieglitz et al.*, 1996] (triangles). Water depths are indicated for each data point resulting from this study and *Oppo and Horowitz* [2000], and the dashed ellipse highlights data from the inferred core of AAIW on the Brazil margin.

Cd_W value of 0.29 nmol/kg by *Oppo and Horowitz* [2000]. The two deepest cores analyzed in this study (1485 and 1627 m) are near the core of this northern source water mass, which was centered at about 1500 m in this region of the South Atlantic (Figure 3) [*Curry and Oppo*, 2005]. Comparison with core top Cd_W results from 1490 and 2397 m (Figure 2b) suggests a shoaling of GNAIW compared to modern NADW, as generally accepted [e.g., *Duplessy et al.*, 1988; *Marchitto et al.*, 1998; *Curry and Oppo*, 2005; *Lynch-Stieglitz et al.*, 2007]. The shallow, low-nutrient LGM water mass that exhibits a Cd_W minimum at 441 m and extends to about 800 m in depth is likely SACW, and it appears to have had a nutrient composition similar to its modern counterpart (Figure 2b). Although the core of LGM AAIW is narrowly defined at 1100 m on the Brazil margin, mixing with these adjacent water masses likely gives rise to the Cd_W depth gradients observed in Figures 2 and 3. There appears to be a steeper gradient between AAIW and SACW than with GNAIW, suggesting a greater degree of mixing with the deeper water mass. The water mass geometry that we infer for the glacial South Atlantic (Figure 3) is strongly similar to that achieved with benthic foraminiferal $\delta^{13}C$ [*Curry and Oppo*, 2005] and provides additional nutrient structure in a region where water masses above GNAIW have not been resolved for Cd [*Marchitto and Broecker*, 2006].

4.3. Water Mass $\delta^{13}C_{as}$

[12] Benthic foraminiferal Cd_W results and $\delta^{13}C$ data were used to calculate $\delta^{13}C_{as}$ (Table 1), which we employed as a conservative water mass tracer in the manner of *Lynch-Stieglitz et al.* [1996] and *Oppo and Horowitz* [2000]. As in these studies, we present the data on a plot of Cd_W versus $\delta^{13}C$ (Figure 4) in order to illustrate $\delta^{13}C_{as}$ variability between glacial age water masses. The three LGM water masses identified in this study exhibit a narrow range of $\delta^{13}C_{as}$ values close to 0‰. The two deepest samples (1485 and 1627 m) plot near North Atlantic [*Boyle*, 1992; *Marchitto et al.*, 1998; *Marchitto and Broecker*, 2006] and other Brazil margin (1567 m) [*Oppo and Horowitz*, 2000] GNAIW results (Figure 4), supporting assignment of this water mass as GNAIW or a mixture of GNAIW and AAIW. The shallow, low-nutrient LGM water mass exhibits $\delta^{13}C_{as}$ values near 0‰ and often slightly negative, which are persistent to the depth of AAIW at 1100 m (Figure 4). The shallowest points at 441 and 462 m likely describe the nutrient composition and $\delta^{13}C_{as}$ signature of SACW, with increasing influences from AAIW mixing with depth.

[13] The high-nutrient LGM water mass on the Brazil margin, which we identify as AAIW, is distinct from the other water masses in Figure 4 due to its elevated Cd_W and reduced $\delta^{13}C$ signature, and exhibits an average $\delta^{13}C_{as}$ of only 0.16‰ over 898–1268 m (0.23‰ in its center from 936 to 1108 m). Core top data from this site suggests a much higher modern AAIW $\delta^{13}C_{as}$ average value of 1.22‰ over similar depths (899–1490 m) (Table 2). Although late Holocene $\delta^{13}C_{as}$ values for the shallowest (899 m) and deepest (1490 m) AAIW cores are regarded as estimates since they are based on $\delta^{13}C$ measurements in proximal sediment cores (938 and 1567 m, respectively), $\delta^{13}C_{as}$ results from the core of the modern water mass are considered robust since both nutrient proxy measurements were conducted on the same core. Importantly, LGM AAIW appears to have had a significantly lower $\delta^{13}C_{as}$ signature than its modern counterpart.

[14] Substantially reduced $\delta^{13}C_{as}$ values suggest that LGM AAIW was formed in a different manner than at present. Lower $\delta^{13}C_{as}$ can imply air/sea exchange of CO_2 under conditions of relative warmth and reduced windiness, neither of which would likely characterize the glacial Southern Ocean. A more likely explanation is that the high-nutrient water mass was in contact with the atmosphere for a shorter period of time than modern AAIW, possibly due to impingement of winter sea ice [*Crosta et al.*, 1998; *Rickaby and Elderfield*, 2005] on the formation area. This inference is in agreement with the hypothesis that Antarctic sea ice expansion during glacial periods drove changes in Atlantic meridional overturning circulation and resulted in modified AAIW formation [*Keeling and Stephens*, 2001]. Alternatively, or in conjunction with sea ice effects, LGM AAIW in the South Atlantic may have developed a reduced $\delta^{13}C_{as}$ signature because it consisted partly of recycled GNAIW, which could have upwelled in the Antarctic region and contributed to the formation of AAIW. If GNAIW upwelled in the Southern Ocean but did not stay in contact with the atmosphere for an extended period of time, it could have re-formed as intermediate water with a higher nutrient content but similar $\delta^{13}C_{as}$ value.

[15] A comparison with paleonutrient data from the Pacific/Indian Ocean sector of the subantarctic suggests that the altered form of AAIW we observe was unique to the

LGM Atlantic Ocean. AAIW bathing the Australian shelf [*Lynch-Stieglitz et al.*, 1996] exhibited much higher $\delta^{13}C_{as}$ values than were observed on the Brazil margin (Figure 4), suggesting that these distinct intermediate water masses were formed in a different manner, with reduced communication between ocean basins. Other proxy records from the southeast Pacific suggest enhanced ventilation of AAIW in that region at the LGM [*Muratli et al.*, 2010], but our finding of reduced $\delta^{13}C_{as}$ values implies reduced ventilation instead for this water mass in the Atlantic basin. Based on these discrepancies, we hypothesize that contributions of AAIW formed in the Indian and Pacific Oceans to the mid-depth Atlantic were greatly reduced at the LGM in favor of AAIW generated within the Atlantic sector. Accordingly, import of intermediate waters into the Atlantic eastward through the Drake Passage via the cold-water return route [*Gordon*, 1986], which feeds NADW formation, may also have been reduced.

[16] Several environmental processes could have imparted $\delta^{13}C_{as}$ errors, although we expect their effects to be minimal at the Brazil margin study site. Preferential loss of Cd during dissolution of foraminifera [*McCorkle et al.*, 1995] would result in lowered Cd_W with constant $\delta^{13}C$, resulting in a negative $\delta^{13}C_{as}$ error. However, the results presented here are not likely to have been compromised by dissolution because the LGM samples were collected from 1627 m and above in the South Atlantic, where waters are less corrosive than in the deeper Pacific (~2500 m) where the effect was observed [*McCorkle et al.*, 1995]. Enhanced sea surface productivity could also affect $\delta^{13}C_{as}$ estimates due to remineralization of resultant abundant organic matter at the sediment surface [*Mackensen et al.*, 1993]. For a constant Cd_W, this process would produce lower benthic foraminiferal $\delta^{13}C$ values by up to 0.5‰, and thus reduce $\delta^{13}C_{as}$ as well. We did not apply such a productivity correction because a finding of reduced LGM organic carbon accumulation in the study area [*Mollenhauer et al.*, 2004] does not support an inference of enhanced primary productivity. Additionally, we did not incorporate a −0.4‰ $\delta^{13}C$ adjustment for the Holocene foraminiferal $\delta^{13}C$ offsets from bottom water observed by *Oppo and Horowitz* [2000], which would affect LGM $\delta^{13}C_{as}$ estimates. However, inclusion of this calibration correction would result in an increased $\delta^{13}C_{as}$ difference between LGM and modern AAIW. Thus, we thus consider our finding of reduced LGM AAIW $\delta^{13}C_{as}$ robust.

[17] Glacial South Atlantic AAIW $\delta^{13}C_{as}$ characteristics imply that glacial-interglacial scale changes in Southern Ocean derived water mass carbon isotopic composition must be interpreted in terms of variable air/sea gas exchange effects in addition to nutrient composition, as suggested by *Martínez-Méndez et al.* [2009]. For example, the $\delta^{13}C_{as}$ reduction of about 1‰ that we infer for AAIW at the LGM is well in excess of the glacial whole ocean $\delta^{13}C$ depletion of 0.3‰ [*Duplessy et al.*, 1988] and is even larger in amplitude than glacial-interglacial scale benthic foraminiferal $\delta^{13}C$ variability observed at intermediate depths in the southwest Pacific [*Pahnke and Zahn*, 2005]. With the suggestion of chemically distinct glacial AAIW in the Atlantic ocean basin, our results also endorse caution in interpreting paleoceanographic nutrient proxy results in terms of mixing with intermediate southern sourced water masses, since there may not be a fixed global glacial upper southern component water end-member. The new Cd_W and $\delta^{13}C_{as}$ end-member values we determine here appear to be specific to the South Atlantic.

5. Conclusions

[18] This study presents the first Cd_W and $\delta^{13}C_{as}$ depth transects for the glacial South Atlantic at depths shallower than 1200 m, in a region critical for determining the structure and formation of AAIW [*Marchitto and Broecker*, 2006]. Constraint of Atlantic intermediate-depth circulation is important, as water mass tracer records suggest rapid (millennial-scale) reorganizations from the last glacial stage to the Holocene [*Zahn and Stüber*, 2002; *Rickaby and Elderfield*, 2005; *Pahnke et al.*, 2008] with near basin-wide changes in AAIW penetration. The water mass geometry presented here is needed to complement existing fixed-depth records, which can be affected by water mass vertical migration and mixing. Our results suggest that AAIW penetrated northward to at least 27°S in the LGM Atlantic at a core depth of 1100 m (Figure 3). The $\delta^{13}C_{as}$ signature of this water mass suggests that it was formed with reduced atmospheric contact, likely due to the presence of sea ice in the subduction area and/or contributions of upwelled GNAIW, and that the AAIW we observe was unique to the Atlantic basin. Inferred changes in AAIW formation at the LGM leading to strong $\delta^{13}C_{as}$ depletion in the South Atlantic support caution in interpreting benthic foraminiferal $\delta^{13}C$ results alone, as well as mixing between this and other water masses.

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