Response of eastern tropical Atlantic central waters to Atlantic meridional overturning circulation changes during the Last Glacial Maximum and Heinrich Stadial 1

Enqing Huang,1 Stefan Mulitza,1 André Paul,1,2 Jeroen Groeneveld,1,2 Stephan Steinke,1 and Michael Schulz1,2

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Benthic foraminiferal δ¹⁸O and Mg/Ca of sediment cores off tropical NW Africa are used to study the properties of Atlantic central waters during the Last Glacial Maximum (LGM) and Heinrich Stadial 1 (HS1). We combined our core top data with published results to develop a new Mg/Ca-temperature calibration for Planulina ariminensis, which shows a Mg/Ca-temperature sensitivity of 0.19 mmol/mol per °C. Estimates of the LGM and HS1 thermocline temperatures are comparable to the present-day values between 200 and 400 m water depth, but were 1.2–1.5 °C warmer at 550–570 m depth. The HS1 thermocline waters (200–570 m depth) did not show any warming relative to the LGM. This is in contrast to previous climate model studies, which concluded that tropical Atlantic thermocline waters warmed significantly when Atlantic meridional overturning circulation was reduced. However, our results suggest that thermocline temperatures of the northeastern tropical Atlantic show no pronounced sensitivity to changes in the thermohaline circulation during glacial periods. In contrast, we find a significant increase in thermocline-water salinity during the LGM (200–550 m depth) and HS1 (200–400 m depth) with respect to the present-day, which we relate to changes in the wind-driven circulation. We infer that the LGM thermocline (200–550 m depth) and the HS1 upper thermocline (200–400 m depth) in the northeastern tropical Atlantic was ventilated by surface waters from the North Atlantic rather than the southern-sourced waters. This suggests that the frontal zone between the modern South Atlantic and North Atlantic Central Waters was probably shifted southward during the LGM and HS1.

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1. Introduction

[2] The upper permanent thermocline waters of the tropical and subtropical Atlantic, usually termed central water masses, are a key component of the upper branch of the Atlantic meridional overturning circulation (AMOC). The renewal of thermocline waters is accomplished by the subduction of surface waters in the mid-to-high latitudes [e.g., Luyten et al., 1983]. Driven by downward Ekman pumping and mixed-layer deepening during wintertime, surface waters are transformed into thermocline waters and subsequently move along isopycnal surfaces toward lower latitudes [Poole and Tomczak, 1999]. By the same mechanism, surface waters from the subtropical gyre can also subduct and ventilate the shallower tropical thermocline, which are subsequently upwelled near the equator and return to the subduction areas forming a closed subtropical cell [e.g., Snowden and Molinari, 2003]. The properties of the ventilated thermocline are therefore sensitive to changes in the atmospheric circulation and ocean surface conditions in the formation areas.

[3] A variety of model simulations suggest that ocean thermocline depths could rapidly adjust to a change in the AMOC geometry and strength. For example, a signal of deep water formation changes in the northern North Atlantic can be rapidly transferred to the equatorial Atlantic in a few years or decades via the propagation of planetary waves [e.g., Huang et al., 2000; Goodman, 2001; Cessi et al., 2004]. A reduction of the North Atlantic deep water (NADW) production can cause a deepening of the tropical Atlantic thermocline [e.g., Huang et al., 2000; Timmermann et al., 2005]. This prediction has later been supported by modern observational data [Zhang, 2007] and paleoceanographic records.
Figure 1. Meridional section of seawater salinity (colors) and potential density (contour lines) along the eastern Atlantic Ocean. The position of the section is indicated in the panel on the right. Data is from the World Ocean Atlas 2009 (WOA2009) [Antonov et al., 2010; Locarnini et al., 2010] and the figure was made by Ocean Data View 4 (R. Schlitzer, available at http://odv.awi.de). Dots denote core locations. The dashed line outlines the Cape Verde Frontal Zone, which represents the transition between the SACW and NACW.

[Lopes dos Santos et al., 2010]. Thermocline temperatures of the northern tropical Atlantic have been found warmer, both on multidecadal [Zhang, 2007] and glacial-interglacial time scales [Lopes dos Santos et al., 2010] when NADW flux was reduced. Modeling studies also predict a pronounced warming of around 1–3°C at the thermocline depths of the tropical Atlantic when the AMOC strength and the NADW production are reduced by freshwater perturbations in the North Atlantic [Zhang, 2007; Chang et al., 2008; Chiang et al., 2008].

[6] Associated with the thermocline adjustment, additional processes also contribute to the heat accumulation in the tropical Atlantic during the AMOC slowdown. First, stronger northeast trade winds over the tropical Atlantic could strengthen downward mixing of heat [Chiang et al., 2008]. Second, because of the strong northward branch of the AMOC in the present upper ocean, the formation of the equatorward branch of the northern Atlantic subtropical cell is suppressed [e.g., Hazeleger and Drijfhout, 2006]. However, weakened AMOC could invigorate the northern Atlantic subtropical cell leading to a transport of warm and salty subtropical-gyre water into the tropical thermocline [Chang et al., 2008; Wan et al., 2010]. Third, a slowdown of the AMOC can trap heat in the tropics and the Southern Hemisphere [Chiang et al., 2008]. Therefore, the tropical thermocline waters are heated up due to a reduction in the AMOC through the abovementioned processes. Because of its high sensitivity and rapid response, thermocline temperature changes in the northern tropical Atlantic are proposed as a possible indicator of the past and present AMOC variations [Zhang, 2007; Lopes dos Santos et al., 2010].

[5] The interpretation of thermocline temperature changes in response to AMOC changes could be complicated by many other factors, such as changes in preformed seawater properties of the subduction regions and latitudinal shifts in the isopycnal outcrops. Thermocline waters of the western North Atlantic subtropical gyre were estimated to be 4°C cooler during the Last Glacial Maximum (LGM, 23–19 ka BP), which has been attributed to significantly cooler conditions in the subduction regions at that time [Slowey and Curry, 1995]. A model study also predicts an equatorward shift of the outcrop regions of isopycnal surfaces in both hemispheres during the LGM, which led to a shoaling of the ventilated thermocline depths [Paul and Schäfer-Neth, 2003, 2004]. Therefore, changes in glacial climate boundary conditions might have significantly influenced tropical thermocline temperatures, and could obscure effects associated with past changes in the AMOC. In order to assess the net result induced by different processes, and to test thermocline temperature changes as a proxy for past AMOC variations, it is crucial to obtain reliable temperature reconstructions for time periods when climate boundary condition were relatively similar whereas the AMOC strength experienced significant changes.

[6] To this end, we utilized benthic foraminiferal δ18O and Mg/Ca to study thermocline-water temperatures and salinities in the northeastern tropical Atlantic during the LGM and Heinrich Stadial 1 (HS1, 17.5–14.7 ka BP). We find that the HS1 thermocline temperatures (200–570 m water depth) did not show any significant warming relative to the LGM. A significant decline in the AMOC intensity from the LGM to HS1 [e.g., McManus et al., 2004; Gherardi et al., 2009] apparently did not leave its imprint in thermocline temperatures of the northeastern tropical Atlantic. Moreover, we find a significant increase in thermocline-water δ18O and salinity both during the LGM (200–550 m depth) and HS1 (200–400 m depth) relative to the late Holocene. Thermocline waters of the northeastern tropical Atlantic were probably influenced by the subducted salty surface waters from the North Atlantic during these two time periods rather than by surface waters from the Southern Hemisphere.

2. Material and Oceanographic Setting

[7] Four gravity cores and their accompanying multicores from the continental slope off NW Africa were analyzed (Figure 1 and Table 1). They were recovered from water depths between 300 and 670 m during the Meteor-Cruise M65/1 in 2005 [Mulitza et al., 2006]. Core material consists
of sandy mud with abundant shells or shell fragments of various microfossils.

[9] Modern bottom waters at the coring locations are influenced by the South Atlantic Central Water (SACW). The temperature-salinity properties of subsurface waters at our coring locations are consistent with that of the SACW (Figure 2). Within the isopycnal surfaces of \( \sigma_0 = 26.3 \) and \( \sigma_0 = 27.3 \), the in situ measurements of seawater temperatures and salinity from four conductivity-temperature-depth (CTD) profiles fit well in a linear relationship (Figure 2), which is characteristic of the Atlantic central waters [Poole and Tomczak, 1999]. The upper part of the SACW (roughly between 100 and 400 m in the tropics) is formed near the subtropical front in the southwestern Atlantic, while the lower part (>400 m) is derived from the Indian Central Water [Poole and Tomczak, 1999; Stramma and Schott, 1999]. Bottom water over the deepest cores GeoB9535–4/5 is also partly influenced by the Antarctic Intermediate Water (Figures 1 and 2). North to our core locations, thermocline waters are influenced by the North Atlantic Central Water (NACW). The transition between these two central water masses is between 20°N and 25°N off the African coast, forming the so-called Cape Verde Frontal Zone in the eastern tropical Atlantic. The SACW is colder and fresher than the NACW within the same isopycnal surfaces, e.g., the SACW at our coring sites is 3.1–3.6°C cooler and 0.7–0.9 psu fresher than the NACW at 30°N within the isopycnal surfaces of \( \sigma_0 = 26.75 \) and \( \sigma_0 = 27.25 \) (Figures 1 and 2). Along the coast, the SACW penetrates further northward with increasing water depth (Figure 1) [Arhan et al., 1994; Poole and Tomczak, 1999].

3. Methods

3.1. X-Ray Fluorescence Core Scanning

[9] The chemical element composition of the core material was measured by the X-Ray Fluorescence core scanner at MARUM, University of Bremen. The X-ray tube voltage and detector sensibility allows the analysis of elements from potassium through strontium [Röhl and Abrams, 2000]. Split core sections were analyzed at a resolution of 1 or 2 cm. The resulting data are element intensities in counts per second, which were further normalized as follows:

\[
\text{Percentage (element)} = \frac{\text{counts (element)}}{\text{total counts (K, Ca, Ti, Mn, Fe, Cu, Sr)}} \times 100\% . \tag{1}
\]

In this study we use the calcium-percentage records to correlate the stratigraphy in each core (Figure 3).

3.2. Radiocarbon Dating

[10] About 8–15 mg of a mixture of shallow-dwelling planktonic foraminifera for each sample was picked for accelerator mass spectrometry (AMS) \(^{14}\)C analyses performed at the Poznan Radiocarbon Laboratory (Table 2). Radiocarbon ages of core GeoB9535–4 were presented previously by Collins et al. [2011]. AMS \(^{14}\)C ages were converted to calendar ages using the “Fairbanks0107” calibration curve [Fairbanks et al., 2005], assuming a constant oceanic surface water reservoir age of 400 years.

[11] We dated one multicore core top sample (GeoB9533–3), which gives an age of 221 ± 83 years BP (Table 2). For each gravity core, the core top age is determined by radiocarbon

![Figure 2. The temperature-salinity diagram of water masses at our core locations and several selected locations of the Atlantic Ocean. The CTD data agree well with the WOA2009 annual-mean data (shown in a thick gray curve) [Antonov et al., 2010; Locarnini et al., 2010] from the same locations. The potential density lines are also shown in thin gray curves.](image-url)
dating, while the LGM and HS1 intervals are basically constrained by two radiocarbon ages, respectively (Figure 3). The sedimentation rate in each core varies between 2 and 3 cm/kyr during the Holocene. However, the sedimentation rates are much higher during the LGM and HS1 (approximately 8–36 cm/kyr). The age of core top samples of gravity core GeoB9533–2 and GeoB9535–4 [Collins et al., 2011] is younger than 2000 years BP. For gravity core GeoB9532–2, we dated the sediment at core depth of 5 cm, which gives an age of 2946 ± 19 years BP. Based on the Holocene sedimentation rate along this core, the age of the core top sample should also be younger than 2000 years BP. In core GeoB9533–2, a 14C age reversal occurs at 120 cm core depth. Based on the visual correlation of four downcore

Figure 3. Downcore calcium percentage records from four gravity cores used in this study. Radiocarbon dates are denoted by arrows in each plot.

<table>
<thead>
<tr>
<th>Lab Number</th>
<th>Core</th>
<th>Sample Depth (cm)</th>
<th>Dating Species</th>
<th>14C Age (years, ±1σ Uncertainty)</th>
<th>Calendar Age (years BP, ±1σ Uncertainty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poz-39025</td>
<td>GeoB9532–2</td>
<td>5</td>
<td>G. ruber, G. sacculifer</td>
<td>3245 ± 35</td>
<td>2946 ± 49</td>
</tr>
<tr>
<td>Poz-39027</td>
<td>GeoB9532–2</td>
<td>80</td>
<td>G. ruber, G. sacculifer, O. universa</td>
<td>14830 ± 140</td>
<td>17020 ± 266</td>
</tr>
<tr>
<td>Poz-32105</td>
<td>GeoB9532–2</td>
<td>95</td>
<td>G. ruber, G. sacculifer, O. universa</td>
<td>15060 ± 110</td>
<td>17432 ± 252</td>
</tr>
<tr>
<td>Poz-32106</td>
<td>GeoB9532–2</td>
<td>115</td>
<td>G. ruber, G. sacculifer, O. universa</td>
<td>17170 ± 120</td>
<td>19919 ± 158</td>
</tr>
<tr>
<td>Poz-39024</td>
<td>GeoB9532–2</td>
<td>135</td>
<td>G. ruber, G. sacculifer</td>
<td>19270 ± 110</td>
<td>22450 ± 118</td>
</tr>
<tr>
<td>Poz-32107</td>
<td>GeoB9533–3</td>
<td>0</td>
<td>G. ruber, G. sacculifer, O. universa</td>
<td>605 ± 30</td>
<td>221 ± 83</td>
</tr>
<tr>
<td>Poz-39028</td>
<td>GeoB9533–2</td>
<td>0</td>
<td>G. ruber, G. sacculifer</td>
<td>2375 ± 30</td>
<td>1917 ± 33</td>
</tr>
<tr>
<td>Poz-39029</td>
<td>GeoB9533–2</td>
<td>100</td>
<td>G. ruber, G. sacculifer</td>
<td>15160 ± 80</td>
<td>17622 ± 215</td>
</tr>
<tr>
<td>Poz-32134</td>
<td>GeoB9533–2</td>
<td>120</td>
<td>G. ruber, G. sacculifer, O. universa</td>
<td>14850 ± 80</td>
<td>17046 ± 184</td>
</tr>
<tr>
<td>Poz-32135</td>
<td>GeoB9533–2</td>
<td>140</td>
<td>G. ruber, G. sacculifer, O. universa</td>
<td>15630 ± 90</td>
<td>18473 ± 127</td>
</tr>
<tr>
<td>Poz-39031</td>
<td>GeoB9533–2</td>
<td>170</td>
<td>G. ruber, G. sacculifer</td>
<td>18250 ± 100</td>
<td>21153 ± 166</td>
</tr>
<tr>
<td>Poz-39034</td>
<td>GeoB9534–5</td>
<td>0</td>
<td>G. ruber, G. sacculifer</td>
<td>3015 ± 35</td>
<td>2742 ± 16</td>
</tr>
<tr>
<td>Poz-39038</td>
<td>GeoB9534–5</td>
<td>70</td>
<td>G. ruber, G. sacculifer</td>
<td>13160 ± 110</td>
<td>14865 ± 157</td>
</tr>
<tr>
<td>Poz-39041</td>
<td>GeoB9534–5</td>
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<td>G. ruber, G. sacculifer</td>
<td>14060 ± 80</td>
<td>15900 ± 142</td>
</tr>
<tr>
<td>Poz-32136</td>
<td>GeoB9534–5</td>
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<td>G. ruber, G. sacculifer, O. universa</td>
<td>16070 ± 100</td>
<td>18862 ± 107</td>
</tr>
<tr>
<td>Poz-32137</td>
<td>GeoB9534–5</td>
<td>125</td>
<td>G. ruber, G. sacculifer, O. universa</td>
<td>17550 ± 120</td>
<td>20328 ± 122</td>
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</tbody>
</table>
calcium-percentage records (Figure 3), we consider that the younger radiocarbon age at 120 cm is unreliable and therefore rejected. Table 3 lists all multicore core top samples and gravity-core core top samples younger than 2000 years BP. The estimated calcification temperatures of benthic foraminifera derived from benthic δ18O agree with modern bottom water temperatures at each core location. This might suggest that the mean hydrographic conditions at our coring locations over the past two thousand years are similar to the present-day. Therefore, core top data of all multicores and several gravity cores (core top samples are younger than 2000 years BP from cores GeoB9532–2, 9533–2 and 9535–4) were used for Mg/Ca-temperature and calcite δ18O calibrations in this study.

3.3. Foraminiferal δ18O and Mg/Ca Analyses

Benthic foraminifera Planulina ariminensis were picked for stable isotopes (4–8 specimens, >400 μm) and Mg/Ca (25–40 specimens, >400 μm) analyses at MARUM, University of Bremen. P. ariminensis is an epifaulal species with an elevated microhabitat [Lutz and Thiel, 1989]. Oxygen isotopes were measured using a Finnigan MAT 252 mass spectrometer equipped with a automatic carbonate preparation device. The isotopic results were converted into international Pee Dee Belemnite (PDB) scale by using the National Bureau of Standards (NBS) 18 and 19 standards. Internal precision for δ18O analysis, based on replicates of an internal limestone standard, was better than ±0.07%.

For Mg/Ca analyses, foraminiferal tests were crushed using two glass plates in order to open the test chambers and then were cleaned following the cleaning protocol of Barker et al. [2003]. Foraminiferal test fragments were rinsed with deionized water and methanol for a few times to remove clays. Between each rinse, samples were ultrasonicated for one minute. After adding an oxidizing reagent (100 μl 30% H2O2 buffered with 10 ml 0.1 M NaOH), samples were put in a sub-boiling water bath for 10 min to remove organic matter. Sample vials were removed from the water bath every 2.5 min in order to release any gaseous build-up by rapping on the vials. The oxidizing step was repeated after replacement of the oxidizing reagent. Thereafter, samples were transferred to new clean vials. After a weak acid leach (0.001 M QD HNO3), samples were dissolved in 0.075 M QD HNO3. The solution was further centrifuged (10 min., 6000 rpm) to remove any insoluble remains and then diluted with deionized water. Finally, the solution was analyzed on a Perkin-Elmer Optima 3300RL ICP-OES equipped with autosampler and ultrasonic nebulizer.

Instrumental precision of the ICP-OES was determined by analyzing an in-house standard solution with a Mg/Ca value of 2.93 mmol/mol and an international limestone standard of ECRM 752–1 with a reported Mg/Ca value of 3.75 mmol/mol [Greaves et al., 2008]. Both standards are matrix-matched with the samples. The in-house standard was run after every five samples showing a long-term standard deviation of ±0.04 mmol/mol. The ECRM 752–1 standard was run twice before analyzing each batch of 50 samples showing a long-term mean value of 3.81 mmol/mol and a standard deviation of ±0.04 mmol/mol. The analytical precision, based on three replicate measurements per analysis, was 0.07% for Mg/Ca (n = 136), while mean reproducibility of the samples (n = 14; separately cleaned and analyzed during different ICP-OES sessions) was ±0.05 mmol/mol (±1 standard deviation). Al/Ca was used to monitor contamination of clays, and Fe/Ca and Mn/Ca to monitor contamination by Fe/Mn oxides and Fe/Mn-rich carbonate coatings. The results show that our Mg/Ca data are not contaminated as the concentrations of Al, Fe and Mn were all below detection limits.

3.4. Planktonic Foraminifera Fragmentation Index

Foraminiferal samples were split into an aliquot containing >250 specimens. Numbers of fragments and complete tests of planktonic foraminifera were counted. The fragmentation index was calculated after [Le and Shackleton, 1992]:

\[
\text{Fragmentation index} = (\text{Fr}/8)/(\text{Fr}/8 + \text{CT})*100\%,
\]

where Fr is number of test fragments of planktonic foraminifera, and CT is number of complete tests of planktonic foraminifera.

3.5. Estimate of Oxygen Isotopic Equilibrium

The predicted δ18O of calcite (Table 3) was calculated from the equation by Shackleton [1974] (the quadratic term in the original equation has only a small effect and was therefore ignored in this study):

\[
\delta^{18}O_{\text{calcite}} = (16.9 - \text{Temperature})/4 + \delta^{18}O_{\text{seawater}} - 0.27.
\]

where temperature is the mean value of four CTD stations GeoB9532–4, 9533–4, 9534–1 and 9535–1. As we do not have any δ18Oseawater measurements of in situ seawater samples, we converted the mean salinity data from four CTD stations into δ18Oseawater based on the modern δ18Oseawater–salinity relationship of the Atlantic central waters (Figure 4):

\[
\delta^{18}O_{\text{seawater}} = (0.46 \pm 0.03) \text{ Salinity} - (15.85 \pm 1.02).
\]

The uncertainty in the coefficients of equation (4) is the standard error. The CTD data extend to a maximum water depth of 628 m. For water below this depth, we extracted annual-mean temperature and salinity data from the WOA2009 database for our calculation [Antonov et al., 2010; Locarnini et al., 2010].

3.6. Seawater δ18O and Paleo-Salinity Estimates

We used the equation after Shackleton [1974]:

\[
\delta^{18}O_{\text{seawater}} = \delta^{18}O_{\text{calcite}} + (\text{Temperature} - 16.9)/4 + 0.27 + 0.22,
\]

to estimate past changes in seawater δ18O. The constant 0.22 ± 0.13‰ is the average offset between our core top P. ariminensis b18O and the predicted b18O of calcite (Table 3). Paleo-salinity estimates were calculated using the equation suggested by Schäfer-Neth and Paul [2004],

\[
\text{Salinity} = \Delta \text{Salinity}_{\text{glacial}} + A*(\delta^{18}O_{\text{seawater}} - \delta^{18}O_{\text{glacial}}) + B,
\]
<table>
<thead>
<tr>
<th>Core</th>
<th>Water Depth (m)</th>
<th>Sample Depth (cm)</th>
<th>P. ariminensis Mg/Ca (mmol/mol)</th>
<th>P. ariminensis δ¹⁸O (PDB, ‰)</th>
<th>Temperature (°C)</th>
<th>Salinity (psu)</th>
<th>Δ[CO₃²⁻/CO₂] calcite (µmol/kg)</th>
<th>Predicted δ¹⁸O (PDB, ‰)</th>
<th>Δδ¹⁸O (Predicted - Measurement)</th>
<th>Calcification Temperature (°C)</th>
<th>ΔT (°C)</th>
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<tbody>
<tr>
<td>GeoB9532-1</td>
<td>301</td>
<td>0–1</td>
<td>2.11</td>
<td>1.24</td>
<td>10.7</td>
<td>35.1</td>
<td>53</td>
<td>1.58</td>
<td>0.34</td>
<td>11.13</td>
<td>0.41</td>
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<td>0–1</td>
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<td>10.7</td>
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<td>53</td>
<td>1.58</td>
<td>0.22</td>
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<tr>
<td>GeoB9532-2</td>
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<td>1.92</td>
<td>1.31</td>
<td>10.3</td>
<td>35.1</td>
<td>51</td>
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<td>0.27</td>
<td>10.83</td>
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<tr>
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<td>35.0</td>
<td>43</td>
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<td>GeoB9533-2</td>
<td>384</td>
<td>0</td>
<td>1.84</td>
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<td>0.01</td>
<td>5.69</td>
<td>0.89</td>
</tr>
<tr>
<td>GeoB9534-4</td>
<td>493</td>
<td>0</td>
<td>1.52</td>
<td>2.16</td>
<td>7.9</td>
<td>34.8</td>
<td>35</td>
<td>2.16</td>
<td>0.00</td>
<td>5.69</td>
<td>−0.96</td>
</tr>
<tr>
<td>GeoB9535-5</td>
<td>666</td>
<td>0–1</td>
<td>1.96</td>
<td>6.6</td>
<td>34.7</td>
<td>31</td>
<td>2.44</td>
<td>0.48</td>
<td>7.56</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>GeoB9535-4</td>
<td>669</td>
<td>2</td>
<td>2.42</td>
<td>6.6</td>
<td>34.7</td>
<td>31</td>
<td>2.44</td>
<td>0.02</td>
<td>5.69</td>
<td>−0.89</td>
<td></td>
</tr>
</tbody>
</table>

Mean Value: 0.22

Standard Deviation (±1σ): 0.13

aΔ[CO₃²⁻/CO₂] was calculated by the CO2sys.xls program [Lewis and Wallace, 2006].
bΔδ¹⁸O (Predicted - Measurement) is the difference between the predicted δ¹⁸O of calcite and the P. ariminensis δ¹⁸O.
cThe calcification temperature is calculated after equation (5).
dΔT is the difference between the calcification temperature and the bottom water temperature.
eMean values of CTD stations GeoB9532-4, 9533-4, 9534-1, 9535-1.
fData from the WOA2009 [Antonov et al., 2010; Locarnini et al., 2010].
Figure 4. Modern $\delta^{18}O_{\text{seawater}}$-salinity relationship of Atlantic central water masses. Data was selected from a global database of seawater $\delta^{18}O$ [Schmidt, 1999b; Bigg and Rohling, 2000; G. A. Schmidt et al., Global Seawater Oxygen-18 Database v1.21, 1999, available at http://data.giss.nasa.gov/o18data/] using the interval [5.9°C; 16.2°C] for temperature and [34.4 psu; 35.8 psu] for salinity [Poole and Tomczak, 1999].

where $A = 2.17$, $B = 34.46$ were adopted from equation (4), assuming that the modern $\delta^{18}O_{\text{seawater}}$-salinity is also applicable for the last glacial period. $\delta^{18}O_{\text{glacial}}$ is the glacial increase in global mean seawater $\delta^{18}O$ due to the buildup of continental ice sheets. $\delta^{18}O_{\text{glacial}}$ equals to $1.0 \pm 0.1%o$ during the LGM [Schrag et al., 2002] when the sea level was 120 m lower than the present [Peltier and Fairbanks, 2006]. If we applied the proportion of 120 m/1.0%o to HS1 when the sea level was 100 m lower relative to the present-day [Peltier and Fairbanks, 2006], then $\delta^{18}O_{\text{glacial}}$ is estimated to be roughly 0.83% during HS1. $\Delta \text{Salinity}_{\text{glacial}}$ is the glacial increase in the global mean seawater salinity due to the sea level lowering and a decrease in the ocean volume. It can be calculated as

$$\Delta \text{Salinity}_{\text{glacial}} = 34.7^* \Delta/(3800 - \Delta),$$

where $\Delta$ is the mean sea level change in m [Schmidt, 1999a]. $\Delta \text{Salinity}$ is thus approximately 1.1 psu during the LGM and 0.9 psu during HS1. We followed the method described in Schmidt [1999a] to calculate the uncertainty of seawater $\delta^{18}O$ and salinity estimates. The following error sources are taken into account: the duplicated measurements of $P. \text{ariminensis}$ $\delta^{18}O$ show a standard error of $\pm 0.1%o$; the core top $P. \text{ariminensis}$ $\delta^{18}O$ shows a nearly constant offset toward lower values from the predicted $\delta^{18}O$ of calcite by $0.22 \pm 0.13%$ (Table 3), $\pm 0.13%o$ was therefore taken into account; the Mg/Ca-temperature estimate has a standard error of $\pm 0.6$°C (see section 4.2). For glacial seawater $\delta^{18}O$ estimate, we still need to include the error of $\delta^{18}O_{\text{glacial}}$, which is $\pm 0.1%o$ for the LGM [Schrag et al., 2002] but is unknown for the HS1 period. Therefore, the standard error of the LGM and the core top seawater $\delta^{18}O$ estimate is $\pm 0.32%o$ and $\pm 0.30%o$, respectively.

The standard error of equation (4) is $\pm 0.12%o$, and the error for the LGM $\Delta \text{Salinity}$ estimate is $\pm 0.05$ psu (the LGM sea level is estimated to be 120 $\pm$ 5 m lowering relative to the present-day [Peltier and Fairbanks, 2006]). Therefore, the standard error of the core top and the LGM salinity estimate is $\pm 0.70$ psu and $\pm 0.74$ psu, respectively. It is practically impossible to calculate the errors of the HS1 seawater $\delta^{18}O$ and salinity estimates. We simply assume that they are equal to the errors of the LGM estimates. However, since the glacial and the deglacial $\delta^{18}O_{\text{seawater}}$-salinity relationships were possibly different from the present-day, the standard errors of the LGM and HS1 seawater $\delta^{18}O$ and salinity estimates could be even larger [Schmidt, 1999a].

3.7. Estimates of Thermocline-Water $\Delta[CO_3^{2-}]$ Values

Thermocline-water $\Delta[CO_3^{2-}]$ values are calculated using the CO2sys_xls program [Lewis and Wallace, 2006]. Input parameters of temperature, salinity, pressure, total silicate and total phosphorous were taken from the WOA2009 [Antonov et al., 2010; Garcia et al., 2010; Locarnini et al., 2010], total alkalinity and total CO2 are from the GLODAP database [Key et al., 2004]. When calculating thermocline-water $\Delta[CO_3^{2-}]$ of the northeastern tropical Atlantic, temperature and salinity of the in situ CTD data (Figure 2) are used instead of those from the World Ocean Atlas 2009 [Antonov et al., 2010; Locarnini et al., 2010]. The equilibrium constants of $K_1$ and $K_2$ were taken from Mehrbach et al. [1973] refitted later by Dickson and Millero [1987]. The dissociation constant for $K_{i\text{HSO}_4}$ is from Dickson [1990]. $[CO_3^{2-}]_{\text{saturation}}$ at a given location and water depth is calculated by $[CO_3^{2-}]_\Omega$, where $\Omega$ is the solubility ratio of calcite. $\Delta[CO_3^{2-}]$ is further obtained by calculating $[CO_3^{2-}]_\Omega$ – $[CO_3^{2-}]_{\text{saturation}}$.

4. $P. \text{ariminensis}$ Mg/Ca-Temperature Calibration

4.1. Evaluating $P. \text{ariminensis}$ Mg/Ca as a Proxy for Thermocline-Water Temperature

Benthic foraminiferal Mg/Ca allows for reconstruction of bottom water temperatures. Earlier studies have established an exponential relationship between $Cibicidoides$ spp. Mg/Ca and temperatures [Rosenthal et al., 1997; Lear et al., 2002; Martin et al., 2002]. However, a later study suggested a strong linear dependence of $Cibicidoides$ pachyderma Mg/Ca on temperature within the temperature range from 6 to 19°C [Marchitto et al., 2007]. The earlier exponential fit between $Cibicidoides$ Mg/Ca and temperatures was probably biased by warm water samples from the Little Bahamas Bank, where foraminiferal tests were contaminated by secondary high-Mg calcite overgrowth [Marchitto et al., 2007; Curry and Marchitto, 2008]. Recent studies reveal that a linear regression between Mg/Ca and temperatures fits for a variety of benthic foraminiferal species [e.g., Rosenthal et al., 2006, 2011; Bryan and Marchitto, 2008; Elderfield et al., 2010]. Moreover, the published exponential relationship of benthic Mg/Ca-temperature [e.g., Rathmann et al., 2004; Healey et al., 2008] could actually be replaced by linear ones. Large inter-genus and inter-species differences in Mg/Ca have also been observed [e.g., Elderfield et al., 2006]. The Mg/Ca-temperature
sensitivity varies from 0.03 mmol/mol per °C for *Hoeeglunda elegans* [Bryan and Marchitto, 2008] to 0.40 mmol/mol per °C for *Hyalinea balthica* [Rosenthal et al., 2011]. Therefore, it is essential to use a species-specific Mg/Ca-temperature calibration rather than a multispecies approach.

[23] An increasing number of studies suggested that the Mg/Ca of benthic foraminifera is not only a function of bottom water temperature but also can be affected by the carbonate-ion saturation state ($\Delta[CO_3^{2-}]$). At the low temperature end (<3°C), the slope of the Mg/Ca-temperature calibration is steeper than that at the high temperature end [Martin et al., 2002; Elderfield et al., 2006; Healey et al., 2008]. This was attributed to a considerable influence of $\Delta[CO_3^{2-}]$ on the Mg uptake of benthic foraminifera [Elderfield et al., 2006; Yu and Elderfield, 2008]. A global ocean data compilation reveals that the Mg/Ca of the epi-benthic species *Cibicidoides wuellerstorfi* from water depths with $\Delta[CO_3^{2-}]$ values below 25 μmol/kg, is positively correlated with ambient seawater $\Delta[CO_3^{2-}]$, showing a sensitivity of 0.008–0.010 mmol/mol per μmol/kg [Elderfield et al., 2006; Healey et al., 2008; Raitzsch et al., 2008; Yu and Elderfield, 2008]. The influence of $\Delta[CO_3^{2-}]$ on the benthic Mg/Ca, therefore, limits the application of the benthic Mg/Ca for reconstruction of temperatures <3°C.

[24] A few studies suggest that there might exist a $\Delta[CO_3^{2-}]$ threshold for changes in benthic foraminiferal Mg/Ca. The current data set indicates that only when $\Delta[CO_3^{2-}]<25$ μmol/kg and $\Delta[CO_3^{2-}]<15$ μmol/kg, the carbonate-ion effect plays an important role on the Mg/Ca values of calcareous species *Cibicidoides wuellerstorfi* [Yu and Elderfield, 2008] and aragonitic species *Hoeeglunda elegans* [Rosenthal et al., 2006], respectively. Yet it is unknown whether such a threshold also exists for the calcareous species *P. ariminensis* and if so, how large the threshold is. Thermocline waters in the North Atlantic are usually supersaturated or near-saturated with carbonate, e.g., bottom water $\Delta[CO_3^{2-}]$ ranges between 31 and 53 μmol/kg at our coring locations (Table 3). The benthic Mg/Ca from thermocline waters might not be complicated by changes in seawater $\Delta[CO_3^{2-}]$ and therefore a promising proxy for reconstruction of thermocline temperatures [e.g., Bamberg et al., 2010]. Nevertheless, an estimate of a possible influence of the carbonate-ion effect on the benthic Mg/Ca samples from thermocline waters is still necessary.

[25] At thermocline water depths, bottom water temperature and $\Delta[CO_3^{2-}]$ are usually well correlated. It is thus difficult to disentangle the effects of temperature and $\Delta[CO_3^{2-}]$ on Mg/Ca [Marchitto et al., 2007]. One solution is to collect samples of benthic foraminifera from areas with different bottom water $\Delta[CO_3^{2-}]$ values but same temperatures. We compare published *P. ariminensis* Mg/Ca data from the Florida Straits [Bryan and Marchitto, 2008] and the Gulf of California [Lear et al., 2002] with our new data from the northeastern tropical Atlantic. Modern thermocline waters of the Florida Straits, the Gulf of California and the northeastern tropical Atlantic between 200 and 700 m have a similar thermal structure (Figure 5a) but very different $\Delta[CO_3^{2-}]$ values (Figure 5b). Therefore, not only do core top samples of these three areas allow to test the influence of temperature and $\Delta[CO_3^{2-}]$ on the benthic Mg/Ca, but also they allow an intercomparison of regional Mg/Ca-temperature calibrations. Our new data (Table 3) cover a temperature range from 7.9 to 10.7°C. Except five samples of the Gulf of California that are from water depths below 500 m with relatively low $\Delta[CO_3^{2-}]$ values of $-$6 to $+$5 μmol/kg, all other samples are located in thermocline waters with $\Delta[CO_3^{2-}]$ values higher than the possible threshold of 25 μmol/kg for calcareous species [Yu and Elderfield, 2008] (Figure 5b).

[26] It should be noted that the samples of Lear et al. [2002] and Bryan and Marchitto [2008] were cleaned using oxidative and reductive steps [Boyle and Keigwin, 1985], while our samples were cleaned using only an oxidative step [Barker et al., 2003]. Mg/Ca ratios in samples cleaned by oxidative and reductive steps are 0.10 ± 0.09 mmol/mol lower than those only cleaned by an oxidative step [Elderfield et al., 2006; Yu and Elderfield, 2008]. Therefore, the Mg/Ca data of Lear et al. [2002] and Bryan and Marchitto [2008] are corrected by 0.10 mmol/mol in order to be comparable to our data.

[27] As shown in Figures 5a and 5c, *P. ariminensis* Mg/Ca of all the three areas follow thermocline temperature changes along water depths. In each area, benthic Mg/Ca and bottom water temperatures can be fit in a linear relationship. The slopes of the three linear regressions range between 0.14 and 0.19 mmol/mol per °C, which are close to each other given their uncertainties. This might indicate a dominant control of temperature on the benthic Mg/Ca. However, absolute Mg/Ca values of the Florida Straits samples are about 0.40 mmol/mol higher than those of the tropical Atlantic samples within the temperature range from 8 to 11°C. In contrast, in a Mg/Ca versus $\Delta[CO_3^{2-}]$ plot, samples of the tropical Atlantic and the Florida Straits fit in a same linear relationship (Figure 5d). In this sense, the benthic Mg/Ca ratios from thermocline waters seemingly are also impacted by the carbonate-ion effect. Several other lines of evidence, however, argue that $\Delta[CO_3^{2-}]$ does not exert an obvious control on the benthic Mg/Ca:

[28] First, the averaged seawater $\Delta[CO_3^{2-}]$ value between 150 and 700 m of the Gulf of California is significantly lower than that of the tropical Atlantic and that of the Florida Straits by 25 and 40 μmol/kg, respectively (Figure 5b). If the 0.4 mmol/mol offset between the Florida Straits and our data was caused by the carbonate-ion effect, then the Mg/Ca data of the Gulf of California should be significantly lower than those of the other two areas. However, within the temperature range from 7 to 14°C, the four Mg/Ca data point of the Gulf of California are still close to either our data or those of the Florida Straits (Figures 5a and 5c).

[29] Second, if the $\Delta[CO_3^{2-}]$ had a profound effect on the benthic Mg/Ca from thermocline waters, the slope of the Mg/Ca-temperature calibration would become steeper toward the low temperature end [e.g., Rosenthal et al., 2006]. However, at least for *P. ariminensis* data within the temperature range from 7 to 14°C, we cannot find such a trend (Figures 5a and 5c). Marchitto et al. [2007] reported another contrary phenomenon that the Mg uptake of *C. pachyderma* from the Florida Straits is possibly suppressed at high levels of carbonate supersaturation. The slope of the *C. pachyderma* Mg/Ca-temperature calibration therefore flattens at temperatures of 12 to 18.6°C [Marchitto et al., 2007]. We do not observe this trend for the available data of *P. ariminensis* either (Figure 5c).

[30] Third, if indeed the carbonate-ion effect could influence the Mg uptake of benthic foraminifera from thermocline
depths, then to what extent might \( \Delta[CO_3^{2-}] \) alter the benthic Mg/Ca signal? The current \textit{P. ariminensis} Mg/Ca data set is still limited. Although all the Mg/Ca samples of the Florida Straits and the northeastern tropical Atlantic are concentrated in the temperature range from 7 to 12°C (Figure 5c), the significant offset between these two data sets might be caused by other reasons rather than the carbonate-ion effect (discussed below). For samples from the Gulf of California, only two Mg/Ca data are available for the temperature range from 7 to 12°C. Therefore, we cannot estimate the Mg/Ca-\( \Delta[CO_3^{2-}] \) sensitivity of \textit{P. ariminensis} by comparing data from thermocline waters with different \( \Delta[CO_3^{2-}] \) values. In previous studies, the Mg/Ca-\( \Delta[CO_3^{2-}] \) sensitivity of benthic foraminifera was also assessed by using samples from waters undersaturated or slightly saturated with respect to carbonate [e.g., Elderfield et al., 2006; Rosenthal et al., 2006].

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**Figure 5.** Comparison of \textit{P. ariminensis} Mg/Ca, bottom water temperatures and \( \Delta[CO_3^{2-}] \) from the Florida Straits, the Gulf of California, and the northeastern tropical Atlantic. (a) Changes of water temperatures and the benthic Mg/Ca with water depth in the three research areas. (b) Changes of seawater \( \Delta[CO_3^{2-}] \) and the benthic Mg/Ca with water depth. (c) \textit{P. ariminensis} Mg/Ca plotted versus bottom water temperatures. (d) \textit{P. ariminensis} Mg/Ca plotted versus bottom water \( \Delta[CO_3^{2-}] \). The best fit linear regressions of two variables were also presented in Figures 5c and 5d. In each plot, diamonds are samples from the Florida Straits [Bryan and Marchitto, 2008], squares from the Gulf of California [Lear et al., 2002] and triangles from the northeastern tropical Atlantic (this study). \textit{P. ariminensis} Mg/Ca of the Florida Straits and the Gulf of California were corrected by +0.1 mmol/mol. Bottom water \( \Delta[CO_3^{2-}] \) values and temperatures of the Florida Straits are in situ measurements [Bryan and Marchitto, 2008]. Seawater temperature profiles of the tropical Atlantic and the Gulf of California are from the CTD and the WOA2009 data [Locarnini et al., 2010], respectively. Bottom water \( \Delta[CO_3^{2-}] \) values of the Gulf of California and the tropical Atlantic were calculated using the CO2sys.xls program [Lewis and Wallace, 2006].
Therefore, we assume that a $\Delta(Mg/Ca)/\Delta([CO_3]^-)$ sensitivity of 0.009 mmol/mol per °C of $C. wuellerstorfi$ [Elderfield et al., 2006] is also applicable to $P. ariminensis$. As discussed above, the slope of Mg/Ca-temperature calibration is not found to be flattened or steepened at high or low $\Delta([CO_3]^-)$ values, respectively (Figure 5). In our study area, the bottom water $\Delta([CO_3]^-)$ difference between the shallowest core GeoB9532–1 (301 m) and a deeper core GeoB9534–4 (493 m) is 18 mmol/kg (Table 3), which is presumed to be able to cause a 0.16 mmol/mol change in the Mg/Ca signal. However, 0.16 mmol/mol can only account for 30% of a total of 0.55 mmol/mol changes in the Mg/Ca between core GeoB9532–1 and GeoB9534–4 (Table 3). This is also the case for samples from the Florida Straits (Figure 5). Therefore, a possible carbonate-ion effect would not be fully able to explain the benthic Mg/Ca changes between different cores in each area.

If the entire data set of $P. ariminensis$ Mg/Ca was determined by both temperature and $\Delta([CO_3]^-)$, we can also try to disentangle the contributions caused by these two factors as follows: In a Mg/Ca versus temperature plot, the global core top Mg/Ca data and temperatures can be fit by a straight line with a slope of 0.15 mmol/mol per °C (Figure S1). We thus arbitrarily adopted this value as the Mg/Ca-temperature sensitivity of $P. ariminensis$. The Mg/Ca variations caused by the temperature effect can therefore be subtracted from the measured Mg/Ca. The residual Mg/Ca values, however, do not show any correlation with thermocline-water $\Delta([CO_3]^-)$ (auxiliary material and Figure S2). This indicates that the offsets between Mg/Ca data from different areas are actually not related to the carbonate-ion effect. Taken together, although we still cannot completely exclude a possible influence of the carbonate-ion effect on $P. ariminensis$ Mg/Ca ratios from thermocline waters, the above estimates suggest that it should be very minor. Temperature seems to be the primary control of changes in Mg/Ca. But one question still remains: why are $P. ariminensis$ Mg/Ca data of the Florida Straits higher than our data by 0.4 mmol/mol (Figure 5c)?

$\Delta([CO_3]^-)$ was calculated by the CO2sys_xls_program [Lewis and Wallace, 2006].

### Table 4. Estimated Bottom Water $\Delta([CO_3]^-)$ Values at Sediment Core Locations in the Gulf of California$

<table>
<thead>
<tr>
<th>Core</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Water Depth (m)</th>
<th>Temperature (°C)</th>
<th>Mg/Ca$^a$</th>
<th>$\Delta([CO_3]^-)$ (mmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGC73</td>
<td>30.57°N</td>
<td>114.10°W</td>
<td>154</td>
<td>14.0</td>
<td>2.77</td>
<td>56</td>
</tr>
<tr>
<td>GGC71</td>
<td>30.68°N</td>
<td>114.12°W</td>
<td>190</td>
<td>13.0</td>
<td>2.47</td>
<td>45</td>
</tr>
<tr>
<td>GGC47</td>
<td>27.93°N</td>
<td>111.80°W</td>
<td>552</td>
<td>8.0</td>
<td>1.53</td>
<td>5</td>
</tr>
<tr>
<td>BC43</td>
<td>27.90°N</td>
<td>111.65°W</td>
<td>655</td>
<td>7.0</td>
<td>1.84</td>
<td>0</td>
</tr>
<tr>
<td>GGC24</td>
<td>26.08°N</td>
<td>110.83°W</td>
<td>1020</td>
<td>4.5</td>
<td>1.02</td>
<td>–5</td>
</tr>
<tr>
<td>GGC16</td>
<td>26.00°N</td>
<td>110.67°W</td>
<td>1295</td>
<td>3.5</td>
<td>1.10</td>
<td>–6</td>
</tr>
<tr>
<td>GGC53</td>
<td>27.62°N</td>
<td>111.93°W</td>
<td>1442</td>
<td>3.0</td>
<td>1.49</td>
<td>–5</td>
</tr>
</tbody>
</table>

$^a$Lear et al. [2002].

$^b$Mg/Ca data was corrected by 0.1 mmol/mol.

$\Delta([CO_3]^-)$ values were suspected to be caused by contamination or diagenetic alteration of secondary high-Mg calcite, which is hard to be removed by chemical cleaning methods. However, because no convincing evidence was found to support such an inference, the reasons for the data offset are still unknown [Marchitto et al., 2007; Curry and Marchitto, 2008]. The elevated ICP-MS values were suspected to be caused by contamination or diagenetic alteration of secondary high-Mg calcite, although this might be the case for $P. ariminensis$ tests from the Florida Straits that are not contaminated by secondary high-Mg calcite, although this would call for further studies by reanalyzing samples of the Florida Straits and the eastern tropical Atlantic using different methods, or by comparing core top $P. ariminensis$ samples from more geographic locations.

### 4.2. Core Top $P. ariminensis$ Mg/Ca-Temperature Calibration

In an attempt to establish a new $P. ariminensis$ Mg/Ca-temperature calibration, we exclude the Florida Straits data as they show a significant offset from our data due to unknown reasons. We combine our core top data only with the data of Lear et al. [2002] in order to cover a broader temperature range. Mg/Ca data from the Gulf of California is relatively scattered at the low temperature end (Figure 5). However, the slope of the Mg/Ca-temperature calibration is not steepened at the low temperature end, which indicates that the scattered data is not likely induced by the carbonate-ion effect. Nevertheless, because previous studies suggest
that the Mg/Ca of calcareous benthic foraminifera is very likely biased by the carbonate-ion effect when bottom water \( \Delta[CO_3^{2-}] \) values are below 25 \( \mu \text{mol/kg} \), and we are more interested in the Mg/Ca-temperature calibration at the high temperature end in this study, we included only samples from sites with \( \Delta[CO_3^{2-}] \) values above this possible threshold. Hence, only two samples from \textcite{Lear2002} were used. These data show a linear relationship (Figure 6):

\[
\text{Mg/Ca} = (0.19 \pm 0.01) \text{ Temperature} + (0.06 \pm 0.08) \quad (8)
\]

\textcite{Marchitto2006} This new calibration covers a temperature range from 8.0 to 14.0°C. The Mg/Ca-temperature sensitivity of 0.19 \( \text{mmol/mol per } ^\circ\text{C} \) is slightly higher than 0.12 \( \text{mmol/mol per } ^\circ\text{C} \) for \textit{C. pachyderma} [\textcite{Marchitto2007}]. The uncertainty in the coefficients of equation (8) is the standard error. The linear relationship between the Mg/Ca and temperatures also suggests that the carbonate-ion effect on the benthic Mg/Ca is very limited over the temperature range of 8.0 to 14.0°C. Otherwise, the calibration slope might become steeper at the low temperature end [\textcite{Rosenthal2006} or flattened at the high temperature end [\textcite{Marchitto2007}]. The standard error of this regression is \( \pm 0.05 \text{ mmol/mol} \); this equals to an uncertainty of the temperature estimate of \( \pm 0.3 ^\circ\text{C} \). At the 95% confidence level, the prediction uncertainty is \( \pm 0.7 ^\circ\text{C} \) within the temperature range from 7.0 to 14.0°C. However, if we considered the propagated error from reproducibility of Mg/Ca samples (\( \pm 0.05 \text{ mmol/mol} \)) and the uncertainty caused by combining data from different chemical cleaning methods (\( \pm 0.09 \text{ mmol/mol} \)) [\textcite{Yu2008}], the total standard error of the Mg/Ca estimate would reach up to \( \pm 0.11 \text{ mmol/mol} \). This equals to an uncertainty of the temperature estimate of \( \pm 0.6 ^\circ\text{C} \). This uncertainty could be even larger if a minor carbonate-ion effect existed. However, as we do not know the exact Mg/Ca-\( \Delta[CO_3^{2-}] \) sensitivity of \textit{P. ariminensis}, it is practically impossible to exclude the carbonate-ion effect on Mg/Ca variations and to estimate the associated uncertainty.

4.3. Fragmentation Index and Past Changes in Seawater \( \Delta[CO_3^{2-}] \) Values

Although a possible carbonate-ion effect on core top samples was estimated to be minor, we further tested whether there were significant changes in past thermocline-water \( \Delta[CO_3^{2-}] \) and whether changes in \( \Delta[CO_3^{2-}] \) might have biased our Mg/Ca-temperature estimates during the LGM and HS1. As we lack proxy records such as foraminiferal B/Ca [\textcite{Yu2007}] to quantify past changes in bottom water \( \Delta[CO_3^{2-}] \), we use the fragmentation index of planktonic foraminifera as a proxy. A recent study revealed that the non-fragmented foraminiferal shell content (equals to the grain size fraction >63 \( \mu \text{m} \)) in pelagic sediments from the equatorial Atlantic is well correlated with seawater \( \Delta[CO_3^{2-}] \) within the \( \Delta[CO_3^{2-}] \) range from \( -10 \) to +40 \( \mu \text{mol/kg} \) [\textcite{Raitzsch2011}]. The fragmentation index is different from but a more precise proxy than the non-fragmented foraminiferal shell content for indicating carbonate-dissolution changes. The results of \textcite{Raitzsch2011} imply that the fragmentation index should also be able to indicate past changes in seawater \( \Delta[CO_3^{2-}] \). The fragmentation index could also be impacted by the sedimentation processes such as reworking of sediment and subsequently downslope transport. Foraminiferal tests are often poorly preserved in reworked sediment. However, except the core top sample of core GeoB9535–5, the fragmentation index is generally low (<23%) in all samples (Figure 7), suggesting that these samples are not originating from re-deposition processes.

The core top fragmentation index increases with water depth (Figure 7). In the upper three cores, the indices remain at a relatively low level of below 23%. In contrast, the core top fragmentation index reaches up to 45% in the deepest core GeoB9535–5. We suggest that this is because the modern bottom water over this core location is partly influenced by the corrosive Antarctic Intermediate Water (Figures 1 and 2). The core top fragmentation indices and modern bottom water \( \Delta[CO_3^{2-}] \) values fit well in an exponential relationship (Figure 7):

\[
\text{Fragmentation index} = 1233.3 \exp(-0.1109\Delta[CO_3^{2-}]).
\quad (9)
\]

The fragmentation index is strongly sensitive to \( \Delta[CO_3^{2-}] \) changes within the \( \Delta[CO_3^{2-}] \) range from 30 to 43 \( \mu \text{mol/kg} \), but is much less sensitive when \( \Delta[CO_3^{2-}] \) > 43 \( \mu \text{mol/kg} \). This result is in line with that of \textcite{Raitzsch2011}, in that the dissolution index becomes insensitive in highly carbonate oversaturated waters as the carbonate dissolution is negligible there. We use equation (9) to convert the downcore fragmentation indices into \( \Delta[CO_3^{2-}] \) values.

During the LGM and HS1, the fragmentation indices remain the same as for the core top in GeoB9532–2 (Figure 7). In all the three deeper cores, the glacial fragmentation indices decreased relative to their core top values. Especially in core GeoB9535–4, the fragmentation indices decreased to 15% during the LGM and to 10% during HS1, respectively. This
indicates a better preservation and elevated bottom water $\Delta[D(CO_3^{2-})]$ levels. We suggest that core GeoB9535–4 was not influenced by the glacial Antarctic Intermediate Water when the sea level was 120 m and 100 m lower during the LGM and HS1, respectively [Peltier and Fairbanks, 2006]. Glacial bottom waters over this core location were presumed to be glacial Atlantic central water masses, which should be more supersaturated with $D(CO_3^{2-})$.

We only present the estimated $D(CO_3^{2-})$ values within the calibration range (Figure 7) and make use of them for the following calculation. We notice that most of the glacial fragmentation indices are below 10%, that is, in a range, in which the fragmentation index- $D(CO_3^{2-})$ sensitivity is small. Therefore, there might be a large uncertainty associated with the glacial bottom water $D(CO_3^{2-})$ estimate. The averaged LGM seawater $D(CO_3^{2-})$ values are 6.6, 9.5 and 8.2 mmol/kg higher than their core top values in core GeoB9533–2/3, 9534–4/5 and 9535–4/5, respectively. If we again adopted a $\Delta(Mg/Ca/[D(CO_3^{2-})])$ sensitivity of 0.009 mmol/mol per $\mu$mol/kg [Elderfield et al., 2006] for P. ariminensis (although possibly it is an overestimate), then increases in the LGM bottom water $D(CO_3^{2-})$ might result in a Mg/Ca overestimate of 0.06, 0.09 and 0.07 mmol/mol, and a temperature overestimate of 0.3°C, 0.5°C and 0.4°C (based on equation (8)) in samples from core GeoB9533–2/3, 9534–4/5 and 9535–4/5, respectively.

The difference between core top and the HS1 fragmentation indices is even larger (Figure 7). Therefore, the HS1 temperature estimate at core GeoB9534–5 and GeoB9535–4 might be possibly biased by the carbonate-ion effect by up to 0.7°C and 0.6°C, respectively. The HS1 fragmentation indices of core GeoB9533–2 and all the glacial fragmentation indices of the shallowest core GeoB9532–2 are beyond the calibration range, and therefore not reliable for a glacial $D(CO_3^{2-})$ estimate. Modern seawater $D(CO_3^{2-})$ values show a nearly linear relationship with water depths between 200 and 400 m at our coring locations. We thus assume that a possible Mg/Ca overestimate of 0.06 mmol/mol and a possible temperature overestimate of 0.3°C caused by the carbonate-ion effect for glacial samples of core GeoB9533–2 also apply to the glacial samples of core GeoB9532–2. However, the averaged Mg/Ca difference between glacial and core top samples is 0.40, 0.38, 0.24 mmol/mol in core GeoB9532–2, 9533–2/3, 9534–4/5, respectively (Tables 3 and 5), which apparently cannot be fully explained by changes in bottom water $D(CO_3^{2-})$ and the carbonate-ion effect at these core locations.

Taken together, the above estimate, although not in a strictly quantitative way, suggests that there were no significant changes in thermocline-water $D(CO_3^{2-})$ during the LGM and HS1 relative to the late Holocene. If the carbonate-ion effect had an influence on the P. ariminensis Mg/Ca, it would bias past Mg/Ca-temperature estimates only at a

![Figure 7](image_url). Planktonic foraminiferal fragmentation indices and the estimated bottom water $D(CO_3^{2-})$ values for selected time slices. The core top fragmentation indices and modern bottom water $D(CO_3^{2-})$ values are well fit in an exponential relationship.
Table 5. LGM and HS1 P. ariminensis Mg/Ca and δ18O Results of Four Gravity Cores

<table>
<thead>
<tr>
<th>Core</th>
<th>Sample Depth (cm)</th>
<th>P. ariminensis Mg/Ca (mmol/mol)</th>
<th>P. ariminensis δ18O (PDB, ‰)</th>
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</tbody>
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5. Downcore Results

5.1. P. ariminensis Mg/Ca-Temperatures of the LGM and HS1

[45] We used the newly developed P. ariminensis Mg/Ca-temperature calibration to estimate bottom water temperature changes at our coring sites for the selected time slices. After correction for changes in sea level, the LGM thermocline temperatures are comparable to the present-day between 200 and 372 m water depth (Figure 8). In contrast, the LGM thermocline temperatures are approximately 1.2°C warmer at intermediate depth (550 m) compared to modern values. The thermal gradient of the LGM water column between 400 and 570 m depth was therefore reduced with respect to the present-day. Thermocline temperature estimates for HS1 are close to those of the LGM. Relative to the present-day, the HS1 thermocline temperatures are about 0.6°C cooler at 217 m depth, 0.8°C warmer at 284 m depth, nearly unchanged at 392 m depth and 1.5°C warmer at 570 m depth (Figure 8). Given the uncertainty of Mg/Ca-temperature estimate, temperature variations at 217 m and 284 m depths during HS1 are not significant with respect to the present-day. The LGM and HS1 warming signal of 1.2–1.5°C at

![Figure 8. Estimated bottom water temperature changes with water depth. Dots are mean values from each core for a specific time interval. Error bars represent one standard deviation (±1σ) of a few individual measurements. Mean temperature data of four CTD stations is shown in black curve. The HS1 and the LGM core water depths are adjusted by −100 m and −120 m, respectively, to account for sea level lowering [Peltier and Fairbanks, 2006]. We did not find enough benthic foraminifera for Mg/Ca analyses from core top samples of cores GeoB9535–4/5.](image-url)
intermediate depths (550–570 m) is larger than the uncertainty of the temperature estimate, and it is reproduced by a couple of individual samples. We therefore consider this warming signal to be robust.

5.2. The δ¹⁸O of P. ariminensis and Reconstruction of Seawater δ¹⁸O and Paleo-Salinity

The core top benthic foraminiferal δ¹⁸O values show an offset of −0.22 ± 0.13‰ from the predicted δ¹⁸O of calcite (Figure 9 and Table 3). LGM and HS1 foraminiferal δ¹⁸O values are enriched in ¹⁸O mainly due to the preferential storage of ¹⁶O in ice sheets during the last glacial period. After correction for the ice-volume effect, however, the LGM and HS1 foraminiferal δ¹⁸O values are still 0.44‰ to 0.77‰ heavier than the modern predicted δ¹⁸O values between 200 and 400 m depth (we mean the predicted δ¹⁸O after correction by −0.22‰, gray line in Figure 9). As there are very limited temperature changes within this depth interval during the LGM and HS1 relative to the present-day (Figure 8), the deviations in δ¹⁸O indicate a significant change in local seawater δ¹⁸O and salinity. At 550–570 m depth, after correction for the ice-volume effect, the LGM foraminiferal δ¹⁸O is 0.36‰ heavier than the modern predicted δ¹⁸O (after correction by −0.22‰).

We further estimated the LGM and HS1 seawater δ¹⁸O and salinity changes. In temperature-δ¹⁸O seawater and temperature-salinity diagrams (Figure 10), the core top estimates are consistent with the characteristics of the modern SACW. The average δ¹⁸O seawater value of the LGM and HS1 thermocline water is 1.7‰ and 1.3‰ higher than at present, respectively. Based on our calculation (see equation (5) and Figure 10c), the ice-volume effect could partly contribute to this increase in glacial δ¹⁸O seawater by about 1.0‰ during the LGM [Schrag et al., 2002] and 0.83‰ during HS1. The average thermocline-water salinity increased by 2.6 psu during the LGM and 1.9 psu during HS1 compared to the late Holocene. This is also partly due to a glacial decrease in global ocean volume, which could result in 1.1 psu increase in global mean seawater salinity during the LGM and 0.9 psu increase during HS1 (see equation (6) and Figure 10d). We note that the HS1 thermocline waters show a clear freshening at 570 m depth (water depth after correction for glacial sea level changes) with respect to the LGM. The whole HS1 central water column shows a strong gradient between 400 and 570 m depth in terms of seawater δ¹⁸O and salinity changes (Figure 10).

6. Discussion

6.1. The Structure of the Glacial Thermocline

In LGM modeling experiments without freshwater perturbations, the ventilated thermocline waters in the tropical Atlantic was predicted to be 2–5°C cooler on average relative to the present-day. These experiments also predicted a shoaling of the thermocline depth [e.g., Paul and Schäfer-Neth, 2003, 2004; Rühlemann et al., 2004]. Foraminiferal δ¹⁸O records confirmed that the LGM thermocline (400–900 m depth) of the western North Atlantic subtropical gyre was 4°C cooler than the late Holocene and the base of the main thermocline was estimated to be 100 m shallower [Slowey and Curry, 1995]. However, our reconstructions do
not support a significant cooling scenario for the glacial northeastern tropical Atlantic thermocline (Figure 8). At our coring locations, a general LGM cooling of the tropical Atlantic thermocline might be offset by changes in the location of the subduction areas (discussed below in section 6.3) and/or in surface water properties over source regions.

6.2. Insensitivity of Thermocline Temperatures of the Northeastern Tropical Atlantic to Thermohaline Circulation Variations under Glacial Boundary Conditions

Climate boundary conditions during the LGM and HS1 were relatively similar. Therefore, it is plausible to compare the LGM thermocline temperatures with those of HS1 and further assess the effect of changing thermohaline circulation on tropical thermocline temperatures. Proxy data suggest that during HS1, the volume transport by the overturning circulation reduced at all water depths in the North Atlantic relative to the LGM [e.g., McManus et al., 2004; Gherardi et al., 2009]. However, the similar thermocline temperature estimates between 200 and 570 m depth during the LGM and HS1 seemingly indicate that the northeastern tropical Atlantic thermocline temperatures did not respond to this significant decline in glacial thermohaline circulation strength.

Several freshwater-hosing experiments using the LGM boundary conditions predict that thermocline waters in the southern subtropical and equatorial Atlantic warmed, whereas thermocline waters in the northern subtropical Atlantic cooled [Rühlemann et al., 2004; Cheng et al., 2007; Brady and Otto-Bliesner, 2011]. The region between the equatorial Atlantic and the northern subtropical gyre is located in a transition area where thermocline temperatures are relatively insensitive to AMOC changes [Rühlemann et al., 2004; Brady and Otto-Bliesner, 2011]. The geographic location of this transition is model-
dependent. For the upper water column between 200 and 600 m depth, the transition area can shift from 5 to 15°C in one model [Rühlemann et al., 2004] to 15–20°C in another [Brady and Otto-Bliesner, 2011]. Our sediment cores (~9°N) are located in this transition area. Therefore, we speculate that the response of thermocline temperatures to glacial thermohaline circulation changes in this area might be too small to be reflected in our Mg/Ca-temperature reconstructions.

Another question is to what extent our data from the ocean margin are representative of the zonal mean conditions of the tropical Atlantic thermocline. Freshwater-hosing experiments using either modern [Zhang, 2007; Chiang et al., 2008; Lopes dos Santos et al., 2010; Heslop and Paul, 2012] or LGM boundary conditions [Brady and Otto-Bliesner, 2011; Schmidt et al., 2012] all confirm that the northeastern and the northwestern tropical Atlantic thermocline temperatures show the same sign of response but different sensitivity to reduced AMOC strength. Therefore, we cannot assume that our temperature reconstructions from the eastern ocean margin represent zonal mean conditions. However, taking modeling results and proxy data together, it is reasonable that at least the northeastern tropical Atlantic thermocline temperatures were rather insensitive to AMOC changes under glacial boundary conditions.

6.3. Possible Southward Penetration of the NACW During the LGM and HS1

Significant increases in glacial central water δ18O and salinity (Figure 10) suggest that there might be pronounced changes in the source regions of thermocline waters during the LGM and HS1. As seawater temperature, seawater δ18O and salinity are conservative properties, we can use these three parameters to trace the possible source regions of the central water mass at our coring sites during the last glacial. The subduction of surface waters into thermocline occurs mostly during wintertime in the mid-to-high latitudes of both hemispheres [Poole and Tomczak, 1999]. Therefore, we mapped the regions in the Atlantic in which winter sea-surface temperature and salinity data from a reconstruction of LGM sea-surface conditions [Schäfer-Neth and Paul, 2004; Paul and Schäfer-Neth, 2003] correspond to our data for the LGM thermocline (Figure 11). In this data set, the seasonal sea-surface temperature is based on the GLAMAP reconstruction, which in turn is derived from planktonic foraminiferal assemblages [Sarnthein et al., 2003, and references therein]. Summer sea-surface salinity in the North Atlantic is estimated from the reconstructed sea-surface temperatures and planktonic foraminiferal test δ18O. With the reconstructed glacial summer salinity and modern ocean data, the glacial-to-modern salinity anomaly in the summer North Atlantic is known. This anomaly is added to the modern monthly salinity data, and the glacial North Atlantic sea-surface salinity field data with a full seasonal cycle are obtained. In the South Atlantic, the LGM salinity is obtained by adding the global glacial-to-modern salinity anomaly of 1.07 psu to the modern monthly salinity data [Schäfer-Neth and Paul, 2004, Paul and Schäfer-Neth, 2003, 2004].

We found that only the characteristics of the wintertime North Atlantic surface water from a range of 32.5–41.5°N match the properties of the tropical central water mass at the LGM (Figures 10b and 11a). However, surface ocean data from the wintertime South Atlantic do not match the properties of the central water mass (Figure 11b). Despite of the rough glacial sea-surface salinity estimates in the South Atlantic and large uncertainties associated with paleo-salinity estimates (Figure 10b), the results at least indicate that central waters in
the northeastern tropical Atlantic probably originated from surface waters of the North Atlantic during the LGM. In that way the LGM Cape Verde Frontal Zone off the African coast was possibly shifted to the south with respect to the present.

[52] We further collected available LGM sea-surface temperature and δ18Oseawater reconstructions from the North Atlantic between 32.5 and 41.5°N and compared them with the properties of the central waters. These data were published by Duplessy et al. [1991] and were later re-calculated by Schäfer-Neth and Paul [2004] using results obtained from newly available planktonic foraminifera transfer functions. We find that δ18Oseawater values derived from the planktonic foraminifer G. bulloides are heavier than that of central waters at our core locations by about 0.5‰ during the LGM (Figure 10a). This is because the calcification temperature of G. bulloides in the North Atlantic is considered to be close to summer sea-surface temperatures [Duplessy et al., 1991]. Reconstructed surface water δ18O results (Figure 10a) are representative of glacial summer seasons. During glacial wintertime, surface waters of the central part of the North Atlantic should be fresher than in summer seasons due to a southward shift of the North Atlantic polar front [e.g., Eynaud et al., 2009]. With respect to the surface waters south of the polar front, surface waters to the north of it were estimated to be 0–0.5‰ more depleted in δ18O during the LGM summer [Duplessy et al., 1991]. Therefore, an increased influx of surface waters from the north to the central part of the North Atlantic might have decreased δ18O values of surface waters during the glacial winter. In that case δ18O values of surface waters in the possible subduction area (32.5–41.5°N) of the wintertime North Atlantic would be in better agreement with those of the tropical central waters.

[53] Evidence of benthic foraminiferal δ13C and Cd/Ca from the western Atlantic support a further penetration of the glacial North Atlantic Intermediate Water to the south during the LGM relative to the present-day [e.g., Curry and Oppo, 2005; Marchitto and Broecker, 2006]. Glacial thermocline waters in the western tropical Atlantic were also significantly influenced by the relatively well-ventilated water mass from the North Atlantic [e.g., Came et al., 2003; Curry and Oppo, 2005]. Here from a different approach, our data suggest that thermocline waters of the northeastern tropical Atlantic were also flushed by the northern-sourced surface waters during the LGM.

[54] The salinity of the HS1 central waters between 200 and 400 m depth seems lower than but statistically indistinguishable from the LGM reconstructions (Figures 10b and 10d), suggesting that the HS1 central waters between 200 and 400 m depth were still mainly influenced by the North Atlantic surface waters. However, a significant freshening of central waters at 570 m depth (Figures 10b and 10d) suggests that the water mass at intermediate depth might have originated from a different surface source during HS1. After correction for the glacial ice-volume effects and ocean volume changes, the properties of the HS1 central waters at 570 m depth coincide with those of the modern SACW (Figures 10c and 10d). This may indicate that the HS1 central waters at intermediate depth were mainly influenced by the southern-sourced surface waters, although the seasonal temperature-salinity properties of the Southern Ocean surface waters for HS1 time period are still not resolved. Our speculation is supported by a biogenic silicon sedimentary record north to our core location: the LGM interval was associated with moderate silicate accumulations off NW Africa possibly due to upwelling of the silica-poor NACW. The HS1 interval, on the other hand, was characterized by an extraordinary increase in silicate accumulations possibly induced by upwelling of the silica-rich SACW [Romero et al., 2008]. Hence, both our data and this previous study suggest a northward intrusion of glacial equivalent of the SACW during HS1, although the influence of the glacial SACW was probably limited in the lower thermocline.

7. Conclusions

[55] We evaluate and confirm the reliability of benthic foraminiferal Mg/Ca of P. ariminensis as a thermocline-water temperature proxy in the northeastern tropical Atlantic both for the late Holocene and the last glacial period. Although a possible influence of the carbonate-ion effect on the benthic Mg/Ca cannot be excluded based on the current data set, it is estimated to be minor.

[56] We find that both the LGM and HS1 thermocline-water temperatures in the northeastern tropical Atlantic were similar to the present-day between 200 and 400 m water depth, but were warmer by 1.2–1.5°C at 550–570 m depth. We do not observe warmer thermocline temperatures during HS1 relative to the LGM. This indicates that the northeastern tropical Atlantic thermocline temperatures were insensitive to changes in thermohaline circulation strength under glacial boundary conditions. However, it appears that the glacial thermocline-water properties were significantly different from the present-day by changes in the wind-driven circulation. We find that the δ18O and salinity of the northeastern tropical Atlantic central waters were significantly increased during the LGM (200–550 m depth) and HS1 (200–400 m depth) with respect to the late Holocene. We also observed the HS1 central waters at intermediate depth (570 m depth) were significant fresher relative to the upper central waters. The temperature-salinity characteristics of the LGM central waters (200–550 m depth) were similar to those of the LGM surface waters from the central part of the North Atlantic. Therefore, we infer that the LGM thermocline in the eastern equatorial Atlantic was possibly ventilated by the northern-sourced surface waters. During HS1, the upper central waters (200–400 m depth) might remain influenced by the northern-sourced surface waters, while the lower thermocline (570 m depth) was possibly ventilated by the southern-sourced surface waters.

[57] Acknowledgments. We thank the crew and scientific party of Meteor Cruise M65/1. Thanks also go to Monika Segl and her team for stable isotope analyses and to U. Röhl and V. Lukies for technical support while using the XRF Core Scanner at MARUM. Matthias Prange, Ute Merkel and Heather Johnstone are thanked for their discussions and suggestions. Three anonymous reviewers’ comments have greatly improved an earlier version of this manuscript. This work was funded through the DFG Research Center/Excellence Cluster “The Ocean in the Earth System.” E.H. is supported by the China Scholarship Council (CSC 2009626073).

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