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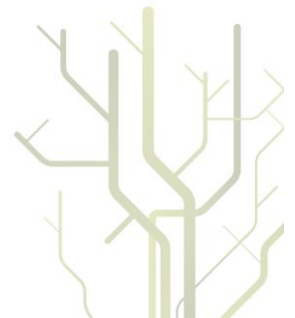FACULTY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF GEOLOGY

Arctic Ocean warmings from the last glaciation to the present:

Implementing and assessing the reliability of planktic foraminiferal paleoreconstructions

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Arctic Ocean warmings from the last glaciation to the present: implementing and assessing the reliability of planktic foraminiferal paleoreconstructions

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Acknowledgements

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This thesis consists of an introduction and five articles. The papers deal with the investigation of past oceanic variability and carbonate preservation and assessment of the reliability of planktic foraminiferal assemblages in paleoenvironmental reconstructions in the Fram Strait (Fig. 1). The scientific papers presented are:

Paper 1

Zamelczyk, K., Rasmussen, T.L, Husum, K., Haflidason, H., de Vernal, A., Ravna, E.K., Hald, M., Hillaire-Marcel, C. **Between two oceanic fronts: Paleoceanographic changes and calcium carbonate dissolution in the central Fram Strait during the last 20,000 years.**

In revision for Quaternary Research

Paper 2

Zamelczyk, K., Rasmussen, T.L., Husum, K., Hald, M. **Marine calcium carbonate preservation vs. climate change over the last two millennia in the Fram Strait: Implications for planktic foraminiferal paleostudies**.

Submitted to Marine Micropaleontology

Paper 3

Zamelczyk, K., Husum, K., Rasmussen, T.L., Godtliebsen, F., Hald, H. **Surface water conditions and calcium carbonate preservation in the Fram Strait during the late Weichselian 29,000-16,000 years BP.**

To be submitted to Paleooceangraphy

Paper 4

Spielhagen, R. F.,Werner, K., Aagaard-Sørensen, S., Zamelczyk, K., Kandiano,E., Budeus, G., Husum, K., Marchitto, T., and Hald, M., 2011. **Enhanced modern heat transfer to the Arctic by warm Atlantic Water.** *Science* 331**,** 450-453.

Paper 5

Werner, K., Spielhagen, R.F., Bauch, D., Hass, H.Ch., Kandiano, E., Zamelczyk, K., 2011. **Atlantic Water advection to the eastern Fram Strait- Multiproxy evidence for late Holocene variability**. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 308 (3-4), 264-276.

1. <u>Introduction and objectives</u>

The impact of climate change is one of the most debated issues in our society and scientific community. Arctic environments are of a great concern, largely because warming is predicted to be of much higher amplitude in high-latitude regions. During the past century, temperatures in these regions have increased almost twice as fast as in other parts of the world, and the recent sea ice loss is faster than predicted by climate models from the Intergovernmental Panel on Climate Change (IPCC, 2007).

In the climate system the ocean plays an important role. It has the capacity to store 1000 times more heat than the atmosphere (Bindoff et al., 2007) and has the ability to redistribute the energy around the globe (Broeker, 1991). With the increasing levels of greenhouse gases and ocean acidification, prediction of future changes in climate is a pressing issue in science. The large uncertainties associated with future climate scenarios stress the need for a better understanding of the mechanisms controlling climate-ocean system. This knowledge depends on the accuracy of instrumental measurements and of geological records.

Geological archives are commonly used to infer information about changes in past dynamics of the ocean-atmosphere-ice system. Marine sediments document the amplitude, rate and timing of natural variability in the climate and ocean system, which span timescales from days to millions of years and provide a measure of the ocean sensitivity to both natural and anthropogenic forcing. In addition, geologic proxies provide insights into processes that are too slow to be captured by decades-long datasets of shipboard and other instrumental measurements.

Reconstructions of past climate and ocean circulation changes from marine sediments rely heavily on the reliability of proxies. The relationship between proxies and their preferable

environmental conditions have been assessed in field calibrations and laboratory studies. Planktic foraminifera is a group of unicellular organisms widely used in paleoceanographic research. Their morphology (shape, number and arrangement of chambers) allows for the identification of the different species (e.g., Kemle-von Mücke and Hemleben, 1999) that are each linked to specific environmental conditions (e.g., Bé and Tolderlund, 1971; Johannessen et al., 1994). Information of their habitat preferences allows reconstructing the paleo-conditions at given locations and timescales. Moreover, the uptake in their shells of different trace elements and isotopes directly from surface seawater reflect the sea water composition and the physical and biological conditions during calcification. Planktic foraminifera shells are composed in 99% by weight of pure calcite, which unfortunately, makes them vulnerable to dissolution. Hence, the record of planktic foraminiferal distribution patterns and various proxies measured in their shells can bear uncertainties that disrupt the interpretation of the sedimentary records.

Numerous studies show that selective dissolution can alter the species composition of foraminiferal assemblages (e.g. Berger, 1970; Thunell and Honjo, 1981; Le and Thunell, 1996). Some species are highly susceptible to dissolution (e.g., *Turborotalita quinqueloba, Globigerina bulloides, Globigerinata glutinata*), whilst others are more resistant to dissolution (e.g., *Neogloboquadrina pachyderma*) (Berger, 1970). Shallow-dwelling species are amongst the most prone to destruction (Malmgren, 1985). Preferential dissolution has been widely recorded in deep sea sediments (Berger, 1970; Peterson and Prell, 1985; Murray and Alve, 1999; Conan et al., 2002). Dissolution effects on foraminiferal shell chemistry and the stable isotope ratios have been studied in sediment and laboratory experiments (Erez, 1979; Rosenthal et al., 2000; Hönisch, 2002; Dekens et al., 2002; Nouet and Bassinot, 2007).

Planktic foraminiferal shells are exposed to destruction by dissolution below the calcium carbonate saturation depth. Above this depth level, dissolution may also occur in the water column and at the sea floor. Dissolution in the upper part of the water column is controlled by the exchange of gasses between the surface water and the atmosphere, the concentration of carbonate ions, alkalinity, productivity, salinity, temperature, mixing processes and in the case of the Arctic region, sea ice cover and brine formation. Dissolution at the sea floor results from $CaCO_3$ undersaturation of pore waters through the addition of metabolic CO_2 by oxidation of organic carbon within the sediment. Emerson and Bender (1981) suggested that release of respiratory CO_2 within pore waters could cause up to 50% calcite dissolution even at the saturation horizon. In situ microelectrode measurements of O_2 and pH confirm that dissolution of $CaCO_3$ within pore waters must be occurring in response to the release of CO_2

(e.g., Hales and Emerson, 1997). It appears that the pore-water induced dissolution is intensified under highly productive regions. Huber et al. (2000) and Heinrich et al. (1998, 2002) showed that carbonate preservation in the northern North Atlantic is linked to the oceanographic regime controlled by two contrasting water masses and sea ice. Also, these works point to supralysoclinal dissolution as the most important factor influencing the pore water chemistry of surface sediments and effecting carbonate preservation in the northern North Atlantic.

The main objective of the present study is to contribute to the understanding of how past oceanographic changes affect the preservation patterns of planktic foraminifera assemblages, hereby to assess their reliability as a proxy for paleoenvironmental recontructions. The study examines the paleoceanographic variations in very high temporal resolution, considers eventual impacts of environmental factors and the concentration of atmospheric CO_2 and quantifies the dissolution effect on carbonates over the last 30,000 years in the Fram Strait. The composite dissolution indices and multi-proxy approach are used to find the apparent interaction between CO_2 concentrations in the atmosphere, oceanic changes and surface productivity. The special focus is on the Atlantic water advection, which governed the past oceanic development and kept the eastern part of the Fram Strait free of ice.

2. Background

2.1. Changes in ocean carbon chemistry and the glacial cycle

Carbon transfer between the ocean and atmosphere is controlled by physical and chemical processes. The cyclicity of organic and inorganic carbon transfer has been proposed to cause glacial-interglacial changes in atmospheric CO_2 (e.g., Sigman et al., 2010). Albeit numerous studies, mechanisms of the carbon transfer in the ocean are still poorly understood. Generally and briefly, the marine carbon system is based on the interrelated chemical reaction of dissolved inorganic carbon forms. When CO_2 (carbon dioxide) dissolves in water it reacts with the water (H_2O) to form carbonic acid (H_2CO_3). This weak acid associates to biocarbonate ion (HCO_3^-), carbonate ion (CO_3^{2-}) and hydrogen ion (H^+). These mechanisms make the ocean a much greater reservoir for carbon than the atmosphere. Biocarbonate represent approximately 90% of the dissolved inorganic carbon, while 9% is carbonate and 1% dissolved CO_2.

In addition to temperature, salinity and pressure, an essential component of the carbonate system of the ocean is alkalinity governed by electrical charge in the ocean and the buffer capacity- i.e. the ability to neutralize acids (Zeebe and Wolf-Gladrow, 2001).

Primary production in the surface water plays a crucial role in the exchange of CO_2 between ocean and atmosphere through the biological carbon pump. This mechanism transfers inorganic and organic carbon to the deep sea. The sea surface organic (soft tissue) production lowers the CO_2 through photosynthesis, while the secretion of calcite and aragonite into shells of planktic foraminifera (and other calcifying organisms) act inversely, and increases pCO_2 at the sea surface (Wollast, 1994). Respiration processes, such as oxidation of organic carbon at the sea floor, release CO_2, which can cause dissolution of calcium carbonate. This process intensifies with increasing pressure with depth and lower temperature.

Cyclic changes in atmospheric CO_2 levels from thousand to millions of years have been suggested to be an important forcing factor for climate change (e.g., Petit et al., 1999) and changes in ocean chemistry (e.g., Sundquist, 1986). On decadal to centennial timescale the exchange of carbon in the ocean is mainly determined by the atmosphere and the productivity. On millennial and longer timescales the deep ocean reservoir becomes an important component of the surface carbon cycle (Zeebe and Ridgwell, 2011). The reservoirs of carbonate sediments, carbonates and alkalinity of the ocean water, in addition to changes in ocean carbon pumps increase the complexity of the marine carbon system (Zeebe and Ridgwell, 2011). Over hundreds of thousands of years surface ocean carbon chemistry varied according to changes of CO_2 in the atmosphere, while the deep sea pH and CO_3^{2-} concentration have been postulated to be relatively stable (Zeebe and Marchitto, 2010). The glacial surface conditions were characterized by lower pH and higher CO_3^{2-} concentration than interglacials (Hönisch and Hemming, 2005; Foster, 2008). Barker and Elderfield (2002) and de Moel et al. (2009) suggested that these changes in ocean carbon chemistry have been responsible for higher shell weights of planktic foraminifera during the last glaciation compared to the Holocene in the North Atlantic and Indian Oceans. Broecker and Clark (2003) used shell weights of planktic foraminifera as a proxy for dissolution in the deep sea sediments, emphasizing the role of CO_3^{2-} concentration of the bottom waters and pore waters in the sediment.

Generally, the Holocene carbon content, before the industrial time, show low-magnitude (260-280 ppmv) variations in atmospheric CO_2 (Monnin et al., 2004) and is therefore postulated to be in a close to steady-state mode (Long-term Ocean-Atmosphere-Sediment Carbon cycle Reservoir model; Zeebe et al., 2011). With the beginning of the industrial epoch, the CO_2 content has increased at a rate not observed in records of hundreds thousands of years in Antarctic ice cores. Over the last 800 000 years concentration of CO_2 in

the atmosphere varied between 172-300 ppmv (Lüthi et al., 2008). In February 2012, it reached 393 ppmv (Mauna Loa Observatory, NOAA), and is still rising.

2.2. Study area

The Fram Strait is situated between the Greenland and Spitsbergen archipelago and constitutes the only deep connection between the central Arctic Ocean and the North Atlantic Ocean. In the deep and narrow channel, exchanges of intermediate and deep waters take place (Rudels et al., 2000). The surface water circulation is basically controlled by two water masses (Fig. 1). The eastern part is occupied by warm and saline Atlantic water transported by the West Spitsbergen Current (Aagaard et al., 1987). This current redistributes heat along its way to the Arctic Ocean (e.g., Gammelsrød and Rudels, 1983) and through surface productivity supplies the underlying sediments with calcium carbonate (Huber et al., 2000). The western part of the Fram Strait is dominated by cold, less saline and ice-loaded water transported by the East Greenland Current along the eastern Greenland slope. Surface sediments below the cold waters are characterized by low carbonate content (Henrich, 1998; Huber et al., 2000).
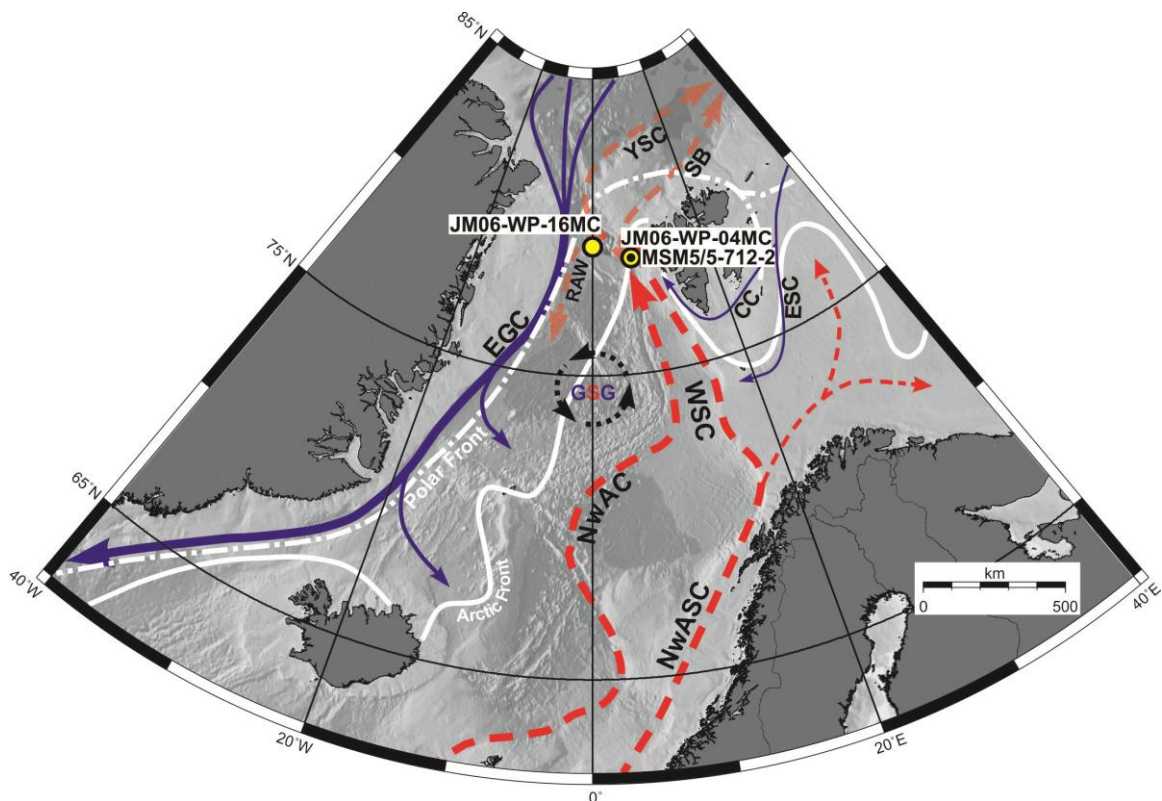
Figure 1. Map showing general ocean circulation pattern, oceanic fronts and sea ice limits in the Fram Strait and the northern North Atlantic (modified from Marnela et al., 2008). Location of cores JM06-04MC and MSM05/5-712-2 are indicated by a double circle and core JM06-16MC by a yellow circle. Abbreviations: NwAC: Norwegian Atlantic Current; NwASC: Norwegian Atlantic Slope Current; WSC: West Spitsbergen Current; ESC: East Spitsbergen Current; CC: Costal Current; YSC: Yermark Slope Current; SB: Svalbard Branch; EGC: East Greenland Current; GSG: Greenland Sea Gyre.

In the central Fram Strait, the dominant water masses form Arctic waters and generate the Polar front in the west and the Arctic front in the east. The two oceanic fronts correspond to the average summer sea ice margin and the maximum sea ice extent in winter, respectively (Vinje, 1977). They determine the geographical position of the marginal ice zone (MIZ) and surface productivity in the summer season (e.g., Smith and Sakshaug, 1990).

3. Materials and methods

Investigated sediment cores were retrieved from the eastern and central Fram Strait (Fig. 1). Two multicores (JM06-16MC and JM06-04MC) were collected by the Norwegian R/V *Jan Mayen* in 2006. The kastenlot corer (MSM5/5-712-2) and the box corer (MSM5/5-712-1) were retrieved by the German R/V *Maria S. Merian* in 2007. Only the lower sediment section of the MSM5/5-712-2 (636-883 cm) was investigated and included in this PhD study. The description and evaluation of methods applied in the PhD project is presented below. Methods used in co-authoring papers 4 and 5 can be found in Spielhagen et al. (2011) and Werner et al. (2011), respectively.

3.1. Lithology and sampling

The sediments in the multicores consisted of hemipelagic mud composed of silt and clay. The investigated interval of core MSM5/5-712-2, apart from silty clays, contained a glacigenic debris flow deposit. In order to obtain a high temporal resolution, the sediment cores were sampled in 0.3 and 0.6 cm intervals in JM06-16MC and JM06-04MC (paper 1 and 2) and 0.5 and 1 cm intervals in core MSM5/5-712-2 (paper 3). The samples were freeze dried and wet sieved at >63μm, >100μm and >1mm size fractions. The sediment samples were weighed before and after freeze drying and the weights of all size fractions were determined. Mineral grains >1 mm representing ice rafted debris (IRD) (Vorren et al., 1983) were counted and using the methods of Ehrmann and Thiede (1985), calculated to flux (numbers of grains/cm^2/year) and concentration (grains/g of dry sediment) of IRD. The lithology of white

clasts found in core MSM5/5-712-2 was studied in thin sections (paper 3). The grain size of silt (4-63 μm) and clay (<4 μm) fractions were analyzed by a Micromeritics SediGraph 5100 in <63 μm fraction (paper 2).

3.2. Geochemical analysis

Total carbon (wt.%TC) and total organic carbon (wt.%TOC) were measured in bulk sediment samples using Leco CS-200 induction furnace at the University of Tromsø. The sample interval was 0.3-5 cm. The $CaCO_3$ content (wt.%) was calculated using the following equation: $CaCO_3 = (TC-TOC)*8.33$ (Espitalié et al., 1977).

3.3. Planktic foraminiferal fauna

After the assessment of preservation of planktic foraminifer shells it was assumed that the distribution of planktic foraminifera reflect the sea surface conditions and is mainly controlled by water mass parameters (i.e. temperature and salinity), food availability and sea ice coverage (e.g. Johannessen, et al., 1994; Carstens et al., 1997).

Planktic foraminiferal analyses were performed in the 100-1000 μm size fraction in the same intervals as sampling resolution (see chapter 3.1). The >100 μm size fraction ensure the presence of small specimens and juvenile forms of subpolar planktic foraminifers such as *G. glutinata, G. uvula, and T. quinqueloba*, which are often not represented in a coarser size fraction (e.g., Bauch, 1994; Carstens et al., 1997; Kandiano and Bauch, 2002). Preparation of the foraminiferal samples mainly followed the method of Feyling-Hanssen (1958). At least 300 planktic foraminiferal specimens were picked from each sample and identified to species level. The concentration (number of foraminifera specimens per gram dry weight sediment, and the relative abundances (%) of individual species of planktic foraminifera were calculated in each sediment core. In addition, the methods described in Ehrmann and Thiede (1985) were applied to calculate the flux of planktic foraminiferal specimens (numbers/cm^{2}/year).

3.4. Quantification of the degree of dissolution

Numerous studies have shown that the planktic foraminifera species assemblages retrieved from sediments can be considerably affected by dissolution (e.g., Ruddiman and Heezen, 1967; Berger, 1970, 1971, 1979; Berger and Parker, 1970; Bé et al., 1975; Adelseck, 1978; Thunell and Honjo, 1981; Conan et al., 2002). Carbonate dissolution is largely associated with ocean circulation and climate (e.g., Archer and Maier-Reimer, 1994; Archer, 1996), and partly governs the carbonate content of a sediment. Therefore, quantification and

assessment of the preservation state of carbonate shells of planktic foraminifer assemblages is important. Unfortunately, every individual dissolution proxy bears some biases most commonly linked to the sensitivity to changes in environmental conditions at the sea surface. In the PhD study, several dissolution indicators are combined to assess the preservation state of planktic foraminifer shells.

The mean shell weight of *N. pachyderma* was used to infer changes in intensity of dissolution in the water column and/or within the sediment. This method was proposed by Lohmann (1995) and has been developed by e.g., Spero et al. (1997), Bijma et al. (1999), Broecker and Clark (2001), Barker and Elderfield (2002), Barker et al. (2004), Beer et al. (2010) as a proxy for bottom and/or surface water carbonate ion concentration. Up to 30 hand-picked clean shells from a narrow size range and without any signs of corrosion or secondary calcite crusts in each sample were weighed using a microbalance with high sensitivity. Mean shell weights were calculated by dividing the weighed mass by the total number of foraminifer shells.

Metzler et al. (1982) suggested that fragmentation is a more valuable indicator of dissolution than weight loss. The degree of foraminiferal fragmentation seems to directly reflect the dissolution-induced weakening of the shell (Conan et al., 2002). The extent of fragmentation of planktic foraminifer shells was used to assess the intensity of dissolution within the sediment. The number of planktic foraminifer shell fragments was counted in sample splits with more than 300 complete shells in the 100 μm -1 mm size fraction. The number of fragments per gram dry weight sediment was calculated. A fragmentation index was calculated according to Berger (1982) and Pfuhl and Shackleton (2004).

Carbonate content (%$CaCO_3$) was used as a proxy for dissolution based on observation that dissolution in deep-sea sediments reflects the decrease in carbonate content with increasing water depth. The interpretation of the $CaCO_3$ content in the sediment is not straightforward, because %$CaCO_3$ can be insensitive to the degree of dissolution until this becomes significant (Broecker and Peng, 1982; Barker et al., 2007). Thus, this proxy was used as a secondary support in the assessment of planktic foraminifera preservation.

Visual inspection of the shell surface of planktic foraminifera was made via the light microscope. Changes in the ultrastructure of foraminifer shells caused by progressive dissolution were documented through the scanning electron microscopy (SEM) (paper 1).

Under conditions of progressing dissolution, planktic foraminifer assemblages are subjected to species-selective removal. Deep-dwelling species form more robust shells which become enriched relative to surface-dwelling species with thin porous shells (e.g., Arrhenius,

1952; Ruddiman and Heezen, 1967; Berger, 1968, 1970; Parker and Berger, 1971). This leads to changes in the species composition as dissolution proceeds and can be correlated with the extent of dissolution. Numerous rankings of species susceptibility have assessed the intensity of dissolution (e.g., Berger, 1968, 1970; Parker and Berger, 1971; Bé et al., 1975; Thunell and Honjo, 1981). However, this indicator is not so simple to interpret, because the planktic foraminifera species composition is also controlled by the environmental conditions at the sea surface (e.g., Carstens et al., 1997; Schiebel and Hemleben, 2005).

3.5. Stable isotope analysis (δ^{18}O and δ^{13}C)

Stable isotopes were measured on the polar planktic foraminifera species *N. pachyderma* from the >100 µm fraction at the IFM-GEOMAR Stable Isotope Laboratory in Kiel (Germany) (paper 2 and 3) and at Stable Isotopes laboratory of the GEOTOP Research Centre at the Université du Québec à Montréal (Canada) (paper 1). Oxygen isotope values recorded in planktic shells are assumed to be primarily controlled by temperature and salinity of the ambient water mass (e.g., Spielhagen and Erlenkeuser, 1994). The carbon isotopic signature is defined by the carbon isotopic ratio of the dissolved inorganic carbon in the water mass, which is primarily governed by processes linked to ventilation rates and primary productivity (e.g., Katz et al., 2010 and references herein). Additionally, carbon isotopes may be influenced by the size of the foraminifera, pH and light intensity (e.g., Oppo and Fairbanks, 1989).

3.6. Chronology

The chronology is based on accelerator mass spectrometry (AMS) ^{14}C dates performed on *N. pachyderma* measured at Poznań Radiocarbon Laboratory. All AMS ^{14}C dates were calibrated to calendar years before present using the OxCal 4.1 program (Bronk Ramsey, 2009a) and the Marine09 calibration dataset (Reimer et al., 2009). A standard reservoir correction of 400 years was applied in all cores. A local correction was applied to core JM06-04 MC (ΔR= 7±11; (Mangerud et al., 2006)). The chronology in core JM06-16MC (paper 1, see below) was supported by stratigraphic tephra horizons. In core MSM5/5-712-2, in addition to radiocarbon dates, a stratigraphic tie point obtained through the correlation of magnetic susceptibility records from Jessen et al (2010) was used. The age models were created by linear interpolation between median probability values of the calibrated AMS[14]C dates.

3.6.1. Tephra analysis (paper 1)

The deposition of tephra provides distinct and widespread stratigraphical marker horizons. The distinct petrographic character and geochemical composition of the tephra shards often allows identification of single volcanic grains with high precision and to link them to known volcanic eruptions (Haflidason et al., 2000).

In order to define the initial fall-out and a possible source of redistribution of volcanic grains, rhyolitic and basaltic shards were counted separately in the 63-100 μm and 100-1000 μm size fractions and the concentration was calculated (Haflidason et al., 2000). Geochemical analyses of 5 out of 30 samples containing tephra grains were carried out at the University of Tromsø and the University of Bergen. Routinely, 5 to 16 points were analyzed on every fragment and the mean of analyses was used in correlation to shards of two known stratigraphic tephra horizons, the Vedde Ash Tephra (Mangerud et al., 1984; Turney et al., 1997) and Hekla 4 tephra (Dugmore et al., 1995).

3.7. SiZer analysis (paper 3)

Statistically significant features in major trends of %$CaCO_3$, mean shell weight and % of subpolar species were evaluated by SiZer analysis (Significance of Zero Crossings of the Derivative, Chaudhuri and Marron, 1999). The method allows identifying features at different levels of smoothing and represents a measure of the true variation observed in the data sets. The SiZer includes graphical presentation of statistically significant decreases or increases detected in levels of smoothing.

4. Summary of papers

Paper 1

Zamelczyk, K., Rasmussen, T.L, Husum, K., Haflidason, H., de Vernal, A., Ravna, E.K., Hald, M., Hillaire-Marcel, C. **Between two oceanic fronts: Paleoceanographic changes and calcium carbonate dissolution in the central Fram Strait during the last 20,000 years.** *In revision for Quaternary Research*

The purpose of the study is to investigate changes in paleoceanography and calcium carbonate preservation from the Last Glacial Maximum through the Holocene to the present in the central Fram Strait. The deep sea sediment core covers the last 20,000 years and is located between the Polar and the Arctic fronts in the marginal ice zone (MIZ). The reconstruction is based on the distribution patterns of planktic foraminifera, mean shell

weights and the degree of fragmentation of shells, stable isotopes and other geochemical and sedimentological parameters. The results show that planktic foraminifera shells are poorly preserved throughout most of the record. Only the interval comprising the early Holocene from c. 10.8 to 8 ka BP shows significantly improved preservation of $CaCO_3$. The dissolution is correlated with the extent of Arctic water and the associated marginal ice zone (MIZ) with high organic productivity. This implies seasonally ice free waters. The general dissolution of planktic foraminifera below the core (prior to 1900 CE) top and the better preservation of small subpolar species in the surface sediments dating from the last century imply a large and significant surface water warming. However, the apparent high-magnitude warming seems to be overestimated due to preservation changes. This study clearly demonstrates the importance of the examination of preservation changes to evaluate results on paleoenvironmental changes at high latitudes.

Paper 2

Zamelczyk, K., Rasmussen, T.L., Husum, K., Hald, M. **Marine calcium carbonate preservation vs. climate change over the last two millennia in the Fram Strait: Implications for planktic foraminiferal paleostudies.**

Submitted to Marine Micropaleontology

Previous investigations based on changes in planktic foraminifera data sets during the last 2000 years show low-magnitude oceanographic changes prior to 1900 CE and an exceptional Atlantic water warming during the last century. Apart from visual examination under the light microscope (paper 4), the two papers (4 and 5), Spielhagen et al. (2011) and Werner et al., (2011) do not include quantification of dissolution and the potential effect of dissolution is not taken into account.

Paper 2 is a high-resolution study on the effects of dissolution on planktic foraminiferal shells and species distribution patterns in a sediment core situated closely to the coring site examined in Spielhagen et al. (2011) and Werner et al. (2011) (paper 4 and 5). The sediment core is located in the eastern Fram Strait below the Atlantic water masses flowing into the Arctic Ocean. The proxy record spans the last 2400 years. The investigation of carbonate preservation is based on mean shell weight of planktic foraminifera specimens, % fragmentation, planktic foraminiferal species distribution and geochemical proxies. The results indicate three periods of poor preservation at 700-850 CE, 1400-1500 CE and from 1800 CE to present. In addition, the ratio between planktic foraminiferal flux and flux of

benthic foraminiferal organic linings (Bonnet, 2009) is used to further elucidate the changes in preservation at the sea floor. The increased ratios at 300 BCE -0 CE, 330-650 CE, 1260-1580 CE and 1900-1995 CE also point to poor preservation at the sea floor. These periods seem to be affected by dissolution of planktic foraminifera species and appear as colder time intervals in the record. In the last century, improved preservation of calcium carbonate coincides with preservation of the small, fragile subpolar species *Turborotalita quinqueloba* and *Globigerinita uvula*. The marked increase of subpolar species and apparent surface water warming after 1900 CE could therefore partly result from the effects of dissolution in sediments prior to 1900 CE rather than solely reflecting a large magnitude warming. Our data suggest that the high-magnitude of climate change in the 20th century, previously recorded in the Fram Strait, is difficult to estimate and is probably overestimated.

Paper 3

Zamelczyk, K., Husum, K., Rasmussen, T.L., Godtliebsen, F., Hald, H. **Surface water conditions and calcium carbonate preservation in the Fram Strait during the late Weichselian 29,000-16,000 years BP.**

To be submitted to Paleooceangraphy

The purpose of this study is to investigate the details of oceanographic variability and to detect, quantify and assess the extent of potential dissolution of calcium carbonates on the western Svalbard slope before, during and after the Last Glacial Maximum. The multi decadal-centennial data resolution of the proxy record provides a good opportunity to evaluate potential driving mechanisms of dissolution in the glacial oceanographic regime in the eastern Fram Strait. The study presents the first record of the mean shell weight of *N. pachyderma* and % of shell fragmentation during the last glaciation in this area. The distribution patterns of the planktic foraminiferal species indicate that warm and saline Atlantic water masses were almost continuously present and caused seasonally ice free waters during glacial summers. This implies the presence of sea surface conditions almost similar to those of today. High abundances of subpolar species and good preservation of calcium carbonate were found during periods of Atlantic water influence. Poor preservation indicated by decreased mean shell weight, low content of calcium carbonate and enhanced shell fragmentation was accompanied by declines in subpolar species abundances and can be linked to changes in the surface water mass distribution. The predominance of Arctic water masses with seasonally enhanced sea ice formation, melt water injections and changes in the carbonate water

chemistry presumably reduced the calcification of planktic shells and favored dissolution of planktic foraminifera. The poor preservation in the Late Weichselian and in the early deglaciation can additionally be linked to high concentrations of atmospheric CO_2. The poor preservation events with marked decreases in planktic subpolar species imply that selective dissolution could influence the composition of fossil assemblages and reduced the reliability of paleoenvironmental reconstructions during the last glaciation.

Paper 4

Spielhagen, R. F., Werner, K., Aagaard-Sørensen, S., Zamelczyk, K., Kandiano, E., Budeus, G., Husum, K., Marchitto, T., Hald, M., 2011. **Enhanced modern heat transfer to the Arctic by warm Atlantic Water.** *Science* 331, 450-453.

In this study, we aim to reconstruct the temperature variability of the Atlantic water advection to eastern Fram Strait over the past ~2000 years. The temperature reconstruction of the Atlantic water is based on two methods. The SIMMAX modern analog technique is applied on planktic foraminifer species counts to calculate temperatures at 50-m water depth, and Mg/Ca ratio is measured of the species *N. pachyderma*. The Mg/Ca paleothermometry in this study is applied for the first time in the Arctic region. The assessment of preservation state of planktic foraminifera shells is based on a visual inspection. Variations in fluxes of subpolar and polar species are used to infer the sea ice conditions, variability on the position of ice margin and water mass distribution.

High abundances of subpolar species and relatively high fluxes of planktic foraminifera from 0 to ~700 CE indicate warm summer conditions with strong Atlantic water inflow. From ~700 CE, a simultaneous reduction in planktic foraminifer fluxes indicates weakening of Atlantic water advection and the influence of sea ice/icebergs in the eastern Fram Strait until ~1400 CE. The Mg/Ca paleothermometry show stable mean temperatures and SIMMAX-based reconstructions indicate higher temperatures at ~700-1400 CE. At ~1500 CE, a very high flux of polar planktic foraminifera and low temperatures indicate cold surface conditions linked to the Little Ice Age period. From 1500 CE, the abundances of planktic foraminifera gradually decrease reaching values near-zero at ~1900 CE, while the mean temperature of the Mg/Ca paleothermometry increases already from ~1700 CE. A ~2 °C temperature increase and high flux of subpolar foraminifer in the youngest sediments, reflecting the past ~100 years, indicate a strong advection of warm Atlantic water to the Fram

Strait. The high temperature and faunal composition changes of planktic foraminifera are most probably linked to the Arctic amplification of global warming.

Contribution to paper 4:

My contribution to the paper as co-author was to carry out the planktic foraminiferal analysis of the >150 µm size fraction, interpret data with co-authors and contribute to the manuscript.

Paper 5

Werner, K., Spielhagen, R.F., Bauch, D., Hass, H.Ch., Kandiano, E., Zamelczyk, K., 2011. **Atlantic Water advection to the eastern Fram Strait- Multiproxy evidence for late Holocene variability**. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 308 (3-4), 264-276.

The aim of this study was to reconstruct climatic variability and examine the strength of the Atlantic water inflow on the continental margin of western Svalbard during the past two millennia. The study is based on an AMS radiocarbon dated box core. Planktic and benthic stable isotopes, planktic foraminiferal paleodata, absolute sea surface temperatures calculated by transfer functions and lithogenic parameters were used to investigate the oceanographic development of the eastern Fram Strait.

The results show a continuous and variable influence of Atlantic water over the last 2000 years. A sharp reduction in planktic foraminifer fluxes around 800 AD and after 1730 AD indicates cool summer conditions with major influence of sea ice/icebergs. High amounts of the subpolar planktic foraminifer species *Turborotalia quinqueloba* in the size fraction 150-250 µm indicate strengthened Atlantic Water inflow to the eastern Fram Strait already after ~1860 AD. Nevertheless surface conditions stayed cold well into the 20th century as indicated by low planktic foraminiferal fluxes. While cold conditions of the terminating Little Ice Age period persisted at the surface, at the beginning of the 20th century the warm and saline Atlantic water already strengthened, hereby subsiding below the cold upper mixed layer. Surface sediments with high abundances of subpolar planktic foraminifers indicate a strong inflow of Atlantic Water providing seasonal ice-free conditions in the eastern Fram Strait during the last few decades.

Contribution to paper 5:

My contribution to the paper as co-author was to carry out the planktic foraminiferal analysis of the >150 μm size fraction, interpret data with co-authors and contribute to the manuscript.

5. Synthesis

In the present PhD study, a multi-proxy approach has been used to elucidate paleoceanographic variability and the calcium carbonate preservation state in the eastern Fram Strait throughout the last 30,000 years. Detailed records of mean shell weight variability combined with fragmentation indices have provided insight into chemistry of surface water and/or sea floor conditions in the Fram Strait. Three time periods representing important oceanographic changes in the Fram Strait have been investigated with a high temporal resolution allowing for an assessment of the extent of dissolution. The results show that the Atlantic water inflow governed the oceanographic development and the exchange of gasses between the atmosphere and surface ocean in the Fram Strait. The quantification of carbonate dissolution shows that planktic foraminiferal assemblages were affected by dissolution during some time intervals throughout the past 30,000 years. This implies that the reliability of sedimentary records of planktic foraminifera is reduced. This study underlines the importance of evaluating the preservation state before applying planktic foraminifera as a paleoceanographic proxy. The main conclusions of the study are:

- The best preserved planktic foraminifera assemblages during the last 30,000 years were found during the Last Glaciation Maximum. Some minor dissolution events occurred during the Last Glacial Maximum as response to seasonally changing physical oceanographic parameters, sea ice formation, increased surface productivity, and melt water pulses. During the deglaciation and the Holocene, the preservation state of carbonates generally deteriorated. This trend was interrupted at 10,800- 8000 BP, where the preservation of planktic foraminifera markedly improved. Changes in preservation are related to the extent and influence of the Arctic water and the marginal ice zone (MIZ) and its associated high organic productivity in the surface water masses.

- The mid to late Holocene was characterized by severe dissolution of sedimentary carbonates. This period shows the poorest preservation of the last 30,000 years.

- During the last century, fluxes and relative abundances of subpolar species increased markedly. The good preservation of small subpolar species in the last 100 years seems to be a consequence of improved preservation in the youngest sediments. These faunal changes coincided with distinctly increased sedimentation rates which appear to have

protected at least some subpolar species from dissolution in the eastern and central Fram Strait.

This study of planktic foraminifera preservation has shown that carbonate dissolution is a common phenomenon in the Fram Strait. In some cases, the carbonate dissolution has changed the composition of foraminiferal fauna and modified the information on climatic and oceanographic development recorded in sediments of the Fram Strait. Unfortunately, the methods applied in this PhD study are not sufficient to identify the cause of dissolution. Nevertheless, the results highlight the necessity for testing the reliability of one of the most important proxies in climatic and oceanographic paleoreconstructions.

6. Future work

In this PhD study, the reconstruction of carbonate preservation and oceanographic variability in the Fram Strait over the past 30,000 years was focused on a high temporal resolution of traditional proxies. However, when using quantitative dissolution indices such as mean shell weight, shell fragmentation, $CaCO_3$ content and susceptibility-based rankings of species, the possible dissolution- triggering factors cannot be narrowly specified. This is due to their dependence on chemical properties of the ambient water and changes in environmental conditions at the sea surface. In recent years, new geochemical proxies in planktic foraminifera have emerged. Apart from the novel but already increasingly applied Mg/Ca paleothermometry, the most promising are $\delta^{11}B$ and B/Ca ratio, proxies for past sea water pH and carbonate ion concentration, respectively.

Boron (B) naturally occurs in two isotopes, ^{11}B (~80%) and ^{10}B (~20%). In seawater, dissolved boron occurs mainly in two forms: boric acid ($B(OH)_3$) and borate ($B(OH)_4^-$. Their relative concentration changes with pH. At low pH, boron predominates in the form of boric acid, whereas at high pH, boron predominates in the form of borate. Since the stable isotope ^{11}B is enriched in boric acid, the isotopic composition of the two forms of boron changes with their relative concentration and shows that $\delta^{11}B$ increases with increasing pH (e.g., Katz et al., 2010). The pH-dependence of boron in calcite shells of planktic foraminifera is also a basis for B/Ca, proxy for carbonate ion concentration of the seawater. Compared to $\delta^{11}B$, the B/Ca measurements have the advantage of being less time consuming (Yu and Elderfield, 2007) and due to the high measurement precision of the B/Ca ratio, the method is very sensitive to pH and carbon system changes in seawater (Ni et al., 2007). Parallel measurements of boron concentration and isotopic composition have the potential to fully assess the sea water carbon

system (e.g., Ni et al., 2007) providing a direct way to calculate the pCO_2 (Hönisch and Hemming, 2005).

Core-top measurements of B/Ca in foraminiferal calcite indicate a strong dependence on pH, CO_3^{2-}, but also on temperature of the ambient seawater (Yu et al., 2007; Foster, 2008). One way to isolate the temperature influence is to use Mg/Ca temperature estimates to extract seawater pH changes from planktic foraminiferal B/Ca records (Yu et al., 2007). However, carbonate chemistry and temperature often change simultaneously and this can complicate the interpretation of the B/Ca ratio in foraminiferal records. An effort to further develop the B/Ca method has been made in laboratory culture experiments (Allen et al., 2009).

The advantage of using new geochemical proxies like the Mg/Ca, B/Ca and $\delta^{11}B$ is that they define important parameters for the solubility of carbonates. The Mg/Ca paleothermometry used together with oxygen isotopes can provide information on changes in ice volume and herewith salinity (e.g., Lea et al., 2000), which is an important factor influencing chemical composition of sea water. The B/Ca and $\delta^{11}B$ proxies for paleo-pH and CO_3^{2-}, in conjunction with mean shell weight of planktic foraminifera offer, a reliable method to infer factors controlling the calcium carbonate preservation state (Lohmann, 1995; Broecker and Clark, 2001). During my PhD study, the assessment of planktic foraminifera shell mass loss over the last 30,000 years in the Fram Strait revealed a clear relationship between the atmospheric CO_2 and the shell weight of planktic foraminifera (Fig. 2). The atmospheric CO_2 - shell weight relationship implies that chemistry changes of sea surface water and its feedback mechanisms could have been of a great importance for the carbon cycle at least on orbital timescales, but apparently also on shorter time scales.

A successful application of these novel proxies to sediment cores from the equatorial Atlantic (Hönisch and Hemming, 2005) and North Atlantic (Yu et al., 2007) holds a great potential for reconstructing paleo-pH and CO_3^{2-} in low productive waters of the Arctic. This is partly due to the small samples required for the analysis (Hemming and Hanson, 1992), but mainly because the Arctic Ocean is very sensitive to climatic and oceanographic changes and highly vulnerable CO_2 absorption due to low water temperature. During the last glaciation, the exchange paths of water masses between the Arctic Ocean and the world ocean were presumably closed, except in the deep Fram Strait. Numerous studies have shown that the oceanic circulation pattern and exchange of atmospheric gases in the Fram Strait was similar to modern conditions and allowed the ocean-atmosphere, and hereby carbon system changes to be recorded almost continuously over the last 30,000 years (e.g., Hebbeln et al., 1994). Therefore, the sediments of the Fram Strait offer a biogeochemical archive for the natural

versus anthropogenic sea water chemistry and calcium carbonate dissolution changes during the glacial-interglacial cycle.
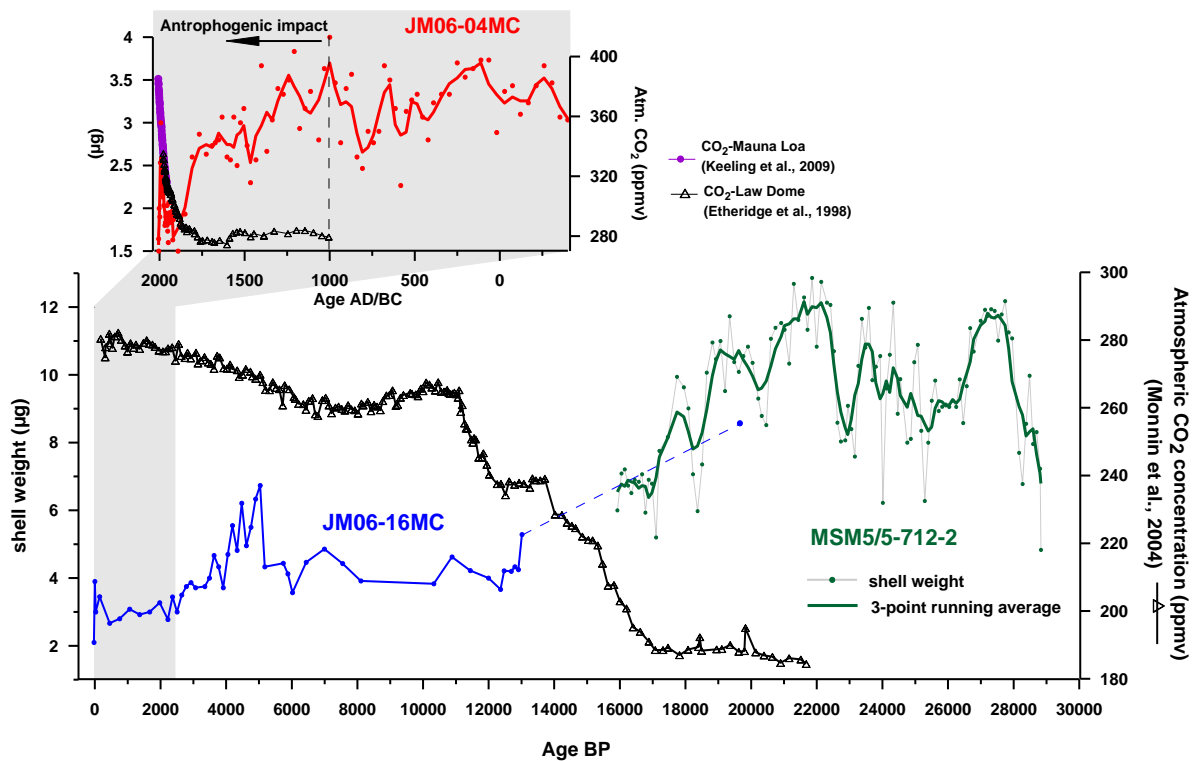

Fig. 2. Shell weight records from three sediment cores investigated during my PhD study (JM06-04 MC, JM06-16MC, MSM5/5-712-2) from the Fram Strait compared to atmospheric CO_2 concentration (Monnin et al., 2004; Etheridge et al., 1998; Keeling et al., 2009). The apparent anti-correlation strongly indicates an ocean-atmosphere link in the eastern and central Fram Strait.

The use of traditional and well-tested methods (described in the thesis) in combination with emerging geochemical approaches (described above) would be the best way to investigate how past ocean chemistry changes influenced planktic foraminifera and subsequently estimate the degree of ocean acidification and its causes. However, before the B/Ca and $\delta^{11}B$ proxies can be applied to sediment cores, uncertainties related to biological, kinetic and thermal controls of the trace element exchange and isotope incorporation during the calcification of planktic foraminifera need to be addressed. Calibration and validation of these proxies can be based on sediment traps and core top samples. Proxies measured in planktic foraminifera from sediment traps at different water depths and in the sediment surface samples at a given temperature and pH, make possible the establishment of the exact interdependence of the B/Ca and $\delta^{11}B$ on the pH, temperature, salinity and other parameters

within the water column and at the water-sediment interface. The application of the two species dominating in the Fram Strait, *Neogloboquadrina pachyderma* (sin.) and *Turoborotalita quinqueloba*, in two size fractions allows studying different life stages and defines the rate of trace element incorporation between juvenile and adult forms. With careful scrutiny and appropriate application, these proxies promise an important contribution to paleostudies of planktic foraminifera trace elements in the high latitudes.

The approach and methods described above will be adopted in a project entitled "Effects of ocean chemistry changes on planktic foraminifera in the Fram Strait: Ocean Acidification from natural to anthropogenic changes". The project has been funded by the Norwegian Research Council and will start in summer 2012. The aim of the project is to reconstruct and quantify the response of planktic foraminifera to chemistry changes in the surface waters of the Fram Strait from the last glaciation to the present. The project aims to increase the understanding of consequences of changes in Arctic Ocean carbonate chemistry due to increased atmospheric CO_2 concentration on calcifying planktic foraminifera. Furthermore, the study will examine the past and present impacts of Arctic Ocean acidification.

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