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A Holocene palaeoceanographic multi-proxy study on the variability of Atlantic water inflow and sea ice distribution along the pathway of Atlantic water

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Sarah MP Berben
A dissertation for the degree of Philosophiae Doctor – August 2014

DISSERTATION FOR THE DEGREE OF PHILOSOPHIAE DOCTOR

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By endurance we conquer!

Acknowledgements

I would like to take the opportunity to thank all the people who supported and guided me throughout this entire PhD journey.

First of all, I would like to thank my supervisor Dr. Katrine Husum for giving me this wonderful opportunity in the first place. Further, I'm very grateful for all of her scientific advice, moral support, patience, freedom and trust to develop my own ideas, not to mention the many loud laughs we had. Secondly, I would like to thank Dr. Steffen Aagaard-Sørensen for the many scientific discussions, constructive feedback and assistance regarding my PhD-work.

The entire CASE group is thanked for the always pleasant and inspiring meetings, training sessions and social gatherings scattered over Europe. Special thanks go to Prof. Simon Belt and the chemical sisters for a warm welcome in Plymouth and a highly enthusiastic guidance in my biomarker adventure. It has been very contagious (*or should I scream contamination!)*. My gratitude is also expressed to my fellow 'ESRs' for the many scientific discussions, supporting friendships and enjoyable stays abroad. In particular, to Diane for being, this entire time, my Tromsø partner in crime!

Thank you to Frank Peeters for an enthusiastic introduction to the fascinating world of paleoceanography and the encouragement to continue. You were so right when you told me *"Saar, ik weet wat je het liefste zou doen, en volgens mij weet je dat zelf ook"*…and that is exactly what I did.

Thanks are also extended to the entire staff at the department of geology, UiT, for their technical and organizational assistance. Special thanks go to Jan P. Holm, Trine Dahl, Julia Sen and Karina Monsen for their always professional and kind help when and wherever I needed it.

To all my colleagues and friends in Tromsø, I would like to say thank you for all the support (in many ways), the different kind of social get-togethers and successful distractions, especially to Noortje for being such a great and always helpful friend from the early beginning. It all contributed to this great experience of living in the Arctic.

Thank you to all my friends and family in Belgium for not forgetting me, taking an interest in what it is again that I actually do, but most of all, for always making it such a pleasure to come back home. Some of you were even crazy enough to come and visit me so far up north which I appreciate a lot.

Finally, the biggest thank you is for my mother and her never-ending support and believe in my (sometimes crazy) dreams and ambitions which is an inspiration on itself.

Tusen takk!

Sarah

Table of contents

Preface

This PhD thesis was carried out from 2011 to 2014 at the University of Tromsø within the Initial Training Network programme "Changing Arctic and Subarctic Environments" (CASE-ITN) funded by the European Commission within the 7th Framework Programme FP7 2007/2013, Marie Curie Actions. The overall aim of the project was to reconstruct and elucidate the Holocene natural variability of physical parameters such as Atlantic water inflow and sea ice distribution in the Arctic and Subarctic environment (Nordic Seas). Further, it provided intensive training sessions (including a marine geology and geophysics cruise in the Fram Strait with the R/V Helmer Hanssen, University of Tromsø) and progress meetings which all resulted in a close collaboration with five institutes across Europe (i.e. University of Bordeaux, Amsterdam, Plymouth, Geomar (Kiel) and the Geological Survey of Norway (Trondheim)). This collaboration also included a personal research stay during spring 2013 at the Biogeochemistry Research Centre, University of Plymouth, focusing on the analyses of sea ice and phytoplankton biomarkers.

Additionally, a Marie Curie "toppfinansiering" was received from the Research Council of Norway, whereas the Norwegian Research School in Climate Dynamics provided funding for their annual all staff meetings, several specialized courses and participation of the 2nd Young Scientist Meeting/4th Open Science Meeting organized by PAGES in Goa, India.

The results of this thesis were presented in 5 posters and 8 talks during national and international workshops, project meetings and conferences. The thesis consists of an introduction and three scientific papers regarding the investigation and reconstruction of the natural variability of Atlantic water inflow and sea ice distribution in the high latitude North Atlantic and adjacent Barents Sea. The scientific papers presented are:

Paper I

Berben SMP, Husum K, Cabedo-Sanz P and Belt ST (2014) **Holocene sub-centennial evolution of Atlantic water inflow and sea ice distribution in the western Barents Sea.** *Clim. Past* 10: 181-198, doi:10.5194/cp-10-181-2014.

Paper II

Berben SMP, Husum K, Navarro-Rodriguez A, Belt ST and Aagaard-Sørensen S **Atlantic water inflow and sea ice distribution in the northern Barents Sea: A Holocene palaeoceanographic evolution.**
Submitted to Paleoceanography

<u>Paper III</u>

Berben SMP, Husum K and Aagaard-Sørensen S **A late Holocene multi-proxy record from the northern Norwegian margin: temperature and salinity variability.**
In prep. Intended for The Holocene

1 Introduction and objectives

Atlantic water is transported through the North Atlantic via the Fram Strait and Barents Sea into the Arctic Ocean where it interacts with sea ice, affects salinity regulation and hence, the Atlantic Meridional Overturning Circulation (AMOC) (e.g. Rudels et al., 1996; Dieckmann and Hellmer, 2008). The latter is of great importance for the global climate and plays an influential role for the relatively warm north-western European climate. Further, the inflow of Atlantic water results in an oceanic heat advection towards the Arctic and mainly defines the Arctic sea ice extent, especially within the high latitude North Atlantic and adjacent Barents Sea (Hopkins, 1991). Nonetheless, the extent of Arctic sea ice is also influenced by different processes such as atmospheric circulation variability, local wind patterns and ice import (Hopkins, 1991). The Barents Sea is considered to be the main gateway of Atlantic water inflow towards the Arctic Ocean and thus, a region characterized by a significant heat exchange between the ocean and atmosphere (Broecker, 1991; Serreze et al., 2007). Furthermore, the dramatic decline in Arctic sea ice cover throughout recent decades is most pronounced within the northern Barents Sea (e.g. Comiso et al., 2008; Screen and Simmonds, 2010) and it has been argued that a recent enhanced advection of Atlantic water inflow has contributed to a further decline in sea ice cover (e.g. Kinnard et al., 2011; Spielhagen et al., 2011; Årthun et al., 2012). Additionally, an increased loss of Arctic sea ice, related to an enhanced Arctic warming, is presumed to had a severe impact on climatic conditions far beyond the Arctic region (e.g. extreme winters in Europe) (Francis et al., 2009; Yang and Christensen, 2012). As such, both Atlantic water and sea ice cover are pivotal elements of the climate system (e.g. Hopkins, 1991; Kvingedal, 2005; Stroeve et al., 2012) with the high latitude North Atlantic, including the Barents Sea, representing a key area for which to focus investigations into ocean-sea ice-atmosphere interactions (Vinje, 2001). In order to obtain a better comprehension of the interaction between Atlantic water inflow and sea ice distribution it is crucial to determine the degree of natural variability and thus, acquire more high resolution palaeo-records of sub-surface water masses and sea ice cover (e.g. Voronina et al., 2001; Polyak et al., 2010).

Previously, climate fluctuations throughout the Holocene (ca. 11 700 – 0 cal yr BP) have been associated with North Atlantic Ocean circulation changes (e.g. Bianchi and McCave, 1999; Bond et al., 2001). In particular, proxy records have indicated several changes of sea ice distribution and surface water masses (i.e. Atlantic, Arctic and Polar water) within the high latitude North Atlantic (e.g. Bauch and Weinelt, 1997; Bond et al., 1997; Jennings et al., 2002; Sarnthein et al., 2003; Hald et al., 2007), the Svalbard margin (e.g. Slubowska et al., 2005; Rasmussen et al., 2007; Spielhagen et al., 2011; Müller et al., 2012; Werner et al., 2013) and the Barents Sea (e.g. Duplessy et al., 2001; Lubinski et al., 2001; Duplessy et al., 2005; Risebrobakken et al., 2010; Risebrobakken et al., 2011; Klitgaard Kristensen et al., 2013). A strong influence of Atlantic water related to the Holocene Thermal Maximum (HTM) has been observed throughout the early Holocene (e.g. Duplessy et al., 2001; Sarnthein et al., 2003; Husum and Hald, 2004; Slubowska et al., 2005; Hald et al., 2007; Slubowska-Woldengen et al., 2007; Risebrobakken et al., 2010). The HTM is primarily attributed to a solar insolation maximum at these latitudes, although various other factors such as land-cover feedbacks and coupled atmospheric-oceanic dynamics and in particular, the northward penetration of relatively warm Atlantic water might have contributed (e.g. Berger, 1978; Koç et al., 1993; Kaufman et al., 2004). Nevertheless, palaeo-temperature reconstructions based on alkenones (Calvo et al., 2002), diatoms (Koç and Jansen, 1994; Birks and Koç, 2002; Andersen et al., 2004) and planktic foraminifera (Andersson et al., 2003; Risebrobakken et al., 2003; Sarnthein et al., 2003) have different temporal signatures of the HTM which are attributed to the influence of regional variations, different depth habitat and/or response time of the various proxies to atmospheric changes (Moros et al., 2004). This emphasizes the important role of atmosphere-ocean interactions (Kaufman et al., 2004; Moros et al., 2004; Hald et al., 2007). After the HTM, a dominance of Arctic water and increased sea ice cover has been observed by marine records in the high latitude North Atlantic (e.g. Sarnthein et al., 2003; Hald et al., 2007), the Svalbard margin (e.g. Rasmussen et al., 2007; Müller et al., 2012; Rasmussen et al., 2012; Werner et al., 2013) and the Barents Sea (e.g. Duplessy et al., 2001; Risebrobakken et al., 2010; Klitgaard Kristensen et al., 2013). This period characterized by cooler conditions is referred to Neoglacial cooling and is consistent with decreasing summer insolation at high latitudes (Wanner et al., 2008). Finally, during the late Holocene, marine records have indicated a reduced influence of Atlantic water inflow, the dominant presence of cold Arctic water and cooler conditions (e.g. Slubowska et al., 2005; Hald et al., 2007; Skirbekk et al., 2010). This general cooling trend has been ascribed to reduced insolation at high latitudes (e.g. Kaufman et al., 2009) and has also been recorded by several terrestrial records such as ice core records from Greenland and Svalbard (e.g. Dahl-Jensen et al., 1998; Divine et al., 2011) and lake and tree records from north-western Europe (e.g. Bjune et al., 2009; Kaufman et al., 2009). Contradictory, marine records also showed evidence of a strengthened inflow of Atlantic water at the Vøring plateau (Andersson et al., 2003; Risebrobakken et al., 2003; Andersson et al., 2010), at the Svalbard margin (Slubowska-Woldengen et al., 2007; Jernas et al., 2013; Werner et al., 2013; Zamelczyk et al., 2013) and in the Barents Sea (Duplessy et al., 2001; Lubinski et al., 2001). Additionally throughout the late Holocene, observations of fluctuating climatic conditions attributed to different causes such as solar forcing, volcanic eruptions (e.g. Bryson and Goodman, 1980; Lean, 2002; Jiang et al., 2005; Wanner et al., 2008) or the North Atlantic Oscillation (NAO) have been found in the Nordic Seas (e.g. Giraudeau et al., 2004; Goosse and Holland, 2005; Nyland et al., 2006; Rousse et al., 2006; Solignac et al., 2006; Slubowska-Woldengen et al., 2007; Semenov et al., 2009) and in north-western Europe (e.g. Lauritzen and Lundberg, 1999; Bjune and Birks, 2008).

These Holocene observations highlight the importance of atmospheric changes as they influence the strength of the surface water masses, the AMOC and hence, Earth's global heat distribution. Nonetheless, the natural variations of Atlantic water inflow and sea ice distribution, including the precise nature and driving forces behind them, are not well constrained. Therefore, the overarching main objective of this thesis is to investigate the natural variability of Atlantic water inflow and sea ice distribution throughout the Holocene by reconstructing a series of new high resolution multi-proxy records of sub-surface water mass properties (i.e. temperature and salinity) and sea ice distribution. In order to obtain a better understanding of potential driving mechanisms, additional focus is placed on: a) the Holocene palaeoceanographic evolution in the western and northern Barents Sea; b) the interaction between surface water masses and sea ice extent; and c) the interplay between Atlantic and Coastal water during the fluctuating climatic conditions of the late Holocene and the possible relationship to the North Atlantic Oscillation.

2 Present day oceanography of the study area

The North Atlantic Current (NAC) transports warm and saline Atlantic water (>2 °C, >35 ‰; Hopkins, 1991) from the south and enters the high latitude North Atlantic as two major topographically steered branches of the Norwegian Atlantic Current (NwAC) (Orvik and

Niiler, 2002) (Figure 1). The western branch enters the Norwegian Sea through the Iceland-Faroe Ridge as the Iceland-Faroe frontal jet (Perkins et al., 1998). The eastern branch passes through the Faroe-Shetland channel continuing its north-eastwards pathway along the Norwegian shelf edge (Orvik and Niiler, 2002). Subsequently, Atlantic water is brought into the Arctic Ocean by different branches of the NwAC. The NwAC continues northwards as the West Spitsbergen Current (WSC) along the western Barents Sea slope into the Fram Strait where it splits into three branches, the Return Atlantic Current (RAC), the Yermak Branch (YB) and the Svalbard Branch (SB) (Manley, 1995) (Figure 1). North of Svalbard, the SB flows as an eastwards sub-surface current beyond the Franz Victoria and St. Anna Trough and thereby influences the Barents Sea by south-westwards advected Atlantic water (Abrahamsen et al., 2006) (Figure 1). The eastern branch of the NwAC turns as the North Cape Current (NCaC) into the Barents Sea where it flows partly northwards as a submerged flow and partly eastwards parallel to the Coastal current system (Loeng, 1991) (Figure 1).

The Norwegian Coastal Current (NCC) transports fresh Coastal water (2 - 13 °C, 32 - 35 ‰; Hopkins, 1991) from the North Sea, the Baltic and the Norwegian coast northwards and parallel between the Norwegian margin and the NwAC (Figure 1). It flows into the south-western Barents Sea continuing along the Norwegian and Russian coastline (Aure and Strand, 2001). Due to the influence of freshwater runoff from the Norwegian mainland it is characterized by low salinities (Blindheim, 1987). The NCC is a density driven current mainly influenced by its salinity distribution and, due to mixing with Atlantic water, its salinity increases, whereas stratification reduces on its pathway northwards. The boundary between Coastal and Atlantic water is formed as a well-defined Coastal front with Coastal water above Atlantic water in the upper 50 to 100 m of the water column as a westwards thinning wedge (Ikeda et al., 1989).

The inflow of Atlantic water into the Arctic Ocean is balanced by the outflow of cold, less saline and ice-loaded Polar water (0 - 2 °C, 33 - 34.4 ‰; Hopkins, 1991). From the Arctic Ocean, Polar water is brought into the Atlantic Ocean by the East Greenland Current (EGC) (Rudels et al., 2005) and into the Barents Sea by the East Spitsbergen Current (ESC) and Bear Island Current (BIC) (Hopkins, 1991) (Figure 1).

Arctic water (~0.5 °C, ~34.8 ‰; Hopkins, 1991) is characterized by a reduced temperature and salinity as well as by a seasonal sea ice cover and is formed when Polar water and Atlantic water meet and mix (Hopkins, 1991). In the northern Barents Sea, Arctic water dominates the area with progressively decreasing temperature and salinity towards the north-east.

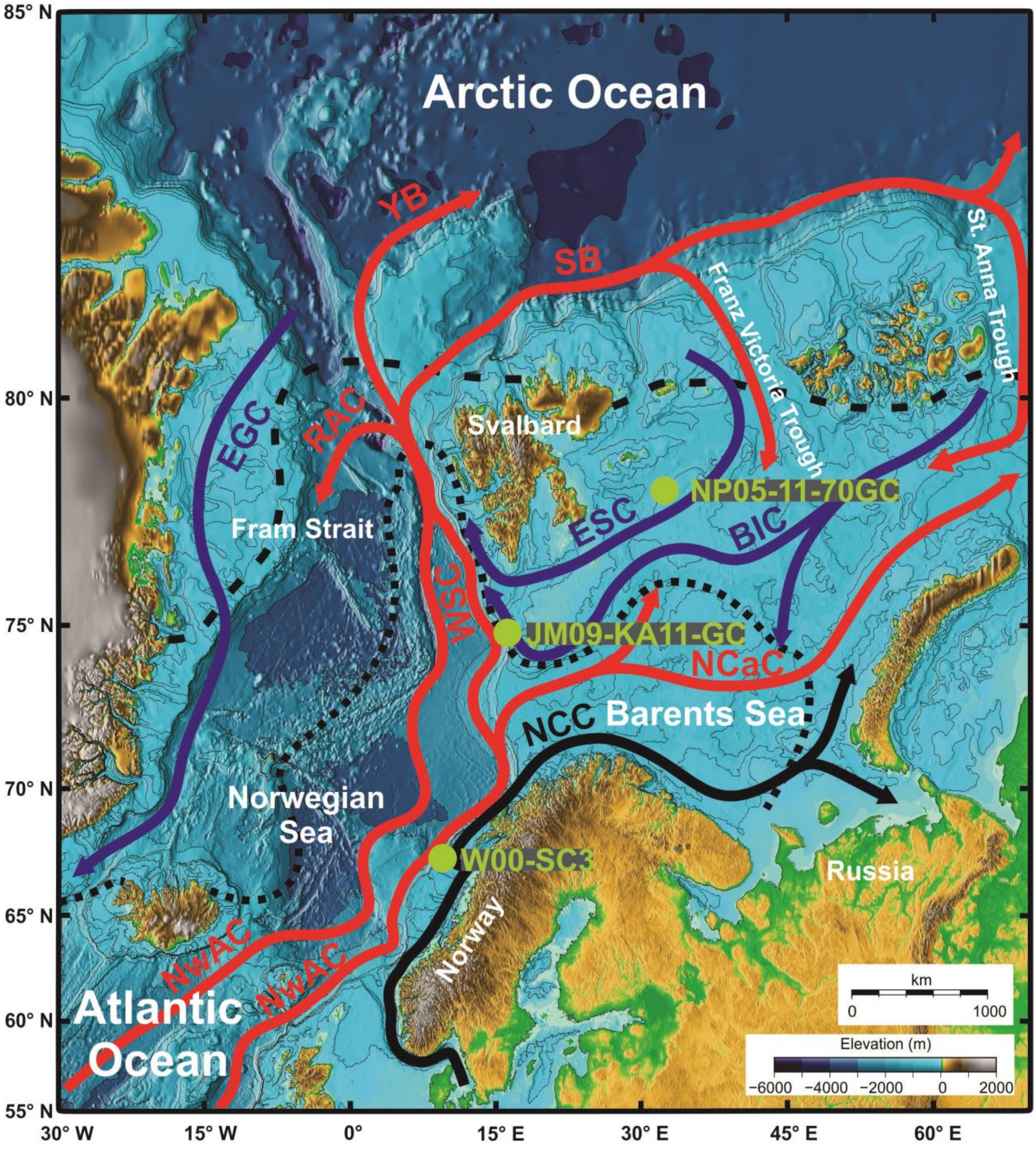

Figure 1: The present day oceanography of the study area is presented on a bathymetric map. The main surface currents and sea ice extent of the high latitude North Atlantic and Barents Sea are indicated. Summer sea ice margin (black dashed). Winter sea ice margin (black dotted). Atlantic water (red): Norwegian Atlantic Current (NwAC), West Spitsbergen Current (WSC), Return Atlantic Current (RAC), Yermak Branch (YB), Svalbard Branch (SB) and North Cape Current (NCaC). Polar water (blue): East Greenland Current (EGC), East Spitsbergen Current (ESC) and Bear Island Current (BIC). Coastal water (black): Norwegian Coastal Current (NCC). The locations of the three marine sediment cores used in this study are indicated with green circles.

One of the main oceanographic features of the Barents Sea are the Oceanic fronts which divide the different water masses by forming boundaries that are defined as a sharp climatic gradient in terms of temperature, salinity and sea ice coverage (Hopkins, 1991; Pfirman et al., 1994). The boundaries between Polar/Arctic and Arctic/Atlantic waters correspond to the Polar and Arctic front, respectively.

In the northern North Atlantic and the Barents Sea, the positions of the Polar and Arctic front are closely related to the overall extent of sea ice distribution and align with the average summer and winter sea ice margins, respectively (Vinje, 1977) (Figure 1). The north-eastern Barents Sea is dominated by Arctic water and characterized by large changes in seasonal sea ice distribution with sea ice mainly formed during fall and winter (Loeng, 1991; Vinje, 2001; Sorteberg and Kvingedal, 2006). Due to cooling and brine rejection during sea ice growth, dense and cold deep waters are formed. In addition, the extensive sea ice formation, subsequent brine rejection in winter and the seasonal melting of sea ice in the summer results in a stable and strong stratification (Wassmann et al., 2006). Contrary, in the south-western Barents Sea the inflow of relative warm Atlantic water affects the sea ice extent which results in a mainly ice-free Atlantic domain (Årthun et al., 2012). The position of the marginal ice zone (MIZ), an area characterized by high surface productivity during the summer season (Smith and Sakshaug, 1990), is strongly influenced by the interplay among the different water masses. A peak algal bloom during spring, as sea ice retreats along the ice edge, is responsible for nearly all the biological primary production in the Barents Sea (Sakshaug et al., 1992).

3 Material and methods

In this thesis, the results of multi-proxy analyses preformed on marine sediment samples are presented and discussed. Along the pathway of Atlantic water, three marine sediment cores were collected (Figure 1). At the northern Norwegian margin (Vøring plateau in front of Trænadjupet, south of the Lofoten) sediment core W00-SC3 (67.24° N, 08.31° E; 1184 m water depth) was retrieved by the SV *Geobay* in 2000 (Laberg et al., 2002) (Paper III). In 2009, sediment core JM09-KA11-GC (74.87° N, 16.48° E; 345 m water depth) was retrieved by the RV *Jan Mayen* in the western Barents Sea (Rüther et al., 2012) (Paper I). Sediment core NP05-11-70GC (78.40° N, 32.42° E; 293 m water depth) was retrieved within the northern Barents Sea, south of Kong Karls Land (Olga Basin) by the RV Lance in 2005 (Paper II).

A description of the methods applied in this PhD thesis is given below. All three papers consist of planktic foraminiferal fauna and their preservation indicators analyses, as well as stable isotope ($\delta^{18}O$, $\delta^{13}C$) measurements of *Neogloboquadrina pachyderma*. Additionally, in paper I and III, summer sub-surface temperatures (SST) were reconstructed via the application of a transfer function. In paper I and II, sea ice and phytoplankton biomarkers were analyzed, whereas in paper III geochemical and trace element analyses were performed.

3.1 Chronology

The chronologies are based on accelerator mass spectrometry (AMS) ^{14}C dates. Eight AMS ^{14}C dates performed on molluscs (Rüther et al., 2012) complemented with five AMS ^{14}C dates on benthic foraminifera were used to develop the depth-age model of JM09-KA11-GC (Paper I). To construct the depth-age model of NP05-11-70GC (Paper II) three AMS ^{14}C dates obtained from benthic foraminifera were used, whereas for W00-SC3 (Paper III) three published AMS ^{14}C dates (Laberg et al., 2002) and one additional AMS ^{14}C date on *N. pachyderma* were used. All AMS ^{14}C dates were calibrated to calendar years Before Present (cal yr BP) using the Calib 6.1.1 software (Stuiver and Reimer, 1993) and the Marine09 calibration curve (Reimer et al., 2009) for NP05-11-70GC (Paper II), and the Calib 7.0.0 software (Stuiver and Reimer, 1993) and the Marine13 calibration curve (Reimer et al., 2013) for JM09-KA11-GC (Paper I) and W00-SC3 (Paper III). For each sediment core a region-specific local reservoir age correction was applied. The calibration was constrained by a 2-σ range and the final depth-age models were developed using linear interpolation. In addition, an extrapolation was applied towards the core top for W00-SC3 (Paper III).

3.2 Planktic foraminifera

The distribution of planktic foraminifera is mainly controlled by water mass properties such as temperature, salinity, nutrition and sea ice cover (e.g. Johannessen et al., 1994; Carstens et al., 1997). The planktic foraminiferal fauna thus reflects the sea surface conditions and is therefore often used to reconstruct sea surface and sub-surface temperatures (e.g. Eynaud, 2011). Quantitative palaeo-temperature estimates can be obtained through the application of a transfer function including a modern training set (e.g. Imbrie and Kipp, 1971; Pflaumann et al., 2003; Kucera et al., 2005). Nonetheless, the composition of foraminiferal assemblages might be modified by carbonate dissolution associated with ocean circulation and climate which can affect planktic foraminifera, in particular smaller species such as *Turborotalita quinqueloba*, *Globigerina bulloides*, *Globigerinita glutinata* and *Globigerinita uvula* (e.g. Berger, 1970; Archer and Maier-Reimer, 1994; Archer, 1996; Zamelczyk et al., 2013).

All samples were freeze-dried, wet-sieved into different size fractions (1000, 100 and 63 µm) and dried in an oven at 40 °C. Due to a low abundance of planktic foraminifera in the bottom samples (90 - 130 cm) of JM09-KA11-GC (Paper I), the planktic foraminifera and sediment in these samples were divided by heavy liquid separation using sodium polytungstate diluted with distilled water to a specific gravity of 1.8 g mL^{-1} following Knudsen (1998). From the 100 - 1000 µm size fraction, planktic foraminiferal assemblages (>300 specimens) were determined following Knudsen (1998). Although a minimum of 300 specimens was aimed for, species-specific relative abundances were calculated for samples containing more than 50 specimens in samples from JM09-KA11-GC (Paper I) and at least 25 specimens in samples from NP05-11-70GC (Paper II) following the recommendations of Forcino (2012). The identification of left and right coiling *N. pachyderma* was achieved following Darling et al. (2006) and thus, the right coiling form is identified as *Neogloboquadrina incompta* (Cifelli, 1961). In addition to the species-specific relative abundances (%), the total planktic foraminiferal concentration (#/g sediment), the total and the species-specific planktic foraminiferal flux (#/cm^2/yr) were calculated, with the latter calculated according to Ehrmann and Thiede (1985).

3.2.1 Preservation indicators

In order to quantify the state of foraminiferal preservation, the potential dissolution of foraminiferal tests was analyzed by measuring the mean shell weight (µg) of *N. pachyderma* (Broecker and Clark, 2001; Barker and Elderfield, 2002; Beer et al., 2010) and calculating the fragmentation (%) of planktic foraminiferal tests (Conan et al., 2002). The mean shell weight was obtained using a Mettler Toledo microbalance (0.1 µg sensitivity). Well-preserved (visually) and square-shaped tests of *N. pachyderma* were chosen from narrow size ranges in order to reduce problems of ontogeny and size difference induced variability (Barker et al., 2004). The fragmentation of planktic foraminiferal tests was analyzed within the 100 - 1000 µm size fraction and calculated following the method of Pufhl and Shackleton (2004).

3.2.2 Transfer function derived summer sub-surface temperature

A transfer function and the Arctic training set of Husum and Hald (2012), based on the >100 µm size fraction, were used in order to reconstruct summer (July-August-September) sub-surface temperature (SST) estimates for a water depth of 100 m. The reconstruction was carried out using the C2 version 1.7.2. software (Juggins, 2010) applying the Weighted Average-Partial Least Square (WA-PLS) and Maximum Likelihood (ML) statistical model with a leave-one-out cross validation (Ter Braak and Juggins, 1993; Telford and Birks, 2005).

3.4 Stable isotope analysis ($\delta^{18}O$, $\delta^{13}C$)

The stable oxygen and carbon isotopic compositions ($\delta^{18}O$, $\delta^{13}C$) of foraminiferal calcite tests reflect several properties of the ambient sea water masses in which they have been calcified. More specifically, $\delta^{18}O$ is controlled by temperature and salinity changes, whereas $\delta^{13}C$ is influenced by the primary production and stratification characteristics of the water mass (e.g. Spielhagen and Erlenkeuser, 1994; Katz et al., 2010).

A stable isotope analysis was carried out on the polar planktic foraminiferal tests of *N. pachyderma*. The tests were selected from narrow size fractions in order to minimize size dependent effects on isotopic composition (Aksu and Vilks, 1988; Keigwin and Boyle, 1989; Oppo and Fairbanks, 1989; Donner and Wefer, 1994; Bauch et al., 2000). All measurements were analyzed using a Finnigan MAT 253 mass spectrometer coupled to an automated Kiel device at the Geological Mass Spectrometer (GMS) Laboratory of the University of Bergen. The ice volume effect was corrected for the obtained $\delta^{18}O$ records of JM09-KA11-GC (Paper I) and NP05-11-70GC (Paper II) according to Fairbanks (1989). These records were not corrected for their species-specific vital effect as published offsets of *N. pachyderma* are often inconsistent (e.g. Kohfeld et al., 1996; Bauch et al., 1997; Stangeew, 2001; Simstich et al., 2003). However, to the $\delta^{18}O$ results from W00-SC3 (Paper III) a vital effect of 0.6 ‰ was applied based on previous suggestions for the Nordic Seas (Simstich et al., 2003) and Norwegian Sea (Nyland et al., 2006).

3.5 Biomarker analysis

The sea ice biomarker IP_{25} is produced specifically by Arctic sea ice diatoms and remains relatively stable in marine sediments (Brown et al., 2011; Belt and Müller, 2013; Stein and Fahl, 2013; Brown et al., 2014). Previous studies indicated that sedimentary IP_{25} concentrations have been consistent with known sea ice trends and thus, provide a tool to reconstruct palaeo sea ice conditions (Belt and Müller, 2013 and references therein). In addition, an integrated analysis of IP_{25} with other phytoplankton lipids such as brassicasterol has been used to distinguish between either open water conditions or perennial ice cover (Müller et al., 2009; Müller et al., 2011; Belt and Müller, 2013).

Samples were freeze-dried and stored at -20 °C prior to the biomarker analysis being performed. The previously described general methodology for biomarker analysis (IP_{25} and sterols) was applied with some modifications (Belt et al., 2012; Brown and Belt, 2012). In order to permit quantification of the biomarkers using gas chromatography-mass spectrometry (GC-MS), three internal standards were added (Belt et al., 2012). A total organic extract (TOE) was obtained following previous descriptions (Belt et al., 2012; Brown and Belt, 2012). The presence of elemental sulfur that interfered with the subsequent chromatographic analyses was removed from the TOE prior fractionation into individual lipids. Subsequently, all individual fractions were analyzed using GC-MS with operating conditions according to Belt et al. (2012). The identification of individual lipids was done on the basis of their characteristic GC retention indices and mass spectra obtained from standards in total ion current chromatogram (TIC). The lipids were quantified by comparison of peak area integrations of selected ions with those of the internal standard in selected ion monitoring (SIM) mode, and subsequently normalized according to instrumental response factors and sediment masses (and total organic carbon content) (Brown et al., 2011; Belt et al., 2012). These ratios were also converted to biomarker fluxes ($\mu g/cm^2/yr$) (Belt et al., 2012). Concentrations of IP_{25} and brassicasterol from NP05-11-70GC (Paper II) were further combined to derive the so-called P_BIP_{25} index that has the potential to provide semi-quantitative estimates of sea ice cover (Müller et al., 2011).

3.6 Geochemical analysis

The weight percentages (wt. %) of total carbon (TC) and total organic carbon (TOC) were analyzed using a LECO SC-444 (ES-2) at the Laboratory of the Geological Survey of Norway (NGU). The calcium carbonate content ($CaCO_3$) was calculated using the equation of Espitalié et al. (1977) (Equation 1).

$$CaCO_3 = (TC - TOC) * 8.33 \qquad \text{[Equation 1]}$$

3.7 Trace element analysis

The incorporation of Mg into planktic foraminiferal calcite is mainly controlled by the ambient sea water temperature (e.g. Nürnberg, 1995). The positive correlation between foraminiferal Mg/Ca ratios and sea water temperature allows for the reconstruction of sub-surface temperature (SST) estimates (e.g. Mashiotta et al., 1999; Elderfield and Ganssen, 2000; Kozdon et al., 2009). Additionally, a combined analysis of Mg/Ca and $\delta^{18}O$ measurements of planktic foraminiferal tests enables the reconstruction of sub-surface salinity (SSS) estimates by using a modern $\delta^{18}O_{seawater}$:salinity relationship (e.g. Thornalley et al., 2009; Elderfield et al., 2010).

Trace element analysis was performed on well-preserved (visually) specimens of *N. pachyderma.* The tests were selected from a narrow size fraction (150 - 250 µm) in order to reduce the possible size-dependent bias on the Mg/Ca measurements (Elderfield et al., 2002). A chemical cleaning procedure, including a reduction step to remove metal oxides and an oxidation step to remove any organic matter, was carried out (e.g. Boyle and Keigwin, 1985). The samples were then analyzed by ICP-MS method for foraminiferal analysis, including simultaneous measurements of Mg, Mn, Al, and Fe, on a Finnigan Element2 at the Marine Science Institute, UC Santa Barbara. In order to identify post cleaning sample contamination which potentially biased the measured Mg/Ca ratios in foraminiferal calcite, tracers of contaminating phases (Fe, Al and Mn) were investigated (Barker et al., 2003).

3.7.1 Sub-surface temperature and salinity

The species-specific temperature:Mg/Ca equation of Kozdon et al. (2009) was used to reconstruct Mg/Ca derived SST estimates. This equation assumes a linear temperature function for the narrow temperature range occupied by *N. pachyderma* which is appropriate for reconstructed temperatures above ca. 2.5 °C. For water masses below 2.5 °C associated with salinities less than 34.5 ‰ the method loses its precision (Kozdon et al., 2009).

SSS estimates were reconstructed based on the δ^{18}O measurements of *N. pachyderma* ($\delta^{18}O_c$) and the calculated Mg/Ca derived SST ($T_{Mg/Ca}$) estimates. The temperature:δ^{18}O equation of Shackleton (1974) modified after O'Neil et al. (1969) and an equation to convert $\delta^{18}O_w$ from VPDB to VSMOW values (Hut, 1987) were rearranged in order to calculate the oxygen isotope ratios of the ambient seawater ($\delta^{18}O_w$) VSMOW. This result in the following equation previously presented by Nyland et al. (2006) (Equation 2).

$$\delta^{18}O_w = \delta^{18}O_c + 0.27 - \left[\frac{4.38 - \sqrt{4.38^2 - 0.4 * \left(16.9 - T_{Mg/Ca}\right)}}{0.2}\right] \qquad \text{[Equation 2]}$$

Subsequently, the salinity (S) to $\delta^{18}O_w$ relation for the central and eastern Nordic Seas by Simstich et al. (2003) (Equation 3) was applied to reconstruct palaeo SSS estimates.

$$\delta^{18}O_w = -12.17 + 0.36 * S \qquad \text{[Equation 3]}$$

4 Summary of papers

<u>Paper I</u>

Berben SMP, Husum K, Cabedo-Sanz P and Belt ST (2014) **Holocene sub-centennial evolution of Atlantic water inflow and sea ice distribution in the western Barents Sea.** *Clim. Past* 10: 181-198, doi:10.5194/cp-10-181-2014.

The NAC brings warm and saline Atlantic water into the Arctic Ocean. This inflow is balanced by the outflow of cold Polar water and by the formation of deep water to the south, which is part of the AMOC. Changes of the AMOC can greatly affect the global ocean circulation and climate, especially in the high-latitude North Atlantic and adjacent Barents Sea where the inflow of warm water, heat exchange and its effect on sea ice formation is essential for the environment and society. It is suggested that the recent decline in Arctic sea ice might have been partly caused by an enhanced advection of Atlantic water into the Arctic Ocean (Kinnard et al., 2011; Spielhagen et al., 2011). To fully understand the nature and driving forces of Atlantic water inflow and its interaction with sea ice, it is crucial to establish the natural range of oceanographic fluctuations within this area.

In this study, a continuous high resolution record from the Kveithola Through, western Barents Sea, is investigated in order to elucidate the Holocene variability of Atlantic water inflow and sea ice distribution. Palaeo SST estimates and temporal changes in sea ice cover are reconstructed by analyzing planktic foraminiferal fauna and their preservation indicators, planktic foraminiferal stable isotopes ($\delta^{18}O$, $\delta^{13}C$) and biomarkers (including IP_{25}).

The resulting multi-proxy data indicates the following palaeoceanographic changes. A dominance of the polar species *N. pachyderma* and low SST values (ca. 4 °C) indicate the existence of cold water and a reduced Atlantic water inflow during the early Holocene (ca. 11 900 – 10 400 cal yr BP). Additionally, the biomarker data argues for a transition from severe sea ice conditions to a marginal ice zone scenario. From ca. 10 900 to 10 700 cal yr BP, the planktic fauna and stable isotope data record a clear cooling event correlating to the Preborial Oscillation. The early-mid Holocene (ca. 10 400 – 7300 cal yr BP) is characterized by an increased influence of Atlantic water. This is indicated by the dominance of *T. quinqueloba*, increased $\delta^{18}O$ values indicative of increased salinity and SST values up to 6 °C. Further, the biomarker data argues for a decline in seasonal sea ice cover. Throughout the mid-late Holocene (ca. 7300 – 1100 cal yr BP) stable conditions with a pronounced influence of Atlantic water are reflected by high abundances of *T. quinqueloba* and relatively warm SST values (ca. 5.9 °C), whereas biomarker data indicates predominantly ice-free conditions at the study site. After ca. 1100 cal yr BP, a higher abundance of *G. uvula* argues for a reduced salinity, whereas biomarker concentrations reflect the reappearance of low-frequency seasonal sea ice. The late Holocene (ca. 1100 – 0 cal yr BP) is further characterized by more unstable conditions as indicated by the rapidly fluctuating proxy records.

Paper II

Berben SMP, Husum K, Navarro-Rodriguez A, Belt ST and Aagaard-Sørensen S **Atlantic water inflow and sea ice distribution in the northern Barents Sea: A Holocene palaeoceanographic evolution.**
Submitted to Paleoceanography

Previous research suggested that the observed Arctic sea ice decline during recent decades might be partly attributed to an enhanced advection of Atlantic water into the Arctic Ocean (Årthun et al., 2012). An increasing loss of sea ice will result in an enhanced Arctic warming and eventually, lead to severe consequences for the climate system. It is thus important to understand the interaction between sea ice and Atlantic water. In the northern Barents Sea, the oceanic fronts dividing different water masses are closely related to the overall extent of sea ice distribution, in particular the average winter and summer sea ice margins.

Therefore, the purpose of this study is to investigate the Holocene natural variability and interaction between Atlantic water inflow and sea ice distribution. This is achieved by multi-proxy analyses performed on a marine sediment core from the Olga Basin, northern Barents Sea. The analyses include planktic foraminiferal fauna and their preservation indicators, planktic foraminiferal stable isotopes ($\delta^{18}O$, $\delta^{13}C$), in addition to sea ice biomarkers (including the P_BIP_{25} index; Müller et al., 2011). The reconstructed sub-centennial record illustrates that the area experienced gradual but distinct changes in seasonal sea ice cover and Atlantic water inflow. Based on these results, different oceanographic scenarios emphasizing the interaction between surface water masses and sea ice distribution are proposed.

The results suggest overall warm subpolar conditions characterized by short spring and long productive summers throughout the early Holocene (ca. 9500 – 5800 cal yr BP). Additionally, the proxy records argue for a strong influence of Atlantic water which contributed to a reduced sea ice extent via an active ocean feedback mechanism. A proxy-specific response is indicated by the different recording times of the Holocene Thermal Optimum between ca. 9300 and 5800 cal yr BP. Throughout the mid Holocene (ca. 5800 – 2200 cal yr BP) an overall cooling trend characterized by cold Arctic water, well-ventilated water masses and an advanced seasonal sea ice cover is indicated. These observations are consistent with the lowered summer insolation likely affecting the sea ice production which resulted in a more southwards position of the sea ice edge. During the late Holocene (ca. 2200 – 0 cal yr BP), the proxy data indicates more unstable palaeoceanographic conditions most likely associated with a more pronounced positive NAO-mode. In addition, both a sub-surface warming linked to the increased inflow of Atlantic water and an extended sea ice cover attributed to decreasing insolation are recorded. This argues for a decoupling between ocean and atmosphere which result in a long spring and short summer season causing the most extended sea ice cover recorded in this study.

<u>Paper III</u>

Berben SMP, Husum K and Aagaard-Sørensen S **A late Holocene multi-proxy record from the northern Norwegian margin: temperature and salinity variability.**
In prep. Intended for The Holocene

The late Holocene is characterized by fluctuating climatic conditions in the Nordic Seas (e.g. Nyland et al., 2006) and north-western Europe (e.g. Lauritzen and Lundberg, 1999; Bjune and Birks, 2008) including the 'Roman Warm Period' (RWP, ca. BCE 50 – CE 400), the 'Dark Ages' (DA, ca. CE 400 – 800), the 'Medieval Warm Period' (MWP, CE 900 – 1500) and the 'Little Ice Age' (LIA, ca. CE 1500 – 1900) (e.g. Lamb, 1977). Previously, shifting NAO conditions have been referred to as a possible forcing mechanism for the observed fluctuating climatic conditions (e.g. Trouet et al., 2009; Olsen et al., 2012). Positive and negative NAO modes affect the westerlies and thereby, the strength of Atlantic water inflow and Coastal water influence along the Norwegian margin (e.g. Sætre, 2007; Hurrell et al., 2013). As it strongly influences north-western Europe climatic conditions, it is of importance to understand the natural variability of Atlantic water inflow in the Nordic Seas.

Therefore, in order to investigate the fluctuating interplay of Atlantic and Coastal water possibly linked to a variable NAO, palaeo SST and SSS estimates are reconstructed throughout the late Holocene. This is achieved by analyses of planktic foraminiferal fauna, preservation indicators, stable isotopes ($\delta^{18}O$, $\delta^{13}C$) and paired Mg/Ca and $\delta^{18}O$ measurements of *N. pachyderma* performed on a marine sediment core from the northern Norwegian margin.

The two independently reconstructed SST-records (i.e. $SST_{Mg/Ca}$ and $SST_{Transfer}$) reveal a discrepancy between their values which is attributed to a combination of several factors. In particular, the low Mg/Ca ratios are primarily caused by the overall poor preservation conditions linked to the continental margin. This resulted in most likely underestimated

$SST_{Mg/Ca}$ and SSS values. Nonetheless, the $SST_{Transfer}$ record corresponds well to modern sea temperatures within the upper 300 m of the water column.

The presented high-resolution multi-proxy data indicates some fluctuating influences of Atlantic and Coastal water at the core site. Period I (ca. 3500 – 2900 cal yr BP) is influenced by relatively cool (ca. 6.9 °C, $SST_{Transfer}$) Coastal water and an enhanced stratification attributed to a dominating negative NAO-like mode. Warmer (ca. 7.3 °C, $SST_{Transfer}$) Atlantic water associated with more favorable preservation and positive NAO conditions dominates throughout Period II (ca. 2900 – 1600 cal yr BP). The RWP might be reflected by the last part of Period II. During period III (ca. 1600 – 950 cal yr BP), the core site experiences stable and relatively cool (ca. 6.6 °C, $SST_{Transfer}$) conditions attributed to an increased influence of Coastal water. This correlates with the colder and dryer DA. A stronger influence of Atlantic water is observed during Period IV (ca. 950 – 550 cal yr BP) and attributed to prevailing positive NAO conditions correlating with the MWP. However, due to the overall late Holocene cooling, Atlantic water was less warm (ca. 6.3 °C, $SST_{Transfer}$) compared to Period II.

5 Synthesis

This study represents multi-proxy high resolution reconstructions of water mass properties of the high latitude North Atlantic and adjacent Barents Sea. They reflect the natural variability of Atlantic water inflow and sea ice distribution over the Holocene. To elucidate the Holocene palaeoceanographic evolution and obtain an improved understanding of driving factors, the interaction between sub-surface water masses, mutually, and sea ice distribution was investigated.

The results illustrate the natural oceanic variability in the Norwegian and Barents Seas, in particular along the pathway of Atlantic water. Additionally, potential forcing mechanisms and aspects of ocean-sea ice-atmosphere dynamics, as part of the climate system, are suggested. Furthermore, using multi-proxy data from the same horizons highlighted the importance of a full comprehension of proxy behaviour as they each have their proxy-specific response to environmental and/or climatic changes. With respect to the analyses of planktic foraminifera, the assessment of preservation conditions has proven to be important for the interpretation of planktic foraminiferal proxy data. In particular, as calcite dissolution affects both faunal assemblages and Mg/Ca ratios of *N. pachyderma*, the palaeo SST estimates might show over or under-estimated values. Finally, the main conclusions of this study are presented below.

The earliest timing of the Holocene (ca. 11 900 – 10 400 cal yr BP) is in the western Barents Sea characterized by a transition from severe sea ice to marginal ice zone conditions and a dominance of cold Arctic water. Both the western and northern Barents Sea experienced overall warm sub-polar conditions including a pronounced influence of Atlantic water and a decline in seasonal sea ice cover during the early Holocene (ca. 10 400 – 7300 and ca. 9500 – 5800 cal yr BP respectively). These palaeoceanographic conditions are attributed primarily to the high summer insolation at these latitudes. Throughout the mid Holocene, contradictory environmental conditions reconstructed for the western and northern Barents Sea indicate the regional different responses to climatic forcing mechanisms. Whereas the northern Barents Sea was characterized by cold Arctic water and an advanced seasonal sea ice extent between ca. 5800 and 2200 cal yr BP, the western Barents Sea was influenced by relatively warm, high saline Atlantic water and predominantly ice-free conditions between ca. 7300 and 1100 cal yr BP. The overall cooling trend associated with the Neoglacial cooling and attributed to the lowered insolation observed in the northern Barents Sea does not seem to affect the western Barents Sea similarly. Eventually, all studies show that the late Holocene experiences an overall period of unstable oceanographic conditions along the pathway of Atlantic water.

Throughout the late Holocene (ca. 2200 – 0 cal yr BP), the northern Barents Sea experienced an enhanced influence of Atlantic water and a seasonal sea ice cover that experienced its greatest extent at any point within the record. Superimposed on this trend, elevated levels of Atlantic water inflow and seasonal sea ice cover were recorded. In the western Barents Sea, a minor cooling trend and the reappearance of low-frequency seasonal sea ice was indicated in addition to rapidly fluctuating oceanographic conditions between ca. 1100 and 0 cal yr BP. The observed fluctuating conditions throughout the late Holocene were investigated in more detail at the northern Norwegian margin. These results show an overall cooling trend throughout the late Holocene (ca. 3500 – 550 cal yr BP) which consist of alternating oceanographic conditions between a dominant influence of Atlantic versus Coastal water. Further, these periods correspond to a dominating positive versus negative NAO mode respectively, with the exception of period III. Seemingly contradictory is the overall cooling trend observed at the northern Norwegian margin and in the western Barents sea versus the well-pronounced increased influence of Atlantic water observed in the northern Barents Sea.

This might be explained by overall more positive NAO conditions resulting in a stronger inflow of Atlantic water northwards but not necessarily in warmer Atlantic water temperatures. The recorded cooler temperatures of Atlantic water are most likely due to a lowered summer insolation.

The investigation of integrated sub-surface water mass and sea ice records suggest that the interaction between Atlantic water and sea ice depends on additionally interfering factors such as insolation and the NAO. In particular for the northern Barents Sea, high insolation throughout the early Holocene resulted in a reduced sea ice cover allowing for a strong heat flux between ocean and atmosphere. This led to an active ocean feedback mechanism that additionally contributed to the decline in sea ice extent. Contrary, throughout the late Holocene, a reduced insolation caused the overall increased sea ice cover that co-existed with an increased influence of Atlantic water. A decoupling between ocean and atmosphere, with the sea ice acting as a barrier between the two, might have prohibited a strong heat flux which resulted in the observed simultaneous sub-surface warming and sea surface cooling. Hereby, the palaeo-records illustrate the complexity of the interacting elements of the climate system leading to different possible natural scenarios of the environmental conditions.

6 Future research

The reconstructed Holocene palaeoceanographic evolution has shown natural fluctuations of Atlantic water inflow and sea ice distribution. Although these results provided new insights, it also highlighted certain issues that deserve more attention in the future.

In this PhD-study, the planktic foraminiferal fauna was analyzed in order to investigate palaeo water mass properties. In particular, the faunal assemblages were used to quantify sub-surface water temperatures via the application of a transfer function. However, the planktic foraminiferal fauna is known to be also influenced by other properties besides temperature (e.g. Johannessen et al., 1994; Carstens et al., 1997). For instance, *T. quinqueloba* has been associated with warm Atlantic water, but is also found nearby the sea ice margin and thus associated with oceanic front conditions (e.g. Volkmann, 2000). With regard to this species, it has been pointed out in this PhD-study that the available nutrients might have played an important role, especially in the Arctic region with the proximity of the sea ice edge and its associated high primary production. Therefore, the resulting transfer function derived SST record (Paper I) possibly contains overestimated SST values. And thus, a more detailed investigation on the preference of high food supply, and consequent incorporation of this knowledge into a modern database, would be appropriated and strengthen transfer function derived SST estimates. This could also lead to a better interpretation of the past influence of Atlantic water whereby a change in strength and temperature are not necessarily occuring at the same time.

Additionally, transfer function derived SST estimates can be biased due to selective dissolution which might alter the species composition of foraminiferal assemblages (e.g. Zamelczyk et al., 2013). In particular, planktic foraminiferal species such as *T. quinqueloba*, *G. bulloides*, *G. glutinata* and *G. uvula* are more sensitive to carbonate dissolution than others such as *N. pachyderma* and *N. incompta* (e.g. Berger, 1970; Archer and Maier-Reimer, 1994; Archer, 1996). Furthermore, calcite dissolution might also be responsible for the removal of Mg-rich parts in foraminiferal tests and thus bias the Mg/Ca ratios (Brown and Elderfield, 1996; Rosenthal et al., 2000; Johnstone et al., 2011). It has been indicated that, beside the calcification temperature, the Mg-uptake is also controlled by environmental factors such as the carbonate ion concentration (Hendry et al., 2009). In this PhD study, preservation indicators such as mean shell weight, planktic foraminiferal fragmentation and sedimentary $CaCO_3$ were analyzed in order to obtain an overview of the preservation conditions. However, these parameters do not identify the responsible factors of dissolution and their connection to environmental conditions. Therefore, a more detailed study of calcite dissolution, its causes and effects is necessary to limit biased palaeo-temperature estimates. For example, an investigation of the B/Ca ratio of foraminiferal calcite, a proxy for past seawater carbonate ion concentration, could contribute to a better understanding of the calcium carbonate preservation state (e.g. Yu and Elderfield, 2007).

To fully examine the dynamics of the density driven AMOC and its involvement in climate changes, it is important to obtain both palaeo SST and SSS estimates (e.g. Thornalley et al., 2009) and thus, a further investigation in order to improve the potential of the Mg/Ca proxy should be carried out. In addition, assuming a future establishment of the species-specific calcification depth, paired Mg/Ca and $\delta^{18}O$ measurements of different species might further deliver SST and SSS data for different water depths. Thereby, it would provide a better understanding of the vertical stratification of the water column.

The biomarker analysis has shown the potential to reconstruct high resolution palaeo seasonal sea ice distribution in the Arctic. Recently, Brown et al. (2014) identified the source of the sea ice biomarker IP_{25}. Nevertheless, to clarify the interpretation of IP_{25} and brassicasterol, the production regulating factors of these biomarkers, in addition to a better knowledge on the source and specificity of brassicasterol, should be better identified (Belt and Müller, 2013). This should be investigated by collecting sea ice and phytoplankton samples from different areas which then contribute to an improved P_BIP_{25} index (potentially region-specific) and thus, a more quantitative assessment of seasonal sea ice cover. In addition, several related biomarkers such as Diene II and Triene could provide additional oceanographic information. Therefore, these biomarkers should be assessed in order to determine their source origin and palaeoenvironmental significance as well as degradation in marine sediments throughout time.

In this PhD study, it was indicated that proxies have their specific responses to oceanographic changes and reflect different elements of the climate system. This led to a better understanding of responsible mechanisms behind the natural variability of Atlantic water inflow and sea ice extent. In order to obtain a better overview of palaeo-environmental conditions, it is important to further identify proxy-specific responses.

Finally, new multi-proxy records along the pathway of Atlantic water (similar to the ones presented here) would strongly contribute to a better spatial interpretation of the sea ice extent and Atlantic water inflow interaction. In addition, similar multi-proxy studies from a broader area in the Arctic Ocean, including the Polar water outflow pathways, might lead to an advanced understanding of sea ice-ocean changes in general and a better constrain of the spatial and temporal variability.

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Paper I

Berben SMP, Husum K, Cabedo-Sanz P and Belt ST (2014) **Holocene sub-centennial evolution of Atlantic water inflow and sea ice distribution in the western Barents Sea.** *Clim. Past* 10: 181-198, doi:10.5194/cp-10-181-2014.

Paper II

Berben SMP, Husum K, Navarro-Rodriguez A, Belt ST and Aagaard-Sørensen S **Atlantic water inflow and sea ice distribution in the northern Barents Sea: A Holocene palaeoceanographic evolution.**
Submitted to Paleoceanography

Paper III

Berben SMP, Husum K and Aagaard-Sørensen S **A late Holocene multi-proxy record from the northern Norwegian margin: temperature and salinity variability.**
In prep. Intended for The Holocene