

Isotopically depleted carbon in the mid-depth South Atlantic during the last deglaciation

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[1] The initial rise in atmospheric CO₂ during the last deglaciation was likely driven by input of carbon from a ¹³C-depleted reservoir. Here we show that high resolution benthic foraminiferal records from the mid-depth Brazil Margin display an abrupt drop in δ¹³C during Heinrich Stadial 1 (HS1) that is similar to but larger than in the atmosphere. Comparing the Brazil Margin results to published records from the North Atlantic, we are unable to account for the South Atlantic δ¹³C data with conservative mixing between northern and southern component water masses. Rapid input of abyssal water from the Southeast Atlantic could account for deglacial δ¹³C anomalies at the Brazil Margin but it would require a reversal in deep water flow direction compared to today. A new mid-depth water mass may explain similar HS1 δ¹³C values in both the North and South Atlantic, but contrasting oxygen isotopic values between the two basins do not support such a scenario. Instead, it appears that δ¹³C behaved non-conservatively during the deglaciation, possibly reflecting the input of carbon from an isotopically depleted source.

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1. Introduction

[2] The rise in atmospheric carbon dioxide between the Last Glacial Maximum (LGM) and the Holocene was first recognized over 30 years ago [Neftel et al., 1982], yet the underlying mechanisms responsible for the CO₂ change remain unclear [Sigman and Boyle, 2000; Sigman et al., 2010]. High resolution ice core records indicate that the initial 30 ppmv increase in CO₂ from ~17 to 16 kyr BP coincided with a decrease in the δ¹³C of atmospheric CO₂ of 0.3‰ [Schmitt et al., 2012]. The synchronicity of the signals suggests that the release of carbon from a ¹³C-depleted reservoir into the atmosphere was a key initiator of the last deglaciation.

[3] Carbon isotope minima were widespread phenomena in the surface and mid-depth ocean during the last deglaciation [Oppo and Fairbanks, 1989; Ninnemann and Charles, 1997; Spero and Lea, 2002; Curry et al., 1988; Peck et al., 2007]. The largest δ¹³C anomalies occurred in the mid-depth North Atlantic. South of Iceland, δ¹³C decreased by ~1‰ at water depths from 1200 m to 2300 m [McManus et al., 1999; Rickaby and Elderfield, 2005; Thornalley et al., 2010]. Similar anomalies occurred at 1300 m in the western tropical Atlantic [Zahn and Stuber, 2002] and 1100 m in the eastern subtropical Atlantic [Zahn et al., 1997]. A variety of mechanisms have been proposed to

explain the carbon isotope minima, including regional brine formation [Dokken and Jansen, 1999; Thornalley et al., 2010; Waelbroeck et al., 2011], greater incursion of southern source intermediate water [Rickaby and Elderfield, 2005], and weakening of the Atlantic meridional overturning circulation [Zahn et al., 1997]. The latter mechanism appears to be consistent with evidence for reduced export of Pa from the North Atlantic relative to the LGM [Gherardi et al., 2009].

[4] The Brazil Margin cores used in this study are ideally located to evaluate the evolution of Atlantic water masses during the deglaciation. In the modern Southwest Atlantic, the cores span the transition between Antarctic Intermediate Water (AAIW), Upper Circumpolar Deep Water (UCDW), and North Atlantic Deep Water (NADW) (Figure 1). During the LGM, the core locations were influenced by Glacial Antarctic Intermediate Water (GAAIW), Glacial North Atlantic Intermediate Water (GNAIW), and Glacial Antarctic Bottom Water (GAABW) [Curry and Oppo, 2005]. Below we show that the Brazil Margin δ¹³C time series display a negative excursion similar to the record of atmospheric δ¹³C during the deglaciation. We then discuss whether the Brazil Margin data can be explained by conservative mixing between northern and southern waters.

2. Methods

[5] The analyses presented in this paper are based on six cores from 1200 m to 2500 m water depth that were retrieved during the KNR159-5 cruise to the Brazil Margin [Curry and Oppo, 2005]. Cores discussed in this paper include 36GGC, 17JPC, 78GGC, 33GGC, 42JPC, and 30GGC (Table 1). Each core was sampled at 4 or 5 cm intervals, and the

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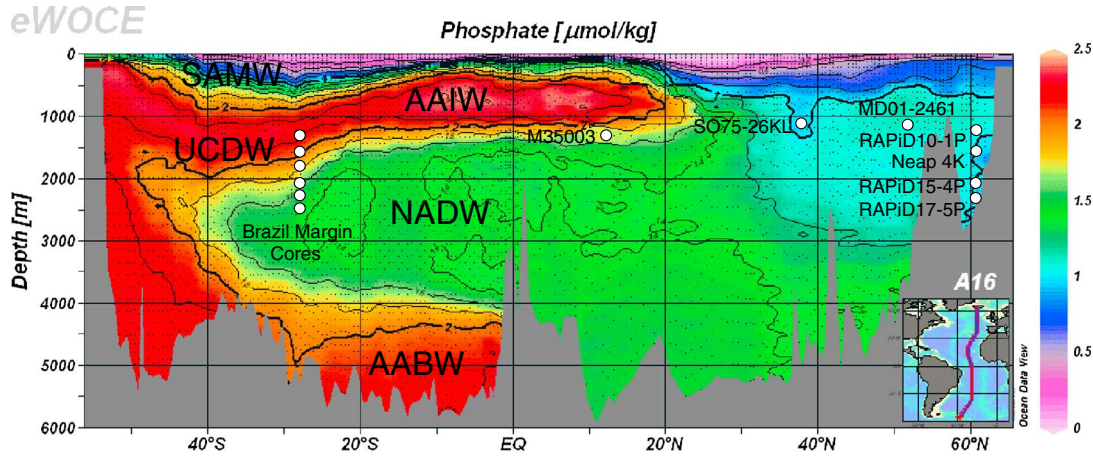


Figure 1. Locations of cores used in this paper superimposed on the phosphate concentration of the World Ocean Circulation Experiment (WOCE) A16 section in the Atlantic Ocean [Schlitzer *et al.*, 2000]. The Brazil Margin cores at 27°S span Antarctic Intermediate Water (AAIW), Upper Circumpolar Deep Water (UCDW), and North Atlantic Deep Water (NADW). Also shown are core locations for NEAP 4K [Rickaby and Elderfield, 2005], RAPiD 10-1P, RAPiD 15-4P, RAPiD 17-5P [Thornalley *et al.*, 2010], SO75-26KL [Zahn *et al.*, 1997], M35003 [Zahn and Stuber, 2002], and MD01-2461 [Peck *et al.*, 2007].

resulting samples were then freeze-dried, washed through a 150 μm sieve, and dried at 40°C.

2.1. Radiocarbon

[6] Planktonic foraminifera (*Globigerinoides ruber* and *Globigerinoides sacculifer*) were picked from the >250 μm size fraction of each sample for accelerator mass spectrometry (AMS) radiocarbon dates. Radiocarbon dating was carried out at the Keck Carbon Cycle Accelerator Mass Spectrometry laboratory at University of California, Irvine, where the samples underwent a 10% leach using 0.01 N HCl to ensure removal of any modern ^{14}C . The foraminifera were then hydrolyzed in 85% phosphoric acid and the resulting CO_2 was combined with hydrogen and iron powder at 560°C to create graphite. The graphite was analyzed using AMS to obtain ^{14}C results.

[7] Modern reservoir ages along the coast of southeastern Brazil are 407 ± 59 years (1σ), equivalent to a ΔR of 7 ± 59 years [Angulo *et al.*, 2005]. For age calibration purposes, we used a ΔR 0 ± 200 years (1σ) to account for unknown changes in reservoir age in the geologic past. Calendar ages were calibrated using Calib v.6.0 (<http://calib.qub.ac.uk/calib/>). The uncertainties in calibrated calendar ages, typically ± 300 years (1σ), are due primarily to our assumed uncertainty in ΔR .

2.2. Stable Isotopes

[8] Benthic stable carbon and oxygen isotopic analyses were based on individual tests of *Cibicidoides* species from the >250 μm size fraction. Analyses were run on a Finnigan MAT 253 triple-collector gas source mass spectrometer coupled to a Finnigan Kiel automated carbonate device at the University of Michigan's Stable Isotope Laboratory. Isotope values were corrected to Vienna Pee Dee Belemnite using National Bureau of Standards (NBS) 19 ($n = 78$, $\delta^{13}\text{C} = 1.94 \pm 0.04\text{‰}$, $\delta^{18}\text{O} = -2.19 \pm 0.07\text{‰}$) and NBS 18 ($n = 12$; $\delta^{13}\text{C} = -5.00 \pm 0.04\text{‰}$, $\delta^{18}\text{O} = -22.98 \pm 0.06\text{‰}$). Samples for cores 42JPC and 36GGC were run at Woods Hole

Oceanographic Institution [Oppo and Horowitz, 2000; Curry and Oppo, 2005].

[9] In addition to NBS 18 and NBS 19, we used the Atlantis II standard ($\delta^{18}\text{O} = 3.42\text{‰}$; Ostermann and Curry, [2000]) to constrain the “heavy” end of the oxygen isotope spectrum. Atlantis II standards run during this study yield a mean $\delta^{18}\text{O}$ of $3.47 \pm 0.08\text{‰}$ ($n = 90$), within one-sigma error of the 3.42‰ value presented in Ostermann and Curry [2000]. Atlantis II $\delta^{18}\text{O}$ values run during analysis of - samples for core 17JPC averaged 3.52‰. In this instance, we subtracted 0.1‰ from the unknowns to compensate for the higher than normal $\delta^{18}\text{O}$ results.

3. Results

3.1. Age Models

[10] Age models for 17JPC, 78GGC, 33GGC, and 30GGC are shown in Figure 2. The age models for 36GGC and 42JPC are presented in Sortor and Lund [2011] and Hoffman and Lund [2012], respectively. Each core has sedimentation rates of 2–3 cm/kyr during the Holocene with higher rates during the deglaciation and LGM, ranging from 5 cm/kyr to 35 cm/kyr (Figure 2). High accumulation rates for 78GGC and 33GGC suggest the core locations were sediment drift sites during the deglaciation and LGM. The cores generally lack modern core tops, with the most recent material dating

Table 1. Locations and Water Depths of Brazil Margin Cores Used in This Paper^a

Core	Latitude (°S)	Longitude (°W)	Water Depth (m)
36GGC	27°31'	46°28'	1268
17JPC	27°42'	46°29'	1627
78GGC	27°29'	46°20'	1820
33GGC	27°34'	46°11'	2082
42JPC	27°46'	46°38'	2296
30GGC	28°08'	46°04'	2500

^aAll cores were retrieved during R/V Knorr cruise KNR159-5.

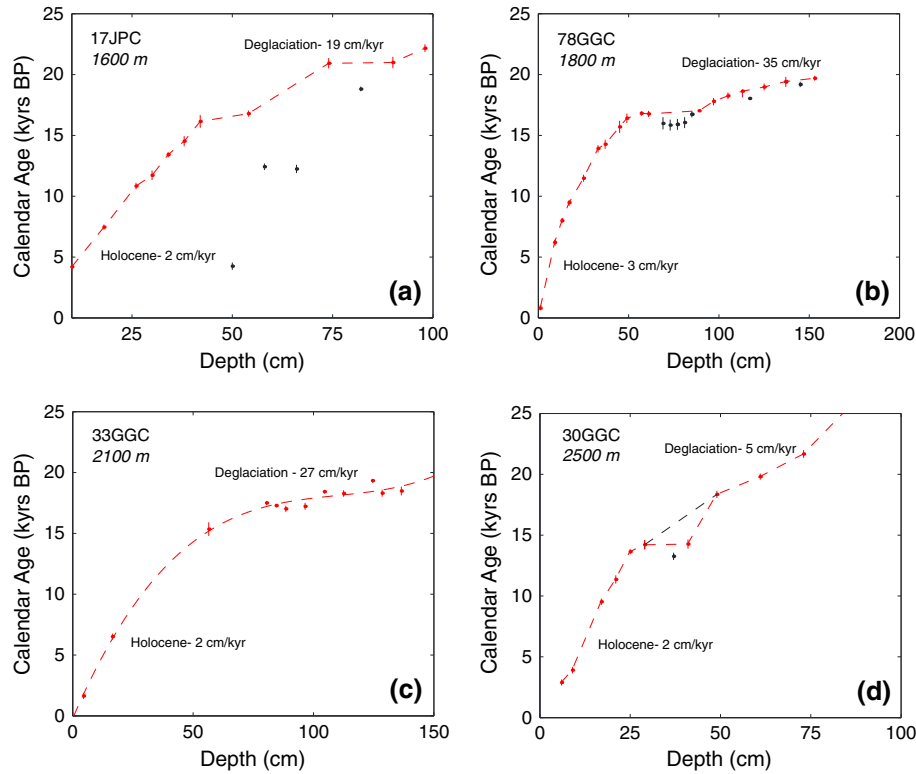


Figure 2. Calendar ages (red circles) and age models (dashed lines) for cores 17JPC, 78GGC, 33GGC, and 30GGC. Error bars for each calendar age represent the $\pm 1\sigma$ uncertainty. Age reversals not included in each age model are shown as black symbols. The plot for 30GGC includes two possible age models depending on which ages are included (see text).

to between 0.5 kyr BP and 3 kyr BP. Nonzero core top ages may be due to a lack of sediment deposition, erosion by deep currents, or an artifact of the coring process.

[11] The radiocarbon results illustrate clear age reversals in cores 78GGC, 17JPC, and 30GGC. Deglacial age reversals have been documented in other cores from the Brazil Margin; *Sortor and Lund* [2011] used stable isotopic data to conclude that reversals in 36GGC were due to deep burrowing. A similar phenomenon appears to have occurred in 78GGC, where anomalously low benthic $\delta^{18}\text{O}$ values from 69 cm to 81 cm coincide with an interval of young radiocarbon ages (Figure 3). The anomalous $\delta^{18}\text{O}$ points have values ranging from 3.5‰ to 3.7‰, indicating they originated from the 35 cm to 45 cm stratigraphic interval. Radiocarbon ages of ~ 13.5 kyr BP in the disturbed section support this interpretation. We exclude these data from the age model for 78GGC. Note that the section of the core with the large decline in $\delta^{13}\text{C}$ (discussed below) occurs prior to the disturbed section. Two additional isolated reversals prior to HS1 (at 145 cm and 165 cm) are also excluded from the age model for 78GGC (Figure 2b).

[12] In the case of 30GGC, there are two possible age models; one that includes the age at 41 cm and one that excludes it (Figure 2d). This age is not a reversal *per se* but would require a drastic change in sedimentation rate. Since there is a clear reversal at 39 cm, we chose to use the age model that excludes both points (dashed black line). Large age reversals in 17JPC at 50 cm, 58 cm, 66 cm, and 82 cm were excluded from the age model for this core.

Age models for 78GGC, 17JPC, and 30GGC were produced by linear interpolation between the remaining calendar ages. Age inconsistencies in 33GGC are subtler than the other cores; many are within error of adjacent dates in the

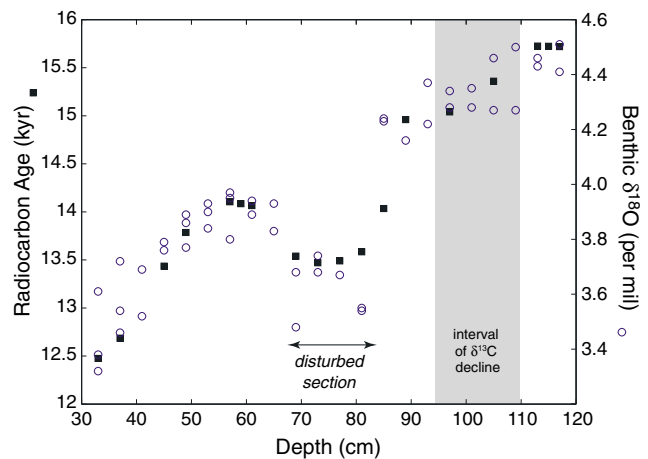


Figure 3. Radiocarbon ages (squares) and benthic $\delta^{18}\text{O}$ results (circles) for the 30–120 cm depth interval in core 78GGC. Both the ^{14}C ages and $\delta^{18}\text{O}$ results indicate the presence of disturbed sediment from 69–81 cm. Both proxies suggest the material originated from the 35–45 cm stratigraphic level. Also shown is the interval of $\delta^{13}\text{C}$ decline at the beginning of HS1.

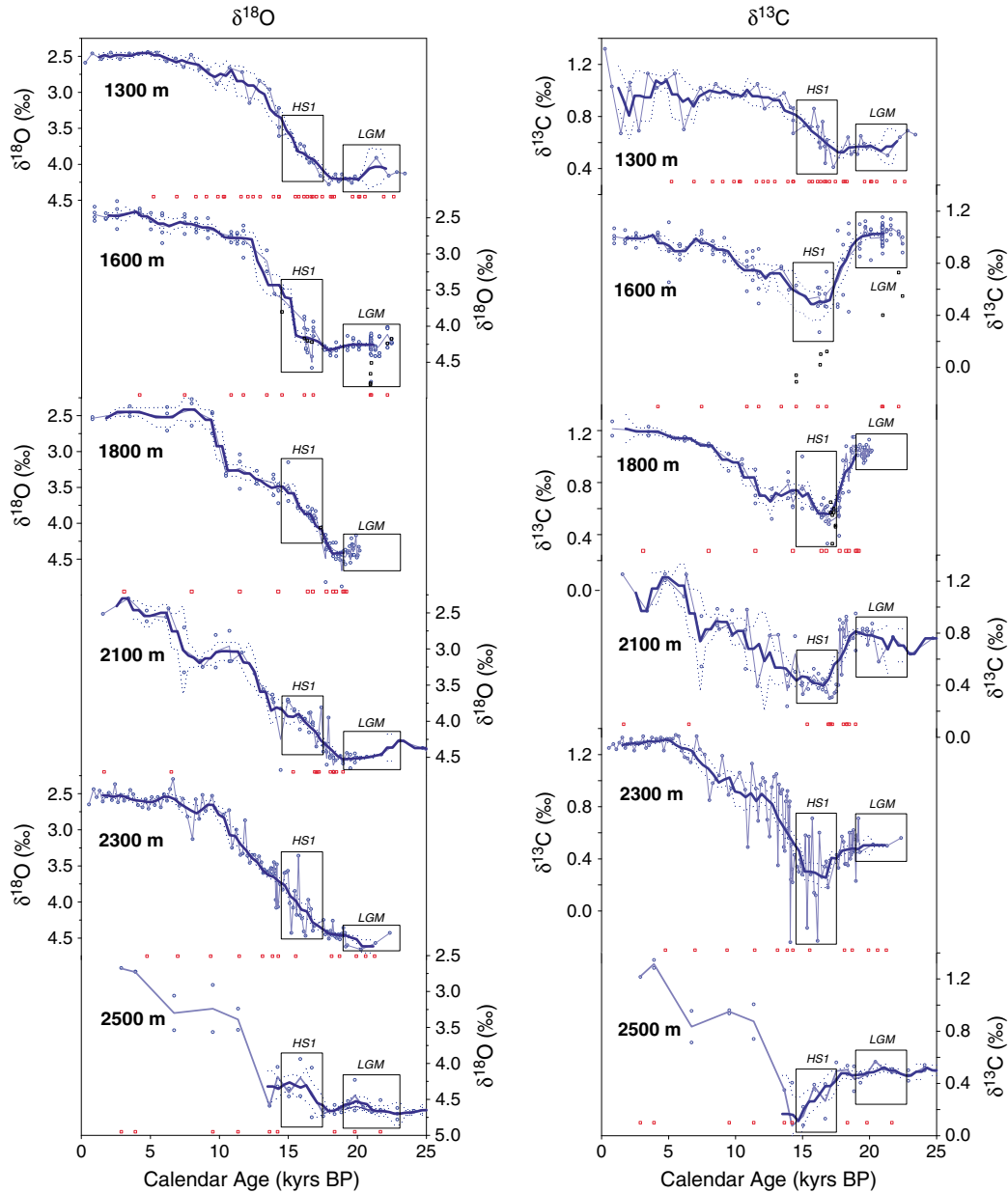


Figure 4. Radiocarbon-constrained $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ time series for the Brazil Margin spanning 1300 m to 2500 m water depth. Each panel includes stable isotopic results for individual foraminifera (circles), the average value at each stratigraphic level (thin line), the 2000-year running mean (thick line), and the standard error (dashed lines). Red symbols denote calendar ages for each core. The running mean at 2500 m water depth is calculated only between 13 and 25 kyr BP due to a lack of high resolution Holocene data. Isotopic values out of stratigraphic order (black squares) were not included in the time averages. Boxes indicate intervals used for calculating mean HS1 (14.5–17.5 kyr BP) and LGM (19–23 kyr BP) values.

stratigraphy (Figure 2c). As a result, we used a polynomial fit to construct the age model rather than linear interpolation between individual points.

3.2. Stable Isotopic Time Series

[13] Benthic foraminiferal $\delta^{18}\text{O}$ time series for the Brazil Margin are shown in Figure 4. The contrast between LGM and Holocene $\delta^{18}\text{O}$ values is $\sim 2.0\text{‰}$ at water depths below 2000 m compared to $\sim 1.8\text{‰}$ above 2000 m, consistent with results spanning the full water column range at the Brazil

Margin [Curry and Oppo, 2005; Lund et al., 2011]. The new radiocarbon constrained records indicate the timing of the LGM to Holocene shift varies by water depth (Figure 4). Above 2200 m, benthic $\delta^{18}\text{O}$ began to decrease at 17.5–18.0 kyr BP whereas below 2200 m, the $\delta^{18}\text{O}$ decrease occurred after 17.0 kyr BP, similar to the depth-dependent timing noted at other Atlantic sites [Waelbroeck et al., 2011].

[14] Benthic $\delta^{13}\text{C}$ in the deepest cores (2300–2500 m) and shallowest core (1300 m) increased by 0.5–0.8‰ between

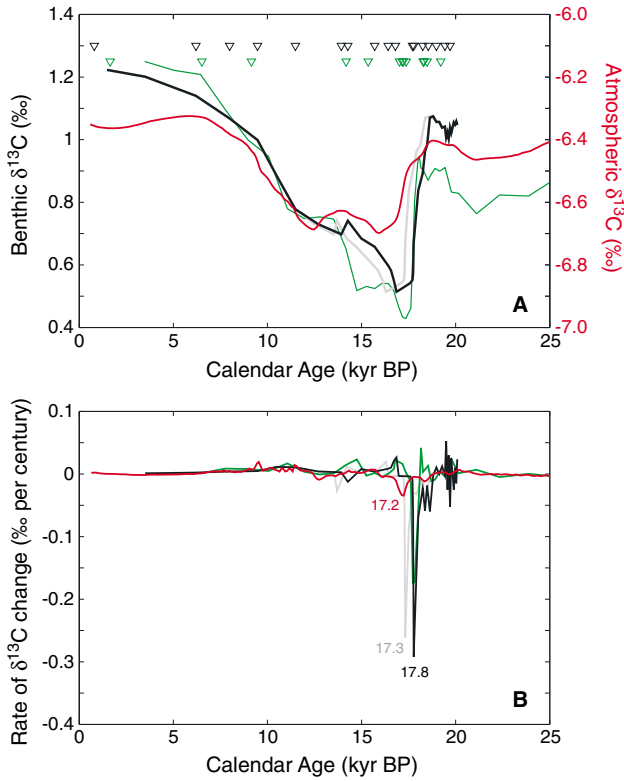


Figure 5. (a) 3-point running mean benthic $\delta^{13}\text{C}$ for 1800 m (black and gray lines) and 2100 m (green line) compared to the atmospheric $\delta^{13}\text{C}$ record from 0–25 kyr BP (red line) [Schmitt *et al.*, 2012]. Results at 2100 m are shifted by +0.1‰ to aid comparison with the record from 1800 m water depth. Two separate curves are shown for the 1800 m, including no change in the regional reservoir age correction ($\Delta R = 0$ years; black line) and a ΔR of 400 years from 12–18 kyr BP (dark gray line). Triangles denote radiocarbon control points. Also shown is the spline fit to the EDC carbon isotopic record (red line). This curve is based on isotopic data from Schmitt *et al.* [2012] using the AICC2012 age model [Veres *et al.*, 2012] (which is similar to that of Parrenin *et al.* [2013]). (a) Rate of $\delta^{13}\text{C}$ change (in ‰ per century) for the time series in panel A. The maximum rate of change for both Brazil Margin records occurs at 17.8 kyr BP, assuming a ΔR of 0 years. If ΔR was instead 400 years, the maximum rate of $\delta^{13}\text{C}$ decline occurs at 17.3 kyr BP. The maximum rate of change for the atmospheric record occurs at approximately 17.2 kyr BP.

the LGM and Holocene, while those in between (1800–2100 m) show little glacial-interglacial difference (Figure 4). The most striking feature of the $\delta^{13}\text{C}$ records is the pronounced negative excursion near the beginning of Heinrich Stadial 1 (HS1; 14.5–17.5 kyr BP). The decrease is largest between 1600 m to 2100 m water depth ($\sim 0.5\text{‰}$), with smaller excursions at 2300 m and 2500 m ($\sim 0.2\text{‰}$). The one exception where $\delta^{13}\text{C}$ increased monotonically during the deglaciation is at 1300 m water depth.

[15] The two high resolution records at 1800 m and 2100 m have $\delta^{13}\text{C}$ histories similar to the atmosphere (Figure 5). Each record displays a pattern of change that resembles a leaning “W”, including an abrupt drop in $\delta^{13}\text{C}$ near ~ 18 kyr BP, a partial recovery by 14 kyr BP, a modest decrease at

12–13 kyr BP, and finally a gradual increase into the mid-Holocene. The magnitude of the oceanic $\delta^{13}\text{C}$ anomalies is $\sim 0.2\text{‰}$ larger than in the atmosphere. For each benthic $\delta^{13}\text{C}$ record, the maximum rate of decline occurred at 17.8 kyr BP, assuming the regional offset in surface water reservoir age (ΔR) was 0 ± 200 years (1σ) (Figure 5). If instead ΔR was 400 years, the maximum rate of $\delta^{13}\text{C}$ change would have happened at 17.3 kyr BP. By comparison, the maximum rate of $\delta^{13}\text{C}$ change in the atmosphere occurred at approximately 17.2 kyr BP. If the age models for these records are correct, it appears that the rapid decrease in $\delta^{13}\text{C}$ at the Brazil Margin either led or was synchronous with the atmosphere.

4. Discussion

[16] The strong correspondence between the Brazil Margin and atmospheric $\delta^{13}\text{C}$ records suggests they are linked by a common mechanism. One possibility is that the Brazil Margin $\delta^{13}\text{C}$ anomalies reflect changes in the composition of northern component water or its proportion relative to southern component water. Alternatively, input of abyssal water from the South Atlantic could have driven the $\delta^{13}\text{C}$ signal. In either case, the apparent changes in circulation represented by the benthic $\delta^{13}\text{C}$ records must have also led to outgassing of ^{13}C -depleted carbon from the ocean in such a way that both the oceanic and atmospheric $\delta^{13}\text{C}$ records had a similar pattern. Below, we first review LGM water mass properties at the Brazil Margin to provide context for the deglaciation. We then evaluate the different circulation mechanisms that could potentially account for the deglacial anomalies.

4.1. LGM Water Mass Proportions

[17] During the LGM, Brazil Margin $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ pairs from 1800 m to 4000 m water depth fall on a mixing line between GNAIW and GAABW (Figure 6a). Assuming $\delta^{13}\text{C}$ values of 1.4‰ for GNAIW [Curry and Oppo, 2005] and -0.2‰ for GAABW [Hoffman and Lund, 2012] (Table 2), the $\delta^{13}\text{C}$ results at 1800 m can be explained by a mixture of 25% GAABW and 75% GNAIW (Table 3). Given that $\delta^{13}\text{C}$ is a non-conservative tracer, it is important to validate these proportions using $\delta^{18}\text{O}$. We do so by estimating the predicted $\delta^{18}\text{O}$ at each depth given the $\delta^{13}\text{C}$ -based proportions and the $\delta^{18}\text{O}$ end-member values for GNAIW and GAABW. Using a $\delta^{18}\text{O}$ of 4.2‰ for GNAIW [Curry and Oppo, 2005] and 4.9‰ for GAABW [Hoffman and Lund, 2012], the predicted $\delta^{18}\text{O}$ at 1800 m is 4.38‰, indistinguishable from observed value of 4.40‰ (Table 3). The predicted and observed LGM $\delta^{18}\text{O}$ values at 2100 m, 2300 m, and 2500 m are also in good agreement.

[18] Between 1100 m and 1600 m, the isotopic data generally fall between GNAIW and GAAIW (Figure 6a). Water at 1600 m depth is composed of $\sim 50\%$ GAAIW and $\sim 50\%$ GNAIW while water at 1300 m appears to consist largely of GAAIW. The offset between observed and estimated $\delta^{18}\text{O}$ for the shallower cores is larger than for the deeper sites (Table 3). This is most likely due to the small contrast in $\delta^{18}\text{O}$ values for GAAIW (4.3‰) and GNAIW (4.2‰) relative to the uncertainty in mean LGM values at each water depth ($\pm 0.05\text{‰}$). Nevertheless, the Brazil Margin data suggest that $\delta^{13}\text{C}$ at mid-depths acted as a largely

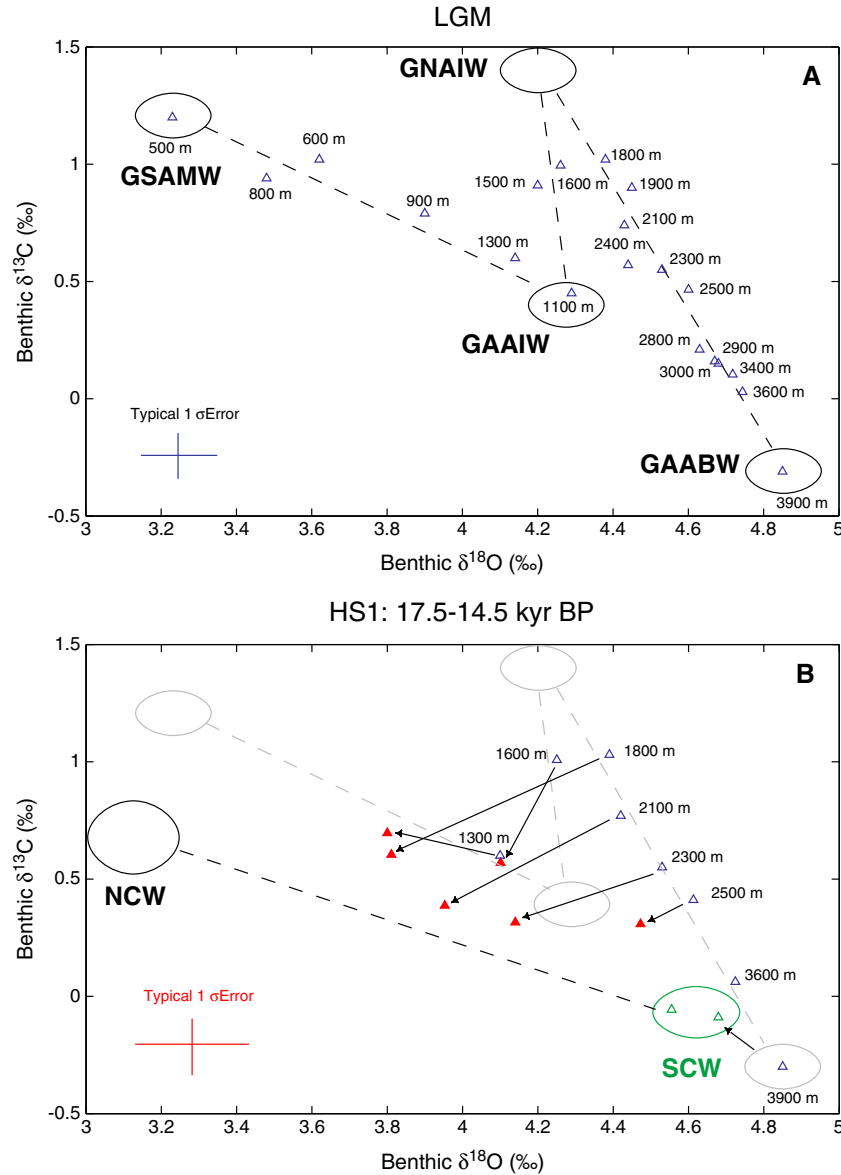


Figure 6. Cross-plots of $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ for the Brazil Margin. (a) LGM cross-plot, including data from *Curry and Oppo* [2005] above 3100 m water depth and *Hoffman and Lund* [2012] below 3100 m. The South-west Atlantic was occupied by four distinct water masses, including Glacial Antarctic Bottom Water (GAABW), Glacial North Atlantic Intermediate Water (GNAIW), Glacial Antarctic Intermediate Water (GAAIW) and Glacial Sub-Antarctic Mode Water (GSAMW). (b) HS1 cross-plot, including Brazil Margin data from 1300 m to 2500 m (this paper) and 3600 m to 3900 m [*Hoffman and Lund*, 2012]. The latter points represent southern component water (SCW). Also shown is the estimated $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ range for northern component water (NCW) during HS1 [*Zahn et al.*, 1997; *Zahn and Stuber*, 2002; *Rickaby and Elderfield*, 2005; *Peck et al.*, 2007; *Thornalley et al.*, 2010]. The mid-depth Brazil Margin results plot above the mixing line between NCW and SCW. A similar pattern occurs when only data from the HS1 $\delta^{13}\text{C}$ minimum are used (not shown).

conservative tracer during the LGM, consistent with results from deeper in the water column [*Hoffman and Lund*, 2012].

4.2. Northern Component Influence During HS1

[19] An apparent reorganization in water mass structure occurred during HS1 (Figure 6b). Between 1800 m to 2300 m water depth, $\delta^{18}\text{O}$ decreased 0.4–0.6‰ while $\delta^{13}\text{C}$ decreased 0.2–0.5‰. In comparison, $\delta^{18}\text{O}$ of southern component water (SCW) decreased by $\sim 0.2\text{‰}$ while its $\delta^{13}\text{C}$

Table 2. Stable Isotope Values for LGM End-Members in the Atlantic^a

End-Member	$\delta^{13}\text{C}$	Error	$\delta^{18}\text{O}$	Error
GAAIW	0.4	0.1	4.3	0.1
GNAIW	1.4	0.1	4.2	0.1
GAABW	-0.2	0.2	4.9	0.1

^aEnd-member values for GAAIW and GNAIW are based on isotope data presented in *Curry and Oppo* [2005]. End-member values for GAABW are based on the results from *Hoffman and Lund* [2012].

Table 3. LGM Proportions of SCW and NCW at the Brazil Margin^a

Water depth (m)	Mixture	LGM $\delta^{13}\text{C}$	LGM $\delta^{18}\text{O}$	% GAAIW or GAABW	% GNAIW	Est. $\delta^{18}\text{O}$	Observed-Estimated $\delta^{18}\text{O}$
1268	GAAIW:GNAIW	0.6	4.20	80	20	4.28	-0.08
1627	GAAIW:GNAIW	0.9	4.30	50	50	4.25	0.05
1820	GAABW:GNAIW	1	4.40	25	75	4.38	0.03
2082	GAABW:GNAIW	0.77	4.50	39	61	4.48	0.02
2296	GAABW:GNAIW	0.55	4.52	53	47	4.57	-0.05
2500	GAABW:GNAIW	0.46	4.60	59	41	4.61	-0.01

^aProportions are estimated using $\delta^{13}\text{C}$ because of the large range in the end-member $\delta^{13}\text{C}$ values. The resulting proportions are then used to estimate the expected $\delta^{18}\text{O}$ at each water depth.

increased $\sim 0.2\text{‰}$ [Hoffman and Lund, 2012]. Northern component water (NCW) underwent the largest isotopic shift, with $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ decreasing by $\sim 1.0\text{‰}$ and $\sim 0.7\text{‰}$, respectively. Assuming HS1 end-member $\delta^{18}\text{O}$ values of 3.1‰ for NCW and 4.6‰ for SCW, the HS1 results from 1800 m to 2300 m water depth can be explained by a mixture of approximately 60% SCW and 40% NCW. Compared to the LGM proportions (Table 3), this represents a substantial reduction in the influence of NCW at the Brazil Margin. Unlike the LGM, however, the HS1 $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ pairs do not fall on a mixing line between NCW and SCW. Projecting the HS1 $\delta^{18}\text{O}$ results to the mixing line, we estimate that $\delta^{13}\text{C}$ for the mid-depth Brazil Margin sites should range from 0‰ at 2500 m to 0.3‰ at 1300 m, about $0.2\text{--}0.4\text{‰}$ lower than observed (Figure 6b).

[20] Given that the Atlantic circulation was probably not in steady state during the deglaciation, a full accounting of isotopic records in the Southwest Atlantic should consider transient changes in NCW and SCW. Unfortunately, surface water reservoir age variability of up to several hundred years in the South Atlantic and more than 1000 years in the North Atlantic [Waelbroeck et al., 2001] precludes reliable quantification of the effect of transient end-member variability on the Brazil Margin records.

4.3. Input of Abyssal Water

[21] The Brazil Margin $\delta^{13}\text{C}$ results imply that water depleted in ^{13}C invaded the mid-depth South Atlantic during the deglaciation. Because the abyssal Southwest Atlantic was characterized by low $\delta^{13}\text{C}$ during the LGM, input of water from the abyss could account for the abrupt changes at mid-depth. The flow path would presumably involve upwelling south of the Antarctic Polar Front [Marshall and Speer, 2012; Anderson et al., 2009] and the subsequent formation and northward advection of a new mid-depth water mass. Just prior to HS1, GAABW in the Brazil Basin had a $\delta^{13}\text{C}$ of $-0.2 \pm 0.2\text{‰}$ [Hoffman and Lund, 2012]. Accounting for the HS1 $\delta^{13}\text{C}$ excursions would require $40 \pm 10\%$ of the water at mid-depth to be replaced by GAABW, assuming no dilution by mixing during its transit to the Brazil Margin.

[22] Input of GAABW would also influence benthic foraminiferal $\delta^{18}\text{O}$. During the LGM, GAABW had a $\delta^{18}\text{O}$ of $4.9 \pm 0.1\text{‰}$ [Hoffman and Lund, 2012]. Rapid addition of $40 \pm 10\%$ GAABW would cause $\delta^{18}\text{O}$ to increase by $0.2 \pm 0.05\text{‰}$, yet the records at 1800 m and 2100 m instead show either no change or a small decrease from the LGM to HS1 (Figure 7). If GAABW was the source of the $\delta^{13}\text{C}$

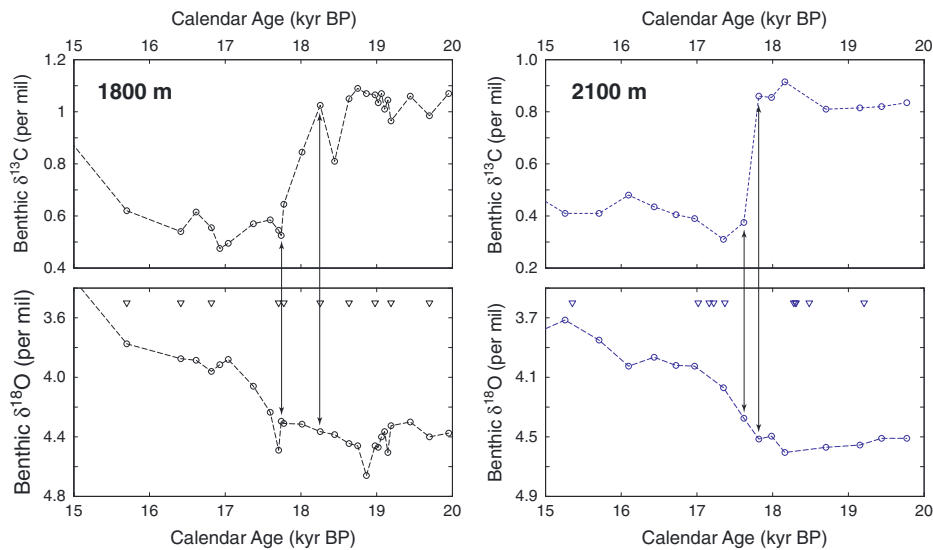


Figure 7. High resolution benthic stable isotopic records for 1800 m and 2100 m water depth at the Brazil Margin for the 15 to 20 kyr BP time interval. The time series are based on the average isotopic value at each stratigraphic level in the core. Triangles denote calendar-calibrated age control points.

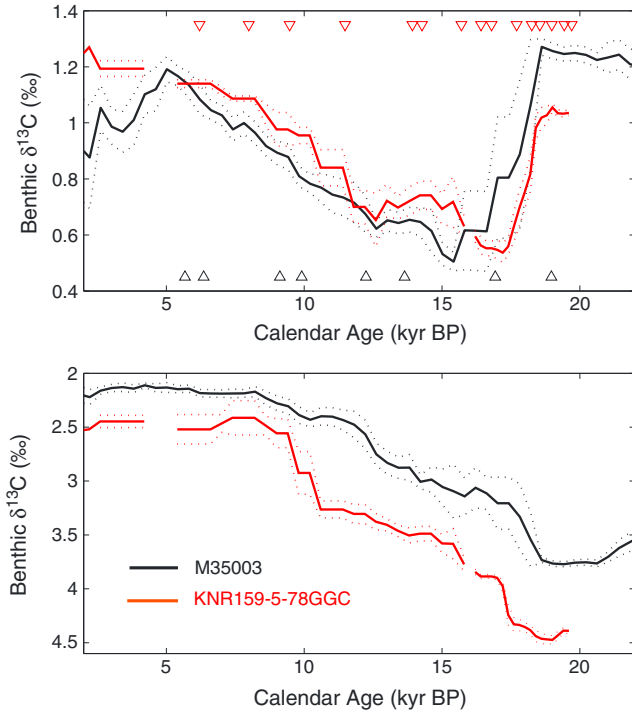


Figure 8. (Top) Radiocarbon-constrained benthic $\delta^{13}\text{C}$ time series for core 78GGC at 1800 m water depth on the Brazil Margin (red) and core M35003 at 1300 m water depth in the western Tropical Atlantic (black) [Zahn and Stuber, 2002]. Results are plotted as 2000-year running mean values (solid lines) and ± 1 SE (dotted lines). The original Zahn and Stuber [2002] age model for M35003 has been updated using CALIB 6.0 (<http://calib.qub.ac.uk/calib/>) and a ΔR of 0 ± 200 years (1σ). (Bottom) Same as top panel but for benthic foraminiferal $\delta^{18}\text{O}$.

anomalies, the associated $\delta^{18}\text{O}$ signal must have been offset by warming or the input of ^{18}O -depleted water from the surface ocean.

[23] Results from the Cape Basin suggest abyssal water in the Southeast Atlantic had a $\delta^{13}\text{C}$ of $-0.9 \pm 0.1\text{‰}$ and $\delta^{18}\text{O}$ of $4.2 \pm 0.1\text{‰}$ [Ninnemann and Charles, 2002; Waelbroeck *et al.*, 2011]. Although benthic $\delta^{13}\text{C}$ in this region may be influenced by epibenthic decay of organic matter [Mackensen *et al.*, 1993] and the $\delta^{18}\text{O}$ results may be biased by the use of common acid bath instrumentation [Ostermann and Curry, 2000; Hodell *et al.*, 2003], the potential influence of this isotopically distinct water mass must also be considered. Accounting for the Brazil Margin $\delta^{13}\text{C}$ anomalies would require $\sim 25\%$ of the water at mid-depths to originate from the Southeast Atlantic. Adding this proportion would cause only a slight ($< 0.1\text{‰}$) decrease in $\delta^{18}\text{O}$, consistent with observations (Figure 7). However, the net advective flow at 1–3 km water depth in the modern South Atlantic is eastward from the Brazil Basin to the Cape Basin, followed by entrainment in the Antarctic Circumpolar Current (ACC) [Sloyan and Rintoul, 2001]. Assuming a similar circulation pattern during the deglaciation, the isotopic signal would need to be transmitted from the Southeast Atlantic via the ACC around Antarctica with little or no dilution by mixing. Although we cannot rule out this possibility, it appears to be an unlikely explanation of the large and abrupt $\delta^{13}\text{C}$ signal at the Brazil Margin.

4.4. A New Mid-Depth Water mass

[24] Carbon isotopic results from the North and South Atlantic suggest a single ^{13}C -depleted water mass occupied mid-depths during HS1. In the western tropical North Atlantic, a region where large changes in reservoir age are unlikely, $\delta^{13}\text{C}$ dropped abruptly at approximately 18 kyr BP, reached a minimum value of $\sim 0.6\text{‰}$ during HS1, and then recovered slowly into the mid-Holocene [Zahn and Stuber, 2002] (Figure 8). This pattern is very similar to that observed at the Brazil Margin. Homogeneous $\delta^{13}\text{C}$ values are observed throughout the mid-depth western Atlantic during HS1 [Oppo and Curry, 2012]. Indeed, vertical profiles from the North and South Atlantic show that the mid-depth records are characterized by a $\delta^{13}\text{C}$ of $0.6 \pm 0.1\text{‰}$ (Figure 9a,b). This pattern is strikingly different than the LGM where the clear north-south contrast in $\delta^{13}\text{C}$ reflects the dominant influence of GNAIW in the North Atlantic. In the South Atlantic, GNAIW manifests itself as $\delta^{13}\text{C}$ maximum near 1800 m water depth.

[25] Unlike $\delta^{13}\text{C}$, benthic $\delta^{18}\text{O}$ profiles from the North and South Atlantic are very different during HS1. At the Brazil Margin, $\delta^{18}\text{O}$ ranges from 3.8‰ at 1300 m to 4.5‰ at 2500 m (Figure 9d). In the North Atlantic, $\delta^{18}\text{O}$ values are lower throughout the same depth interval, spanning from 3.1‰ to 4.1‰ (Figure 9c). At the Brazil Margin, HS1 $\delta^{18}\text{O}$ values decreased by 0.1‰ to 0.5‰ relative to the LGM, whereas in the North Atlantic, the $\delta^{18}\text{O}$ decrease is much larger, ranging from 0.5‰ to 1.0‰. The results suggest the $\delta^{18}\text{O}$ anomaly originated in the North Atlantic, perhaps due to influx of ^{18}O -depleted melt water. The different $\delta^{18}\text{O}$ histories in the two basins are also apparent in the time series in Figure 8. Throughout the LGM and deglaciation, benthic $\delta^{18}\text{O}$ in the western tropical Atlantic is consistently 0.5‰ to 0.8‰ lower than at the Brazil Margin even though the $\delta^{13}\text{C}$ history in the two locations is nearly identical. The $\delta^{18}\text{O}$ data highlight the existence of two separate water masses at mid-depth, in contrast to the $\delta^{13}\text{C}$ results. Given that $\delta^{18}\text{O}$ is a conservative water mass tracer [Lund *et al.*, 2011], it appears that another process is necessary to account for the $\delta^{13}\text{C}$ minima.

[26] What could cause a similar $\delta^{13}\text{C}$ history in the North and South Atlantic? Air-sea gas exchange with a ^{13}C -depleted atmosphere would cause the $\delta^{13}\text{C}$ in the source regions for northern and southern component water to decrease. If this were the case, the signal must have somehow been amplified given the larger oceanic $\delta^{13}\text{C}$ anomaly (Figure 5). Temperature-driven amplification [e.g., Broecker and Maier-Reimer, 1992] is unable to account for the larger oceanic change because such a process would yield opposite $\delta^{13}\text{C}$ signals in the ocean and atmosphere [Spero and Lea, 2002; Ninnemann and Charles, 1997].

[27] The timing of the Brazil Margin $\delta^{13}\text{C}$ anomalies also appears to be inconsistent with an atmospheric driver. The mean ventilation age at 2000 m water depth in the modern Southwest Atlantic is approximately 400 years [Gebbie and Huybers, 2012]. If enhanced Southern Ocean upwelling and formation of a new water mass created the $\delta^{13}\text{C}$ minima, the shift in atmospheric $\delta^{13}\text{C}$ should lead mid-depth records by several hundred years. Instead, the oceanic records either lead or are synchronous with the atmosphere (Figure 5). An

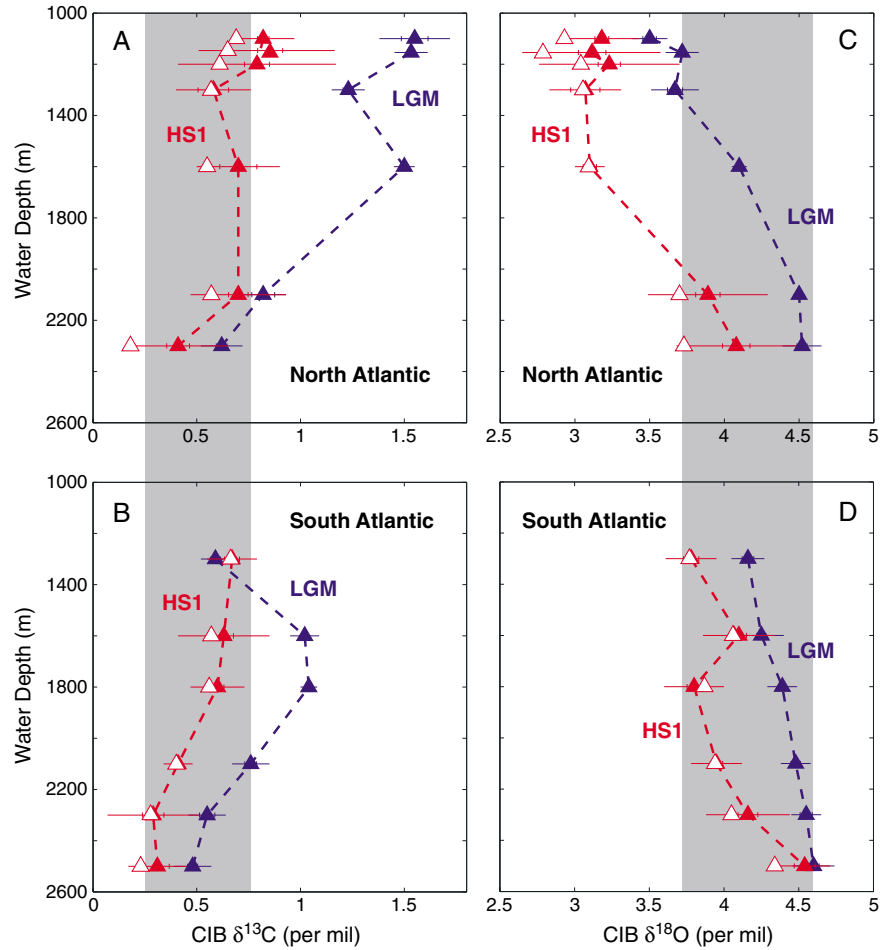


Figure 9. (Left-hand column) Vertical profiles of benthic foraminiferal $\delta^{13}\text{C}$ for the LGM (19–23 kyr BP; blue) and HS1 (red) in the North and South Atlantic. Solid red symbols are the average $\delta^{13}\text{C}$ for 14.5–17.5 kyr BP. Horizontal lines represent the \pm one-sigma uncertainty, and small vertical lines are the standard error. In most cases, the standard error is smaller than the size of the triangle symbol. Open red symbols represent the average $\delta^{13}\text{C}$ during the HS1 $\delta^{13}\text{C}$ minima in each core. The South Atlantic profiles are based on data presented in this paper while the North Atlantic profiles are compiled from published records (Table 4). (Right-hand column) Same as left-hand column except for benthic foraminiferal $\delta^{18}\text{O}$. The $\delta^{18}\text{O}$ results indicate there were two separate water masses in the North and South Atlantic during HS1 while the $\delta^{13}\text{C}$ data suggest there was a single dominant water mass that spanned the entire basin.

increase in surface ocean ΔR at the Brazil Margin in excess of 500 years is necessary for the atmosphere to feasibly lead the oceanic signal. Large shifts in ΔR seem unlikely at the latitude of the Brazil Margin where subtropical convergence causes a ΔR of 0 years today [Angulo *et al.*, 2005]. Given

age model uncertainties, establishing the exact phasing of the atmospheric $\delta^{13}\text{C}$ relative to 2000 m water depth will require the development of high-resolution planktonic $\delta^{13}\text{C}$ records from the Brazil Margin. Regardless of the relative timing, however, the magnitude of the oceanic anomalies

Table 4. Locations of Published High-Resolution Records From the North Atlantic Used in This Paper

Core	Location	Latitude ($^{\circ}\text{N}$)	Longitude ($^{\circ}\text{W}$)	Water Depth (m)	Reference
SO75-26KL	Iberian Margin	37 $^{\circ}$ 49'	09 $^{\circ}$ 30'	1099	[Zahn <i>et al.</i> , 1997]
MD01-2461	SW Ireland Shelf	51 $^{\circ}$ 45'	12 $^{\circ}$ 55'	1153	[Peck <i>et al.</i> , 2007]
M35003	Tobago Basin	12 $^{\circ}$ 5'	61 $^{\circ}$ 15'	1299	[Zahn and Stuber, 2002]
NEAP 4K	Björn Drift	61 $^{\circ}$ 30'	24 $^{\circ}$ 10'	1627	[Rickaby and Elderfield, 2005]
RAPiD-10-1P	South Iceland Rise	62 $^{\circ}$ 59'	17 $^{\circ}$ 35'	1237	[Thornalley <i>et al.</i> , 2010]
RAPiD-15-4P	South Iceland Rise	62 $^{\circ}$ 18'	17 $^{\circ}$ 8'	2133	[Thornalley <i>et al.</i> , 2010]
RAPiD-17-5P	South Iceland Rise	61 $^{\circ}$ 29'	19 $^{\circ}$ 32'	2303	[Thornalley <i>et al.</i> , 2010]

indicates the atmosphere was not the primary driver of common $\delta^{13}\text{C}$ variability in the North and South Atlantic.

4.5. Non-Conservative Behavior of $\delta^{13}\text{C}$

[28] Our discussion of water masses during the LGM and HS1 is based on the assumption advection and diffusion are the primary factors that influence benthic foraminiferal $\delta^{13}\text{C}$. Although benthic $\delta^{13}\text{C}$ at the Brazil Margin acted conservatively during the LGM and Holocene [Hoffman and Lund, 2012], it may have acted non-conservatively during the deglaciation. The enigmatic nature of the Brazil Margin isotopic results and the apparent ubiquity of the HS1 $\delta^{13}\text{C}$ anomaly in the Atlantic suggest that another source of carbon may have been involved. Biological remineralization of marine organic carbon is an unlikely culprit because it would cause $\delta^{13}\text{C}$ to be lower than expected from water mass mixing rather than higher (Figure 6b). Evaluating other potential carbon sources will require high-resolution reconstructions from a range of locations to determine whether the isotopic anomalies are consistent with an alternative reservoir.

5. Conclusions

[29] Mid-depth benthic foraminiferal records from the Brazil Margin display abrupt negative $\delta^{13}\text{C}$ anomalies similar to the atmosphere during the last deglaciation. The magnitude of the Brazil Margin $\delta^{13}\text{C}$ signal is larger than in the atmosphere, similar to the pattern in published $\delta^{13}\text{C}$ records from the North Atlantic. These findings strongly point towards the ocean as a source of the deglacial atmospheric $\delta^{13}\text{C}$ anomaly.

[30] Broadly speaking, the coherence between the Brazil Margin and atmospheric $\delta^{13}\text{C}$ records can be explained in one of two ways. One possibility is that changes in the oceanic circulation simultaneously altered the water mass distribution in the Southwest Atlantic and influenced the outgassing of ^{13}C -depleted carbon from the abyssal ocean. Alternatively, input of ^{13}C -depleted carbon from another source could have moved both the upper ocean and atmosphere towards more depleted values. We evaluate the first possibility by comparing the Brazil Margin results with stable isotopic constraints for Atlantic water masses during the LGM and HS1. During the LGM, stable isotopic results from mid-depths can be explained in terms of conservative mixing between northern and southern component waters. During HS1, however, we are unable to easily account for the Brazil Margin results with a simple two end-member mixing model. A new mid-depth water mass characterized by low $\delta^{13}\text{C}$ is apparently required.

[31] Given that GAABW had low $\delta^{13}\text{C}$ values during the LGM, it is logical to invoke input of water from the abyss as a source of ^{13}C -depleted water. By mass balance, the $\delta^{13}\text{C}$ anomalies would require a large fraction of the water at mid-depths to be pure GAABW from the Southwest Atlantic. Input of this quantity of GAABW would also cause $\delta^{18}\text{O}$ to increase, yet little change is observed. The influence of GAABW could be minimized via warming or the input of ^{18}O -depleted water, but it is unlikely that such compensation would perfectly offset the abyssal signal. Water from the deepest Southeast Atlantic could be a feasible source of

low $\delta^{13}\text{C}$ but the flow path required (from the Cape Basin to the Brazil Basin) is opposite that observed in the modern South Atlantic.

[32] Input of abyssal water may help explain the Brazil Margin results but it does little to reconcile conflicting stable isotope data in the North and South Atlantic. Similar absolute $\delta^{13}\text{C}$ values throughout the Atlantic imply that a single water mass dominated the mid-depths during HS1. However, $\delta^{18}\text{O}$ results from the same cores show a strong meridional gradient in $\delta^{18}\text{O}$, with isotopically depleted values in the north and comparatively enriched values to the south. Given that $\delta^{18}\text{O}$ is a conservative tracer, these data suggest two distinct water masses influenced the mid-depth Atlantic during HS1. Benthic foraminiferal $\delta^{13}\text{C}$, on the other hand, is a non-conservative tracer that is influenced by advection, diffusion, and the input of carbon from other sources. Given that biological remineralization of marine organic matter does not appear to be a viable explanation of the $\delta^{13}\text{C}$ anomalies, another source of carbon external to the ocean-atmosphere system may have been involved.

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