Calibration, validation and application of the foraminiferal Mg/Ca

Reconstructing the intermediate water masses structure and origin in the Western Tropical Atlantic

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Scientific environment

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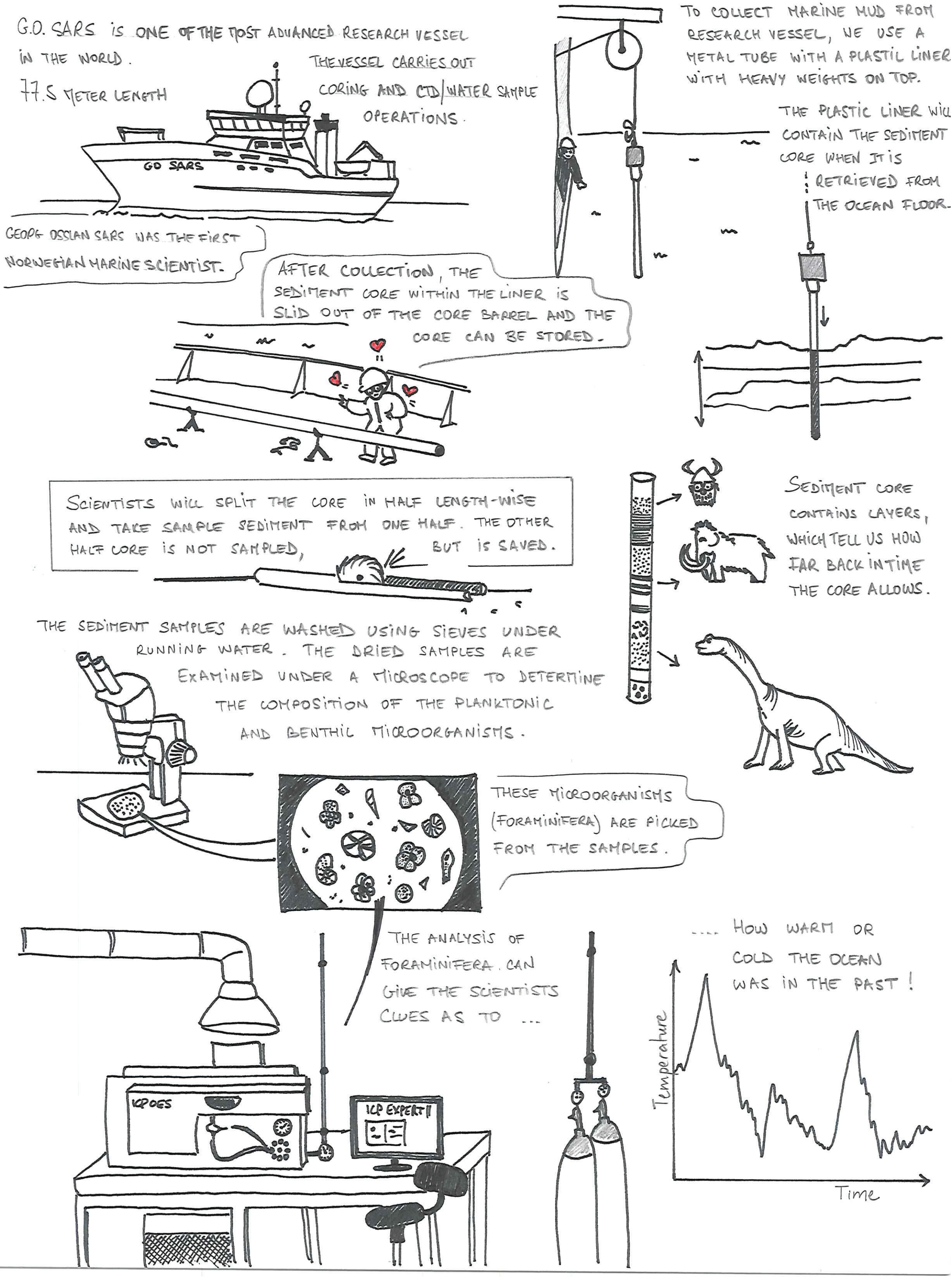
WHAT IS PALEOCLIMATOLOGY? IT IS THE STUDY OF PAST CLIMATES. SINCE IT IS NOT POSSIBLE TO GO BACK IN TIME AND THE USE OF SATELLITE IS A RECENT NEW TECHNOLOGY, SCIENTISTS USE PROXIES TO INTERPRET PALEOCLIMATE AND ITS VARIABILITY.



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This is the time to thank all of you that contributed to make this thesis possible and undeniably enjoyable…

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Bergen, November 2014

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Abstract of dissertation

The Atlantic Meridional Overturning Circulation (AMOC) plays a central role in the northward distribution of heat. It is a key mechanism in the climatic system that needs to be further understood. Most studies focused on surface or deep water conditions. Relatively little is known about the role of subsurface, thermocline and intermediate waters, where heat uptake and/or transport occur. Our aim is to give a better representation of the hydrography during the past by reconstructing the upper water column from surface to intermediate waters. Understanding of how changes in the upper water masses properties is crucial for determining the role of oceanic heat distribution involved in the AMOC and is the main objective of this PhD project.

The Western Tropical Atlantic is a sensitive oceanic region connected with surface and intermediate waters that flow from the Southern Hemisphere into the North Atlantic and a deep water mass from the Northern Hemisphere. This region is unique in identifying the upper limb pathway of the AMOC and associated water masses.

In this context, using sediment cores from depth transects is therefore crucial for estimating not only the magnitude of change but, particularly the orientation of water mass distribution change. Seven coring sites have been retrieved that fall along a depth transect extending from 600 to 1000 m water depth.

Main strategy is to use different planktonic species having different depth habitat to reconstruct the upper surface to about 200-400 m water depth, and furthermore benthic species from depth of the coring sites to reconstruct water mass changes further below to 1000 m.

The PhD project has two major objectives. The first is to calibrate and validate relationship between Mg/Ca ratio and temperature in benthic foraminiferal shells. Mg/Ca ratio in several benthic foraminifer species from core-tops were analysed to develop Mg/Ca calibrations over the 0-6 degrees Celsius temperature range in the Atlantic Ocean (**Paper I**). Apart from temperature, other factors may exert additional influences on foraminiferal Mg/Ca. For that purpose, the effect of the seawater

carbonate chemistry on the magnesium incorporation into the foraminiferal calcite have been investigated for the benthic foraminifer species *Cibicidoides wuellerstorfi* (**Paper II**).

In the second part of this project, we have applied the improved *C. wuellerstorfi* Mg/Ca-temperature calibration to examined surface, subsurface, thermocline and intermediate water conditions during the last deglaciation. Combining with water densities estimates and ventilation ages, we are trying to bring important insights on discerning sources of subsurface and intermediate waters (**Paper III**).

This PhD work introduces a relatively new concept of investigating the hydrology along a core section in the upper water column. Looking to the future, we recommend a parallel strategy of applying proxies with refinements in methods and understanding of mechanisms that control the proxy.

Contents

1 Introduction

This PhD work has been accomplished within the Research Council of Norway (RCN) and the ESF-Euromarc project "Response of tropical Atlantic surface and intermediate waters to changes in the Atlantic meridional overturning circulation" (RETRO). The research presented in this thesis advances our understanding of the behaviour and the role of surface and intermediate oceanic circulation in the tropical Atlantic Ocean during the last deglaciation. This study is based on analysis and interpretation of geochemical multi-proxy records from marine sediments. The PhD thesis consists of an introduction, three papers and a conclusion/perspectives section. The introduction provides the scientific background and the main purposes of this study and summarizes the articles presented in the thesis. The last section concludes with some discussions and further investigations.

The three manuscripts included in this thesis are listed below:

PAPER 1: Refining benthic foraminiferal Mg/Ca-temperature calibration using core-top from the western tropical Atlantic: Implication for paleotemperature estimation. Manuscript published in G^3 (May 2013).

PAPER 2: Revisiting the carbonate ion saturation effect on Mg/Ca in the benthic foraminifer *C. wuellerstorfi* in the Atlantic Ocean. Manuscript in preparation.

PAPER 3: Deglacial evolution of surface to intermediate water mass characteristics in the western tropical Atlantic. Manuscript in preparation.

The first paper presents new benthic foraminifera Mg/Ca calibrations. The second paper is focused on the carbonate system and how the benthic foraminiferal *C. wuellerstorfi* Mg/Ca ratio can be affected or not by the carbonate ion saturation. The third paper is a compilation of benthic and planktonic Mg/Ca-temperature and $\delta^{18}O$ signal over the last deglaciation. These results are used to reconstruct temperature and hydrological changes along a western tropical Atlantic section covering a depth range from surface to 1000 m water depth.

2 Scientific background

Changes in ocean circulation are known to have played a critical role in the Earth's climate evolution during the last deglaciation (Figure 1), between the Last Glacial Maximum (LGM 26-19 kyr; e.g. *Clark et al.*, 1999) and the present warm interglacial period, the Holocene (~10-0 kyr) (*Clark et al.*, 2002; *McManus et al.*, 2004; *Rahmstorf*, 2002, 2006). This deglacial evolution in the North Atlantic included cold episodes, the Younger Dryas and Heinrich 1 events, affecting ocean properties and consequently global climate (*Broecker*, 1994; *Hu et al.*, 2004; *Marcott et al.*, 2011). However, many of the mechanisms involved in the Atlantic Meridional Overturning Circulation (AMOC) changes during the deglaciation remain unresolved.

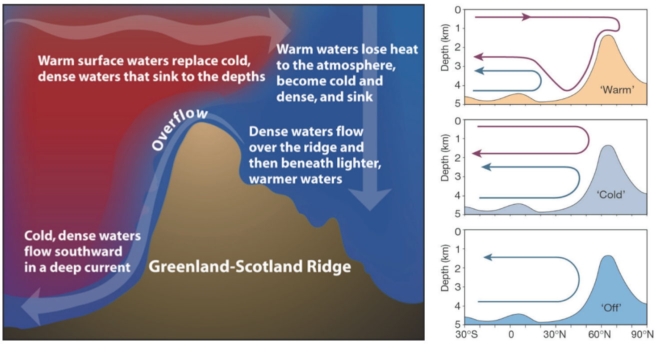

Figure 1: (**left panel**) Simplified sketch of the NADW formation and water distribution accross the Greenland-Scotland Ridge (source: www.whoi.edu; by E.P. Oberlander) and (**right panel**) schematic representation of the three modes of ocean circulation during different times of the last glacial period (*Rahmstorf*, 2002).

Freshwater forcing from melting ice in the North Atlantic has been suggested as a key mechanism (*Broecker*, 1994; *Clark et al.*, 2012; *Hu et al.*, 2009; *Zhang*, 2007), but it is still debated how and to what degree do the deglacial meltwater pulses impact the ocean circulation. Similarly, a slowing of the overturning circulation in the North Atlantic Ocean is expected to reduce northward heat transport in the ocean and to induce warming in the Souhern Ocean and particularly in the thermocline tropical Atlantic, as described as the bipolar see saw mechanism (Figure 2) (*Arz et al.*, 1998, 1999; *Chang et al.*, 2008; *Cheng et al.*, 2007; *Chiang et al.*, 2008; *Dahl et al.*, 2005; *Manabe and Stouffer*, 1997; *Ruhlemann et al.*, 2001; *Ruhlemann et al.*, 2004; *Stouffer* *et al.*, 2006; *Vellinga and Wood*, 2002; *Weldeab et al.*, 2006; *Zhang*, 2007). Furthermore, this tropical heat retention might have played an important role in abrupt climate changes during the last deglaciation.

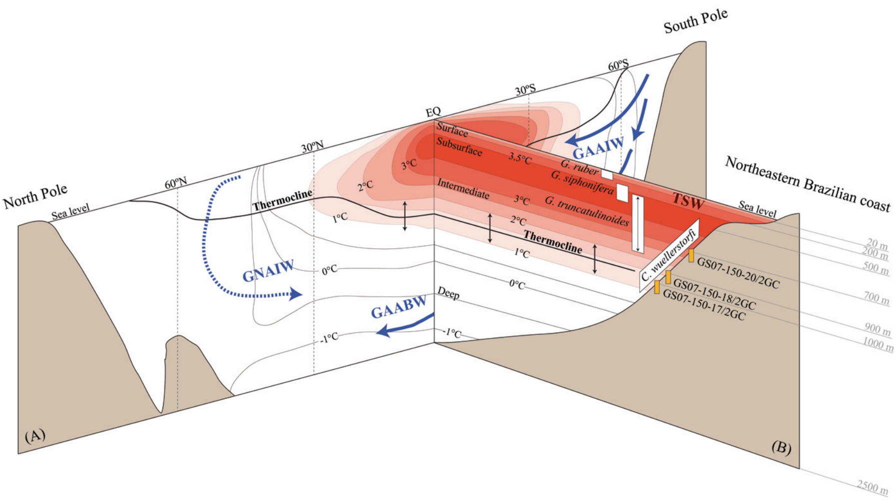

Figure 2: (**A**) Schematic Atlantic Ocean section during abrupt cold events in the North Atlantic. The thermocline, which is presented by a black line indicates the highest temperature gradient. Zonal mean temperature anomaly in the Atlantic Ocean averaged over the last 401st to 500th year, which is presented by gray lines in the profile (A and B), shows heat anomaly centered to the intermediate tropical water depth (adapted from *Manabe and Stouffer*, 1997). (**B**) Chart of the Brazilian transect shows the core-top and down-core used to reconstruct the climate variability (see paper III for further details). TSW: Tropical surface water, GNAIW: Glacial North Atlantic intermediate water, GAABW: Glacial Antarctic bottom water, GAAIW: Glacial Antarctic intermediate water.

Unfortunately, crucial evidence of changes in the ocean's most active water: the intermediate ocean is lacking. **How did intermediate ocean circulation vary across the last deglaciation?** One of the objectives of this PhD project is to remedy to this unresolved issue.

3 Response of tropical Atlantic surface and intermediate waters to AMOC changes

3.1 RETRO project

The aim of the research project RETRO is to reconstruct circulation changes within the surface, thermocline, intermediate and deep waters in the tropical Atlantic Ocean during periods of reduced AMOC, in order to understand the controlling mechanisms linking the high and low latitudes. One of RETRO goals is to investigate large changes in tropical ocean parameters during the transition from the LGM to the present interglacial. This thesis is part of this context.

RETRO focuses on three different depth layers in order to assess the response of the tropical Atlantic climate under different AMOC states: the surface and the subsurface, the intermediate depth including the permanent thermocline, and the deep waters.

- **What mechanisms affect the upper limb/branch of the AMOC?**
- **How these changes in intermediate waters can affect the climate generally or locally?**
- **What is the role of the thermocline and intermediate waters on the abrupt climate changes during the last termination?**

We aim to give insight into these research questions.

3.2 Strategy for reconstructing the tropical thermocline structure

Constraining the different thermocline/intermediate water mass regimes at present and during the past is challenging. One of the objectives of this PhD work is to examine and describe surface, subsurface and intermediate temperature and density changes associated with an AMOC change.

- **Can we show thermocline/intermediate layers warming as predicted by models?**

- **What was the spatial extent of the warming along the water column?**
- **What was the state of the intermediate circulation during extreme reduction in the deeper branch of the AMOC?**

This work will expose some hypothesis.

The work presented in this thesis is based on sediment cores retrieved during a scientific cruise on aboard of the Research Vessel G.O. SARS in December 2007. To investigate the western tropical Atlantic hydrology, geochemical analyses of planktonic and benthic foraminifera were performed to reconstruct temperature, $\delta^{13}C$ and seawater $\delta^{18}O$ variations in the water column down to 1000 m depth. Three different species of planktonic foraminifera cover the upper to thermocline part of the water column (Figure 3 box 1). Benthic foraminiferal species represent conditions in the lower part of the water column, and more specifically at the depth of the core sites (from 600 to 1000 m depth) (Figure 3 box 2).

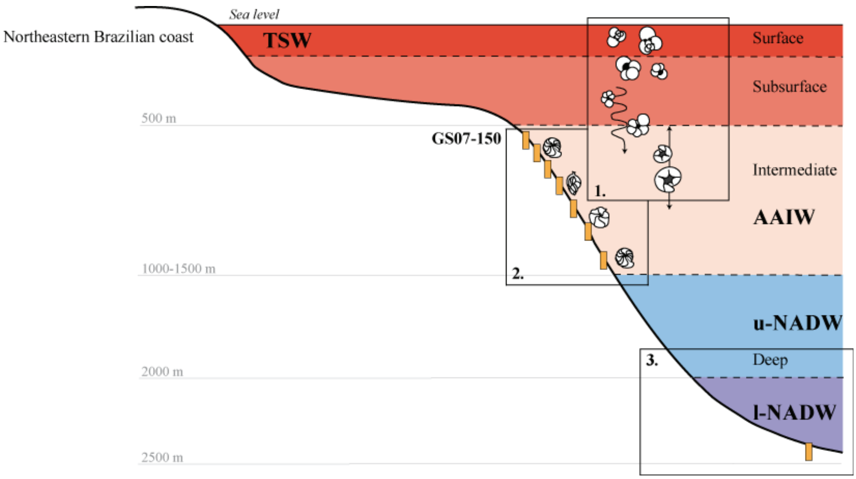

Figure 3: Chart of the western tropical Atlantic Ocean showing the location of the core-top and down-core. TSW: Tropical Surface Waters, AAIW: Antarctic Intermediate Water, u-NADW and l-NADW: Upper and Lower North Atlantic Deep Waters, GNAIW: Glacial North Atlantic Intermediate Water, AABW: Antarctic Bottom Water, STG and SPG: Subtropical and Subpolar gyres. Box 3 represent another goal of the RETRO project in reconstructing the AMOC changes at deep level. This approach is not in the near scope of this thesis.

The studied sites are located within the main northward flow of the intermediate Atlantic current, the Antarctic Intermediate Water (AAIW) bathing a depth range between ~500 and 1100 m in the equatorial sector (Figure 4). AAIW is a major water mass of the upper overturning branch of the AMOC. AAIW is thought to play a key role in the meridional heat transport and contribute to or even trigger abrupt AMOC reorganizations (*Stouffer et al.*, 2007; *Weaver et al.*, 2003). However, the behaviour of AAIW under glacial conditions is not well constrained. Our study increases the understanding of this key oceanic component.

The deepest core sites are also influenced by the upper branch of the North Atlantic Deep Water (u-NADW), which is characterized by a deep southward flow of more saline waters (Figure 4).

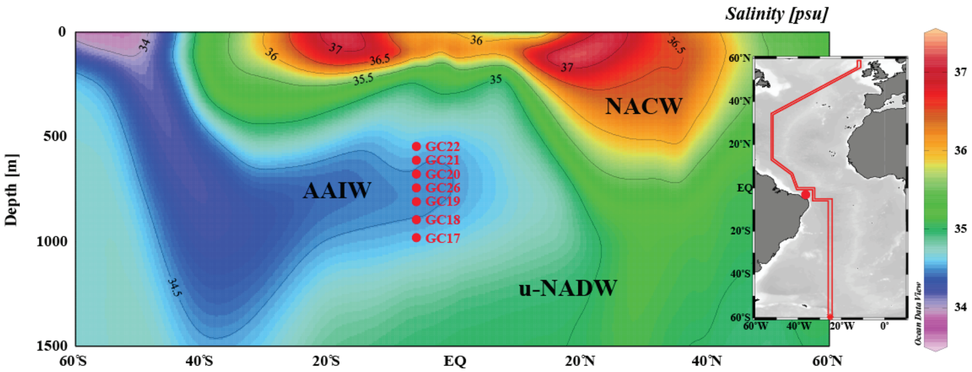

Figure 4: Meridional section of seawater salinity (colors and contour lines) along the western Atlantic Ocean and the northeastern Atlantic Ocean. The position of the section is indicated in the panel on right. Data are from the World Ocean Atlas 2009 (*Levitus et al.*, 2009) and the figure was made by Ocean Data View 4 (R. Schlitzer, available at http://odv.awi.de). Red dots denote core locations. NACW: North Atlantic central water, AAIW: Antarctic intermediate water, u-NADW: Upper North Atlantic deep water.

The study area is ideal to reconstruct the western tropical Atlantic hydrology, in that the sites are sensitively situated to monitor changes in the upper-water column. Moreover, the chosen location is unusual in that its exhibits very minor changes in salinity and in carbonate chemistry, suggested complicating factors in temperature reconstruct using Mg/Ca paleothermometry. This allows the opportunity to better reconstruct the temperature variability. In order to test the thermocline and intermediate water temperature changes associated with AMOC variations during the past, it is first crucial to establish a reliable temperature reconstructions. To this end, one of the objectives of this work is to establish a new benthic foraminiferal Mg/Ca-temperature calibrations in the western tropical Atlantic and to constrain the uncertainties linked to the Mg/Ca proxy (see section Results overview for further details).

4 Results overview

The sensitivity of the tropical climate to global changes has previously been suggested (*Lea et al.*, 2003) but needs further investigation. This can be done by reconstructing the evolution of the thermocline structure. Therefore, methods for reconstructing the tropical thermocline are of major importance to better assess changes in tropical climate and interaction between tropical and extra-tropical climatic conditions.

The challenge regarding paleoproxies relies on the interpretation of produced data. Are they truly representative of the past environment? In that sense, the major difficulty about proxies is to fully understand the parameter that is indirectly measured, the processes involved in the acquisition of such parameters and also to understand the past environment. Most paleovariables cannot be reconstructed directly. For instance, the salinity, together with the temperature are key parameters to reconstruct seawater density changes, which drive the intermediate and deep ocean circulation. Combining foraminiferal $\delta^{18}O$ and Mg/Ca theoretically allow the reconstruction of seawater temperature and $\delta^{18}O$ that is linked to seawater salinity (for more details, see the following sections). Those proxies are, however, controlled by different parameters that need to be fully understood.

This thesis represents an effort to fully constrain a proxy for temperature reconstruction: the foraminiferal Mg/Ca ratio. Our study aimed at reducing the uncertainties linked to the method, at testing and advancing new hypothesis on the foraminiferal Mg/Ca being mainly controlled by temperature. Paper I and II focus mainly on benthic foraminiferal Mg/Ca ratio as a proxy for past temperature reconstructions. A refining of the benthic Mg/Ca calibrations over the warmest part of the cold end-member (between 4 and 6ºC) has been examined (**Paper I**) and the carbonate ion saturation effect on the benthic Mg/Ca has been investigated (**Paper II**). Finally, the tropical climate evolution during the last deglaciation is described in **Paper III**.

4.1 Mg/Ca as a proxy of paleotemperature

The reconstruction of sea surface/subsurface and bottom water temperatures as well as salinities is a key step for a complete understanding of the hydrological component of the climate system during past perturbed states. Independent temperature estimates from Mg/Ca ratios, in combination with the oxygen isotopic composition of the foraminiferal calcite ($\delta^{18}O_{calcite}$), can help constrain the oxygen isotopic composition of seawater ($\delta^{18}O_{seawater}$), which itself reflects changes in the local hydrography (*Duplessy et al.*, 1991; *Waelbroeck et al.*, 2002). The use of Mg/Ca paleothermometry on planktonic foraminifera for reconstructing sea surface temperatures is now widespread (*Anand et al.*, 2003; *Groeneveld and Chiessi*, 2011; *Lea et al.*, 1999; *Mashiotta et al.*, 1999; *Nurnberg et al.*, 1996; *Russell et al.*, 2004; *von Langen et al.*, 2005), but extensive studies during the last decades have also suggested that the same method may be applied to benthic foraminiferal species, in order to generate records of bottom water temperature (BWT) in a wide range of temperatures (*Elderfield et al.*, 2006; *Healey et al.*, 2008; *Kristjansdottir et al.*, 2007; *Lear et al.*, 2002a; *Lear et al.*, 2002b; *Marchitto et al.*, 2007a; *Martin et al.*, 2002; *Rosenthal et al.*, 2006; *Rosenthal et al.*, 2011; *Skinner et al.*, 2003; *Yu and Elderfield*, 2008).

The incorporation of Mg into foraminiferal shells is likely related to temperature through both thermodynamics and physiological processes (*Bentov and Erez*, 2006; *Erez*, 2003; *Lea et al.*, 1999; *Rosenthal et al.*, 1997). Interspecies differences – species-specific vital effect – in shell Mg/Ca have been observed in planktonic (*Anand et al.*, 2003; *Lea et al.*, 1999) and benthic foraminifera (*Elderfield et al.*, 2006; *Lear et al.*, 2002a; *Rosenthal et al.*, 1997). Empirical calibration and understanding of influential parameters other than temperature are vital to the application of Mg/Ca as a paleotemperature proxy. Planktonic foraminifera have been calibrated by core-top (*Dekens et al.*, 2002; *Elderfield and Ganssen*, 2000; *Lea et al.*, 2000; *Nurnberg*, 1995), sediment trap (*Anand et al.*, 2003; *McConnell and Thunell*, 2005) and laboratory culture studies (*Lea et al.*, 1999; *Mashiotta et al.*, 1999; *Nurnberg et al.*, 1996) (see *Barker et al.*, 2005 for an overview); and most of these studies have demonstrated a 9-10% exponential increase in Mg/Ca per degree Celsius in most species. The response of benthic Mg/Ca to temperature is less well constrained. With the exception of recent progress in culturing benthic foraminifera (*Hintz et al.*, 2006a; *Hintz et al.*, 2006b), benthic foraminiferal Mg/Ca has been calibrated exclusively by the comparison of core top samples to bottom water temperatures.

Paper I focuses in a refinement of species-specific Mg/Ca-temperature calibrations using six benthic species and indicates that among the six benthic species used, the epifaunal *C. wuellerstorfi* has the highest potential for reconstructing the BWT from 0 to 6ºC. However, an increasing number of studies suggests that the Mg/Ca of benthic foraminifer is not only a function of temperature but also can be affected by the carbonate ion saturation (*Elderfield et al.*, 2006; *Healey et al.*, 2008; *Martin et al.*, 2002; *Raitzsch et al.*, 2008; *Yu and Elderfield*, 2008).

4.2 Carbonate ion concentration and saturation states

Most of the benthic calibrations support the effect of temperature on foraminiferal Mg/Ca. However, there are still questions regarding the accuracy of these calibrations (*Lear et al.*, 2002a; *Martin et al.*, 2002; *Rosenthal et al.*, 1997; *Russell et al.*, 1994). Studies that focus exclusively on *Cibicidoides wuellerstorfi* suggest that the slope of the Mg/Ca-temperature calibration is steeper than that of the mixed *Cibicidoides* spp. calibration (*Elderfield et al.*, 2006; *Lear et al.*, 2002a). The difference between *C. wuellerstorfi* and the mixed species calibration has led many to highlight seawater carbonate saturation as a potentially significant control on Mg incorporation into the test of this particular species (*Lear et al.*, 2004; *Martin and Lea*, 2002; *Martin et al.*, 2002). Using a global compilation of core-top dataset, *Elderfield et al.* (2006) suggested that Mg/Ca ratio is reduced at low carbonate ion saturation (here after $\Delta\left[CO_3^{2-}\right]$). Then, they propose and establish the first empirical relationship between the $\Delta\left[CO_3^{2-}\right]$ and Mg/Ca in *C. wuellerstorfi*, based on core-top samples. Since then, an increasing number of studies evaluating the effect of $\Delta\left[CO_3^{2-}\right]$ on the Mg/Ca of benthic foraminifera have been conducted (*Healey et al.*, 2008; *Raitzsch et al.*, 2008; *Yu and Elderfield*, 2008). Published studies show that Mg/Ca in *C. wuellerstorfi* and *Cibicidoides kullenbergi* shells are strongly affected by low $\Delta\left[CO_3^{2-}\right]$, for BWT less than 4ºC (*Elderfield et al.*, 2006; *Raitzsch et al.*, 2008; *Yu and Elderfield*, 2008). *Yu and Elderfield* (2008) further assessed the influence of BWT and $\Delta\left[CO_3^{2-}\right]$ on core-top samples from accross the global ocean. They suggest that *C. wuellerstorfi* Mg/Ca ratios show a weak correlation with BWT, whereas *C. kullenbergi* Mg/Ca ratios show no correlation with changes in BWT or $\Delta\left[CO_3^{2-}\right]$. Those conclusions suggest that these species are less sensitive to the temperature than previously expected (*Healey et al.*, 2008; *Raitzsch et al.*, 2008; *Yu and Elderfield*, 2008) and questions the use of Mg/Ca for past temperature reconstructions. *Yu and Elderfield* (2008) therefore recommend separating the temperature signal and the effect on the epifaunal benthic Mg/Ca ratios. This is difficult because temperature and $\Delta\left[CO_3^{2-}\right]$ are often well correlated in the ocean.

In order to extract the temperature signal in benthic foraminiferal Mg/Ca, the **Paper II** investigates the carbonate ion saturation effect on the Mg/Ca in the benthic foraminifer *C. wuellerstorfi*, based on existing Atlantic Mg/Ca dataset and by adding new results from the western tropical Atlantic. The new line of reasoning is to isolate the temperature effect on the Mg/Ca to see if there is any residual effect explained by $\Delta\left[CO_3^{2-}\right]$. Consequently, we have separated the data into bins with narrow temperature ranges, which can then be used to look for relationships with $\Delta\left[CO_3^{2-}\right]$. Based on our results, we find a minor effect of $\Delta\left[CO_3^{2-}\right]$ on Mg/Ca when examining Atlantic sites characterized by similar temperatures. This suggests rather opposite results than those obtained from the study of *Yu and Elderfield* (2008). This study also provides evidence that the temperature is exerting a controlling effect on the foraminiferal *C. wuellerstorfi* Mg/Ca.

The conclusions from **Papers I** and **II** highlight a new angle in the Mg/Ca proxy as a tool for paleotemperature reconstructions. These studies suggest that the sensitivity of temperature and carbonate chemistry on *C. wuellerstorfi* Mg/Ca differs from previous study.

4.3 Evolution of thermocline and intermediate water masses in the western tropical Atlantic during the last deglaciation

One of the objectives of this thesis was to reconstruct the upper and intermediate water masses structure and circulation in the western tropical Atlantic during the last deglaciation. Our understanding of the northward cross-equatorial transport of thermocline and intermediate waters and its role in the interhemispheric climate anomalies is limited and largely debated in paleoclimate investigations. While some studies comfirm a greater Atlantic Intermediate Water (AAIW) fraction during episodes of reduced AMOC, others suggest a reduction.

Recent studies invoke a connection between the high-latitude North Atlantic climate change and the Southern Ocean circulation change to explain the deglacial episodes (*Anderson et al.*, 2009; *Lee et al.*, 2012; *Toggweiler and Lea*, 2010) via the abrupt changes in the northward flow of AAIW (*Came et al.*, 2008; *Marchitto et al.*, 1998; *Pahnke et al.*, 2008; *Rickaby and Elderfield*, 2005; *Thornalley et al.*, 2011a; *Thornalley et al.*, 2011b). However, controversy persists (*Huang et al.*, 2014; *Xie et al.*, 2012, 2014).

Paper III focuses on planktonic and benthic foraminiferal paired Mg/Ca-δ^{18}O and δ^{13}C records from a depth transect on the northeastern Brazilian margin, to reconstruct the changes from surface to intermediate waters during the last deglaciation. This study also presents radiocarbon measurements in paired deep dwelling- and surface habitat planktonic foraminifera to reconstruct the apparent ventilation age at the thermocline depth in the western tropical Atlantic.

Our new records provide crucial details of intermediate depth circulation changes over the last Glacial-Interglacial cycle and their relationship to other records of Northern and Southern Hemisphere ocean-climate change (Figure 5).

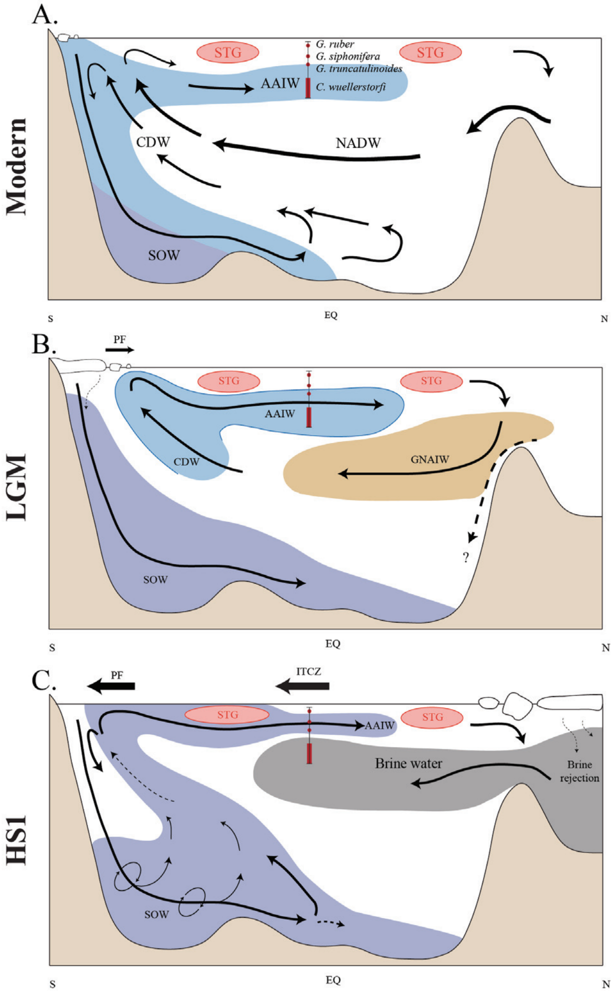

Figure 5. Schematic illustration of hypothesized changes in the western tropical Atlantic overturning across the last deglaciation. (**A**) the modern overturning; (**B**) LGM overturning; (**C**) HS1/YD overturning; The supply of North Atlantic deep water is seriously reduced, the Southern Ocean warms due to the bipolar seesaw, Antarctic sea ice retreats, upwellings are enhanced. See Paper III for futher details.

The main conclusions of this study are as follows:

1. Our records reveal that the LGM was accompanied by a warming episode ~21-20 kyr ago in the top 1000 m water depth, corresponding to an early phase of deglacial warming. The intermediate waters record a warming of 1-2ºC relative to the present day.

2. A heat build-up in the western tropical Atlantic starting 19 kyr ago suggests a rapid response of the surface waters to the bipolar seesaw mechanism, whilst subsurface waters are not responded at least for the earlier half of the Antarctica deglacial warming 1 episode (W-1).

3. Our data collectively suggest that the upper-water column and thermocline waters (100-700 m water depth) of the western tropical Atlantic have contained a large part of the Southern component water mass during the last deglaciation and particularly during HS1 and the YD (Figure 5C). We propose that warm AAIW never ceased to flow northward during the last deglaciation as has been suggested in other studies. Based on Mg/Ca and thermocline ventilation ages records, it is likely inflow at the intermediate depth shawled to thermocline waters during periods of reduced AMOC. Benthic Mg/Ca temperature reconstructions indicate a cooling during both HS1 and to a lesser extent during the YD. The large decoupling between the surface/subsurface, thermocline and intermediate waters certainly suggests large changes in local hydrology at intermediate depth possibly due to water masses reorganization (see Paper III for further details).

4.4 List of papers

PAPER I

Refining benthic foraminiferal Mg/Ca-temperature calibration using core-top from the western tropical Atlantic: Implication for paleotemperature estimation

Tisserand, A. A., T. M. Dokken, C. Waelbroeck, J.-M. Gherardi, V. Scao, C. Fontanier, F. Jorissen (2013)

Geochemistry, Geophysics, Geosystems (G^3)

PAPER II

Revisiting the carbonate ion saturation effect on Mg/Ca in the benthic foraminifer *C. wuellerstorfi* in the Atlantic Ocean

Tisserand, A. A., T. M. Dokken, J.-M. Gherardi, C. Waelbroeck, F. J. C. Peeters

Manuscript in preparation

PAPER III

Deglacial evolution of surface to intermediate water mass characteristics in the western tropical Atlantic.

Tisserand, A. A., T. M. Dokken, L. T. Oppedal, F. J. C. Peeters

Manuscript in preparation

5 Perspectives

Our new understanding provides the basis of future investigations.

Variations in Southern Ocean surface properties are communicated through the subtropical southern hemisphere and into the tropics via the intermediate water masses. A significant contribution of the intermediate water masses participates into the North Atlantic thermohaline overturning. However, the understanding of the mechanisms controlling the vertical structure of the tropical thermocline, which is a key area to reconstruct the inflow and the return flow of the upper limb of the AMOC, is far from complete.

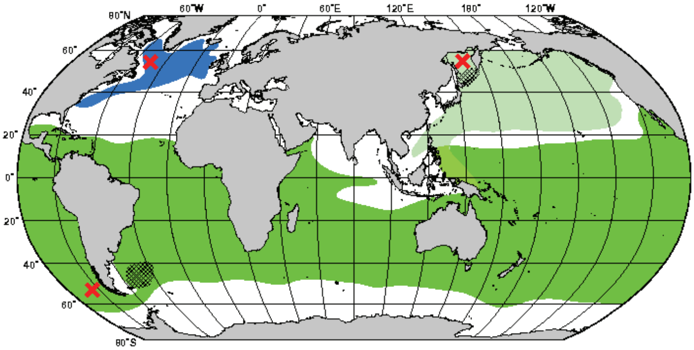

Figure 6: Schematic map showing the distribution of intermediate water masses, as defined by their respective salinity minima: Antartic Intermediate Water (dark green), Labrador Sea Water (blue), North Pacific Intermediate Water (light green). Red crosses denote their main formation regions. AAIW is formed in the southeastern Pacific (red cross), just west of southern Chile, from where it spreads to the entire southern hemisphere and tropics throughout the globe (*Talley*, 1999).

In order to reduce the uncertainties in climate reconstructions, we need records from other tropical deep transects and from the Southern Ocean, that are not well constrained (Figure 6, dark green area).

A large improvement to the already improved Mg/Ca-temperature calibration based on benthic foraminiferal species, would be to enlarge the dataset from the intermediate waters, but not confined to the tropics. The warmest part of the *C.*

wuellerstorfi Mg/Ca calibration is, today, made with few coring sites from the same area (see Paper I for further details). Increasing the number of locations and of data in this temperature range, and when possible, in the thermocline area, would considerably reduce uncertainties.

The question of whether carbonate ion saturation affects the Mg/Ca ratio of the benthic foraminifer *C. wuellerstorfi* is an important question (see section 4.2. for more details). The general consensus is that carbonate ion saturation is the dominant influence on *C. wuellerstorfi* Mg/Ca and that it is actually insensitive to BWT changes. In the manuscript **Revisiting the carbonate ion saturation effect on Mg/Ca in the benthic foraminifer *C. wuellerstorfi* in the Atlantic Ocean**, we have challenged this assertion and used a compilation of core-top data from the Atlantic Ocean to argue that there is not a significant carbonate ion saturation effect on *C. wuellerstorfi* Mg/Ca. Temperature, salinity and carbonate ion are often well correlated in the ocean. To deal with this problem, we have separated the data into bins with narrow temperature ranges to look for relationships with carbonate ion saturation. This paper II has been submitted to EPSL. The main issue concern the choice to limit the analysis to the Atlantic Ocean. However, in line with referee comments, the editor expressed interest in seeing a future resubmission alone similar lines which take a global analysis of available data. Consequently, we will continue this analysis with a global dataset. If we still find no significant influence from carbonate ion saturation based on all of the available data, then this study would show a very important result.

Some aspects of the deglaciation reconstruction could be improved (see Paper III for further details). In order to establish a strong statement of the water mass source affecting the thermocline and intermediate waters during HS1 and the YD, planktonic foraminiferal radiocarbon ^{14}C ages may be replicated and extended at higher resolution. Benthic radiocarbon ^{14}C ages have been employed to reconstruct intermediate water ventilation age in the WTA and a joined manuscript has been submitted (*E. Freeman et al.*, *manuscript submitted*).

During my PhD training, I was led to work with other topics. This work is not included in this thesis, but deserves an outlook in this section. Three papers where I am involved have been published, presenting results from the long-core MD03-2705 from the Mauritanian coast. This core is largely influenced by the dust input from the Sahara. These three papers try to evaluate and detect the African climate dynamics:

- Malaize B., Jullien E., **Tisserand A. A.**, Skonieczny C., Grousset F. E., Eynaud F., Kissel C., Bonnin J., Karstens S., Martinez P., Bory, A., Bout-Roumazeilles V., Caley T., Crosta X., Charlier K., Rossignol L., Flores J. A., Schneider R., 2012. The impact of African aridity on the isotopic signature of Atlantic deep waters across the Middle Pleistocene Transition, Quaternary Research, 77, 182-191.
- Matsuzaki K. M. R., Eynaud F., Malaize B., Grousset F. E., **Tisserand A. A.**, Rossignol L., Charlier K., Jullien E., 2011. Paleoceanography of the Mauritanian margin during the last two climatic cycles: From planktonic foraminifera to African climate dynamics, Marine Micropaleontology, 79, 67-79.
- **Tisserand A. A.**, Malaize B., Jullien E., Zaragosi S., Charlier K., Grousset F., 2009. African monsoon enhancement during the penultimate glacial period (MIS 6.5 similar to 170 ka) and its atmospheric impact, Paleoceanography, 24, PA2220.

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