Arctic Ocean benthic foraminifera preservation and Mg/Ca ratios

Implications for bottom water palaeothermometry

Natalia Barrientos

Academic dissertation for the Degree of Doctor of Philosophy in Marine Geology at Stockholm University to be publicly defended on Thursday 31 May 2018 at 10.00 in De Geersalen, Geovetenskapens hus, Svante Arrhenius väg 14.

Abstract

Reconstructions of Arctic Ocean palaeotemperatures are needed to disentangle natural variability from anthropogenic changes and understand the role of ocean heat transport in forcing or providing feedbacks on Arctic climate change. Despite known complications with calcareous microfossil preservation in Arctic Ocean sediments, calcareous benthic foraminifera can be common in interglacial sequences. However, thus far they have been underutilized in palaeoceanographic studies. This thesis explores the application of the Mg/Ca palaeothermometry proxy for reconstructing bottom water temperatures (BWT) in the Arctic Ocean during the late Quaternary. This method, which is supported by previous empirical studies demonstrating a strong temperature control on trace Mg inclusion into foraminiferal shell calcite, has been applied in many ocean regions and time intervals. Until now its application in the Arctic Ocean has been sparingly explored.

The results of this doctoral thesis are based on benthic foraminifera retrieved from marine sediment cores covering a wide geographical Arctic Ocean area including both the shallow and vast continental shelves and slopes to the intermediate-to-deep waters of the Lomonosov Ridge and Morris Jesup Rise. These provide the first benthic foraminifera Mg/Ca ratios from the central Arctic Ocean region. In the first study, mechanisms that could affect Mg incorporation in Arctic benthic foraminifera are investigated using oceanographic field data and six 'live' modern Arctic species (*Elphidium clavatum*, *Nonionella labradorica*, *Cassidulina neoteretis*, *Oridorsalis tener*, *Cibicidoides wuellerstorfi* and *Quinqueloculina arctica*). The result is new species-specific Mg/Ca–BWT field calibrations that provide important constraints at the cold end of the BWT spectrum (-2 to 1°C) (Paper I). Using the new Mg/Ca–BWT equation for *E. clavatum*, a palaeotemperature record was generated for the late Holocene (past ca. 4100 yr) from the western Chukchi Sea. The data showed BWT fluctuations from -2 to 1°C that are interpreted as showing pulses of warmer Pacific water inflow at 500–1000 yr periods, thus revealing multi-centennial variability in heat transport into the Arctic Ocean driven by low latitude forcings (Paper II). Complications with foraminiferal calcite preservation that limit Mg/Ca palaeothermometry in the Arctic were discovered and these are tackled in two additional papers. Anomalously high Mg content in benthic foraminifera from the central Arctic Ocean is linked to diagenetic contamination as a result of the unique oceanographic, sedimentary and geochemical environment (Paper III). Lastly, the dramatic post-recovery dissolution of foraminifera from a Chukchi Shelf sediment core during core storage is investigated and attributed to acidification driven by sulphide oxidation in this organic rich and calcite poor shelf setting (Paper IV).

The findings of this thesis demonstrate that benthic foraminiferal Mg/Ca-palaeothermometry can be applied in the Arctic Ocean and capture small BWT change (on the order of -2 to 2°C) even at low temperatures. In practice, preservational complexities can be limiting and require special sample handling or analysis due to the high potential for diagenetic contamination in the central Arctic Ocean and rapid post coring calcite dissolution in the seasonally productive shelf seas. This Ph.D. project is a component of the multidisciplinary SWERUS-C3 (Swedish-Russian-US Arctic Ocean Climate-Cryosphere- Carbon Interactions) project that included an expedition with Swedish icebreaker *Oden* to the East Siberian Arctic Ocean.

Keywords: *Arctic Ocean, benthic foraminifera, Mg/Ca-temperature, calcite preservation.*

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Cover: video snapshot of Expedition SWERUS-C3 multicore station 34 (84.276°N, 148.713°E). It shows the seafloor of the Arctic Ocean (Lomonosov Ridge) at 886 m of water depth. Video provided by Björn Eriksson

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To my aunt Gemma

Sila, ᓯᓚ, Inuktitut term, reflects a symphony of climatic forces in Inuit Qaujimajatuqangit (Inuit traditional knowledge):

"the Sun's solar winds and spots, the Earth's orbital cycles, oceans and atmosphere whose movements are steered by the Earth's rotation, air masses and ocean circulations that redistribute heat and moisture at their different rates, ice and regional topography, the breath of plants and animals, and the greenhouse gas metabolism of industrial societies."

Leduc (2007)

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Svensk sammanfattning

Rekonstruktioner av Arktiska oceanens temperaturvariationer över längre tidsperspektiv utgör en viktig nyckelinformation om man skall kunna skilja en naturlig variabilitet ifrån förändringar orsakade av antropogen påverkan och för att förstå betydelsen av havets värmetransport för klimatförändringen i Arktis. Trots kända problem med bevarande av kalskaliga mikrofossil i Arktiska sedimentkärnor så är det relativt vanligt att interglaciala sedimentsekvenser innehåller rikligt med bentiska kalkskaliga foraminiferer. Dessa bevarade kalkskaliga mikrofossil har hittills använts mycket sparsamt i studier av Arktiska oceanens paleoceanografiska utveckling. Denna avhandling utforskar en så kallad paleotermometer, som bygger på att förhållandet mellan Mg och Ca (Mg/Ca) i bentiska foraminiferers kalkskal är kopplat till den vattentemperatur som rådde då skalen bildades. Förhållandet av Mg/Ca används i denna avhandling för att rekonstruera Arktiska oceanens bottenvattentemperaturer under senkvartär tid. Metoden är väl etablerad och har använts för många paleoceanografiska studier i de flesta delar av världshaven, men har ännu inte utforskats för Arktiska oceanen.

De marina sedimentkärnor som har analyserats täcker ett stort geografiskt område av Arktiska oceanen. De kommer ifrån de grunda kontinentalsocklarna och deras sluttningar samt ifrån medeldjupa till djupa delar av Lomonosovryggen och Morris Jesup Rise. I den första studien (Paper I) undersöks mekanismer som kan påverka hur Mg inkorporeras i de bentiska foraminiferernas skal med hjälp av oceanografiska data och sex 'levande' moderna arktiska arter (*Elphidium clavatum*, *Nonionella labradorica*, *Cassidulina neoteretis*, *Oridorsalis tener*, *Cibicidoides wuellerstorfi* och *Quinqueloculina arctica*). Artspecifika kalibreringar av Mg/Ca-bottenvattentemperaturer har tagits fram vilka ger viktiga begränsningar för hur metoden kan användas vid kallare temperaturer (-2 till 1°C). En av de framtagna ekvationerna för Mg/Ca-bottenvattentemperatur har tillämpats i den andra studien (Paper II) för att rekonstruera temperaturvariationer i en sedimentkärna från Tjukterhavet under den senare delen av holocen, mera specifikt de senaste ca 4100 åren. Bottenvattnet där kärnan kommer ifrån har varierat mellan ca -2 och 1°C och variationerna föreslås här vara kopplade till mellan 500 och 1000 år långa pulser av varmare vatteninflöden från Stilla havet via Bering sund.

Problem relaterade till bevarandet av de bentiska foraminiferernas kalkskal i sedimentkärnorna från den centrala delen av Arktiska oceanen uppdagades vilka påverkar användningen av Mg/Ca som en paleotermometer. Dessa problem hanteras i de två sista studierna (Paper III och IV). Oväntat höga halter av Mg i de bentiska foraminiferernas skal från centrala Arktiska oceanen kopplas till en diagenetisk kontamination som beror på specifika oceanografiska och sedimentgeokemiska förhållanden (Paper III). I det sista arbetet (Paper IV) visas hur upplösning av kalk sker i en kärna från Tjukterhavet efter att den tagits upp och öppnats på grund av oxidation av sulfidmineral. Sedimentationsmiljön för denna kärna från det grunda Tjukterhavet kan karaktäriseras som rik på organiskt material men fattig på kalk.

I denna avhandling har det visats att Mg/Ca som palaeotermometer kan användas på kalkskaliga bentiska foraminiferer från Arktiska oceanen för att rekonstruera relativt små temperaturvariationer; i storleksordningen mellan -2 till 2°C. I praktiken begränsas metoden av komplexa diagenetiska processer i den centrala delen av Arktiska oceanen och av att kalkupplösning sker i sedimentkärnor som tagits upp från de grunda Arktiska shelfhaven. Detta kräver vidare utveckling av specifika provhanteringsmetoder. Avhandlingsarbetet har utgjort en del av den tvärvetenskapliga SWERUS-C3 (Swedish-Russian-US Arctic Ocean Climate-Cryosphere-Carbon Interactions) projektet där en expedition med isbrytaren *Oden* ingick 2014 till de Östsibiriska delarna av Arktiska oceanen.

List of papers and author contributions

This thesis comprises four manuscripts, listed below, prefaced by an overview chapter (kappa) describing the aims of the Ph.D. project, the wider background, methodological approaches and manuscript contents. Paper I (accepted for publication in the Special Issue of *Geochimica et Cosmochimica Acta*, dedicated to the memory of Prof. Harry Elderfield – a pioneer of Mg/Ca palaeothermometry) is published and reprinted with permission from Elsevier. Paper II has been submitted to *Geology* and is currently under revision. Papers III and IV are manuscripts soon to be submitted.

Paper I: Barrientos, N., Lear, C.H., Jakobsson, M., Stranne, C., O'Regan, M., Cronin, T.M, Gukov, A.Y., Coxall, H.K., 2018. Arctic Ocean benthic foraminifera Mg/Ca ratios and global Mg/Ca-temperature calibrations: new constraints at low temperatures. Geochimica et Cosmochimica Acta, in press. https://doi.org/10.1016/j.gca.2018.02.036.

Paper II: Barrientos, N., Coxall, H.K., Lear, C.H., Pearce, C., Muschitiello, F., O'Regan, M., Stranne, C., de Boer, A., Cronin, T.M., Semiletov, I., Jakobsson, M., (*in revision*). Late Holocene variability in Arctic Ocean Pacific Water inflow through the Bering Strait. Geology.

Paper III: Barrientos, N., Coxall H.K., Lear, C.H., O'Regan, M., Mörth, C.-M., Jakobsson, M., (*manuscript*). Mg/Ca ratios in late Quaternary benthic foraminifera from the central Arctic Ocean.

Paper IV: Barrientos, N., Jakobsson, M., Mörth, C.-M., Pearce, C., Miller, C., O'Regan, M., Brüchert, V., Johansson, C., Coxall, H.K., (*manuscript*). Post-recovery dissolution of calcareous microfossils in sediments from a highly productive Arctic marine environment.

Publication status as of April 5, 2018.

I was lead author of the four manuscripts for which I carried out all foraminiferal analysis, constructed all figures and maps and led the writing in close collaboration with the coauthors. The CTD data used in the papers were synthesized by Christian Stranne. In Paper II, Francesco Muschitiello conducted and led interpretation of the cross-wavelet analysis. In Paper III, Matt O'Regan performed the PCA analysis and Carl-Magnus Mörth provided key insights into interpretation of the geochemical data. In Paper IV, Christof Pearce provided TOC, N, and XRF analysis and Clint Miller conducted the porewater chemical analysis. Volker Brüchert, Cal-Magnus Mörth and Clint Miller contributed substantially to the geochemical interpretation of the results.

This Ph.D. was funded by Swedish Research Council (VR) grant 2012-1680 awarded to M. Jakobsson, H. Coxall and C-M Mörth. The field data were acquired during the SWERUS-C3 (Swedish – Russian – US Arctic Ocean Investigation of Climate-Cryosphere-Carbon Interactions) 2014 expedition, with icebreaker Oden, funded by the Knut and Alice Wallenberg Foundation (KAW) and the Swedish Polar Research Secretariat (SPRS). This Ph.D. benefited from 3 student-support grants from the Bolin Centre for Climate Research at Stockholm University.

The following 5 additional papers, in which I was a contributing author, were published during my Ph.D. but are not included as a part of this thesis.

Gemery, L., Cronin, T., Poirier, R., Pearce, C., **Barrientos, N.**, O'Regan, M., Johansson, C., Koshurnikov, A., Jakobsson, M., 2017. Central Arctic Ocean paleoceanography from ~ 50 ka to present, on the basis of ostracode faunal assemblages from SWERUS 2014 expedition. Climate of the Past. Clim. Past, 13, 1473–1489.

Jakobsson, M., Pearce, C., Cronin, T.M., Backman, J., Anderson, L.G., **Barrientos, N.**, Björk, G., Coxall, H.K., De Boer, A., Mayer, L.A., Mörth, C.M., Nilsson, J., Rattray, J.E., Stranne, C., Semiletov, I., O'Regan, M., 2017. Post-glacial flooding of the Bering Land Bridge dated to 11 cal ka BP based on new geophysical and sediment records. Climate of the Past, 13, 991–1005.

O'Regan, M., Backman, J., **Barrientos, N.**, Cronin, T., Gemery, L., Kirchner, N., Mayer, L., Nilsson, J., Noormets, R., Pearce, C., Semiletov, I., Stranne, C., Jakobsson, M., 2017. The De Long Trough: a newly discovered glacial trough on the East Siberian continental margin. Climate of the Past, 13, 1269-1284. Doi: 10.5194/cp-13-1269-2017.

Pearce, C., Varhelyi, A., Wastegård, S., Muschitiello, F., **Barrientos, N.**, O'Regan, M., Cronin T.M., Gemery, L., Semiletov, I., Backman, J., Jakobsson, M., 2017. The 3.6ka Aniakchak tephra in the Arctic Ocean: A constraint on the Holocene radiocarbon reservoir age in the Chukchi Sea. Climate of the Past, 13, 303–316.

Jakobsson, M., Nilsson, J., Anderson, L.G., Backman, J., Bjork, G., Cronin, T.M., Kirchner, N., Koshurnikov, A., Mayer, L., Noormets, R., O'Regan, M., Stranne, C., Ananiev, R., **Barrientos Macho, N.**, Cherniykh, D., Coxall, H.K., Eriksson, B., Floden, T., Gemery, L., Gustafsson, O., Jerram, K., Johansson, C., Khortov, A., Mohammad, R., and Semiletov, I., 2016. Evidence for an ice shelf covering the central Arctic Ocean during the penultimate glaciation, Nature Communications, 7, 10365.

TABLE OF CONTENTS

Arctic Ocean benthic foraminifera preservation and Mg/Ca ratios

Implications for bottom water palaeothermometry

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1. Introduction

The Arctic Ocean, despite being the smallest of the world's oceans, plays an important role in regulating Earth's climate. Direct radiative forcing that melts Arctic ice, leading to albedo change and other climate system feedbacks, is clearly important. Compelling evidence shows that this polar ocean exhibits higher sensitivity to global environmental change compared to other regions of the planet, after experiencing anomalous warming over the last century (Serreze et al., 2000; Peterson et al., 2002; Semiletov et al., 2004; Steele et al., 2008; Polyakov et al., 2012). As early as 1896, the concept of higher variability in Arctic surface temperatures produced by changes in CO_2 concentration had already been proposed by the Swedish scientist Svante Arrhenius (Arrhenius, 1896). A century later this mechanism was formally called "Arctic amplification" referring to the double warming in the Arctic region since 1950s compared to mid-latitudes (Serreze et al., 2009; Serreze and Barry, 2011). This polar amplification is largely driven by climate system feedbacks that yet remain poorly understood (Serreze and Barry, 2011). This is in part because the relative roles of direct radiative melting of sea ice from atmospheric forcings compared to oceanic interactions and the warming contributions from natural variability compared to anthropogenic forcing are weakly constrained (Francis et al., 2005; Ding et al., 2017).

As evidenced by the wealth of satellite data the Arctic cryosphere is shrinking (Fig. 1). Even now as this is written, March 2018, the central Arctic Ocean has experienced the greatest warming ever recorded, an anomaly among anomalies that resulted in temperatures approximately 35°C above historical averages for February. This current warming has been linked to atmospheric changes but the ocean is thought to play an important role. Among the main oceanic changes having tremendous environmental impacts are (i) a shift in the boundary between Arctic surface Eurasian and Pacific waters, (ii) sea ice thinning leading to younger sea ice ages, (iii) higher Atlantic layer temperatures with shifting depths and (iv) higher melting of the Greenland ice-sheet, which is a major source of freshwater to the Arctic Ocean (Polyakov et al., 2007, Dmitrenko et al., 2008; Hartmann et al., 2013).

Another concern associated with warming Artic Ocean waters is the threat methane release form methane hydrates stored on shelves and slopes as an additional source of greenhouse gases with the potential to add to global warming (Fig. 2). Predictions are that increasing Arctic Ocean temperatures by only a few degrees could destabilize C-rich methane hydrates present on the shelf and slopes and become a source of CH_4 or CO_2 to the atmosphere (Fig. 2) (Romanovskii et al., 2005; Reagan and Moridis, 2007; Spielhagen et al., 2011; Thatcher et al., 2013; Stranne et al., 2016). Arctic Ocean palaeotemperature records, thus, are important for better understanding these interactions in the past and for modeling future global climate system feedback processes.

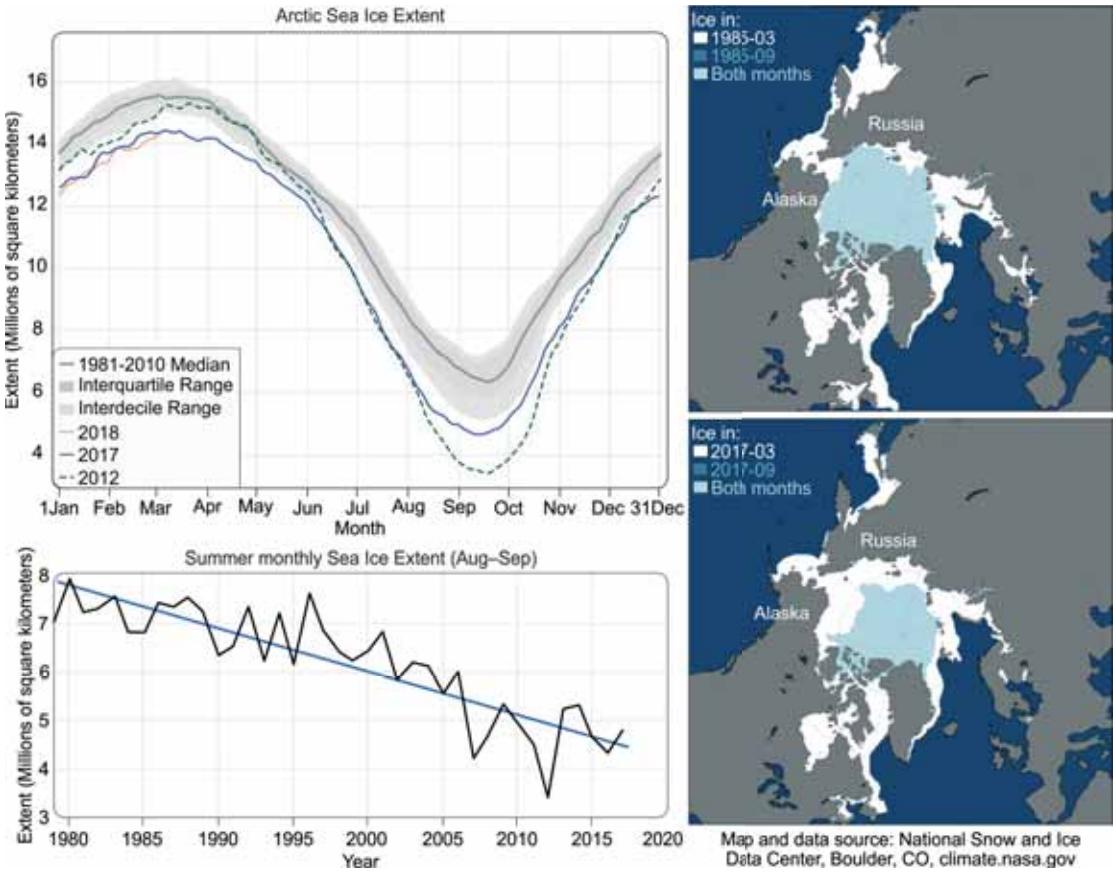

Figure 1. Trends in sea ice decline over the last four decades from satellite observations (1979–2017). August-September summer sea ice extent shows a clear decline of 13.2 % per decade depicting the resulting Arctic amplification. Credit: NSIDC/NASA.

There are only a few proxy methods available for reconstructing past ocean bottom water temperatures (BWT). Benthic foraminifera Mg/Ca palaeothermometry has been shown to be a valuable tool for reconstructing past BWT since the Mg/Ca ratio in foraminiferal calcite is largely temperature dependent (Izuka, 1988; Nürnberg et al., 1996; Lear et al., 2000). Importantly, unlike the foraminiferal $\delta^{18}O$ proxy, Mg/Ca ratios are independent of changes in the global or local meteoric water budgets associated with seasonal or longer term Quaternary glacial transitions (Spielhagen et al., 2004). The Mg/Ca bottom water palaeothermometry has had limited application in the Arctic Ocean but the presence of benthic foraminifera in multiple core records and a strong desire to reconstruct temperatures provided motivation to try.

Like all proxies, benthic foraminifera Mg/Ca-palaeothermometry has its own complications and these are particularly relevant to the Arctic Ocean case. Firstly, previous field and laboratory based Mg/Ca–BWT investigations have shown that shell calcite Mg/Ca ratios are best described by an exponential relationship with temperature, resulting in low sensitivity at low temperatures in the range found in Arctic bottom waters (form -2 to 1°C) (Fig. 2). Moreover, Mg partitioning into calcite has shown to be influenced by factors other than temperature, namely bottom water carbonate ion concentration, especially at low temperatures (Martin et al., 2002, Elderfield et al., 2006). Finally, anecdotal reports from Arctic researchers (e.g. L. Polyak, pers. comm.) have hinted at diagenetic effects in the Arctic

Ocean that might modify 'original' foraminiferal calcite thus hampering the use of the Mg/Ca–BWT method in the Arctic Ocean. Therefore, a proper evaluation of the potential of benthic foraminifera Mg/Ca palaeothermometry for reconstructing BWT in the Arctic Ocean is needed.

The idea for this project builds upon studies that successfully reconstructed interglacial-to-glacial BWT by applying Mg/Ca palaeothermometry in ostracods from central Arctic Ocean sediments (Fig. 2) (Farmer et al., 2011; 2012; Cronin et al., 2012). Cronin et al. (2012) findings implied that the halocline deepened by 300 m and that the Atlantic water deepened ~500 m and warmed by average 2°C within the timeframe of study. Nevertheless, benthic foraminifera outnumber ostracods in Arctic marine sediments and thus, this Ph.D. thesis was designed to investigate the Mg/Ca-BWT proxy application in this other group of marine calcifiers.

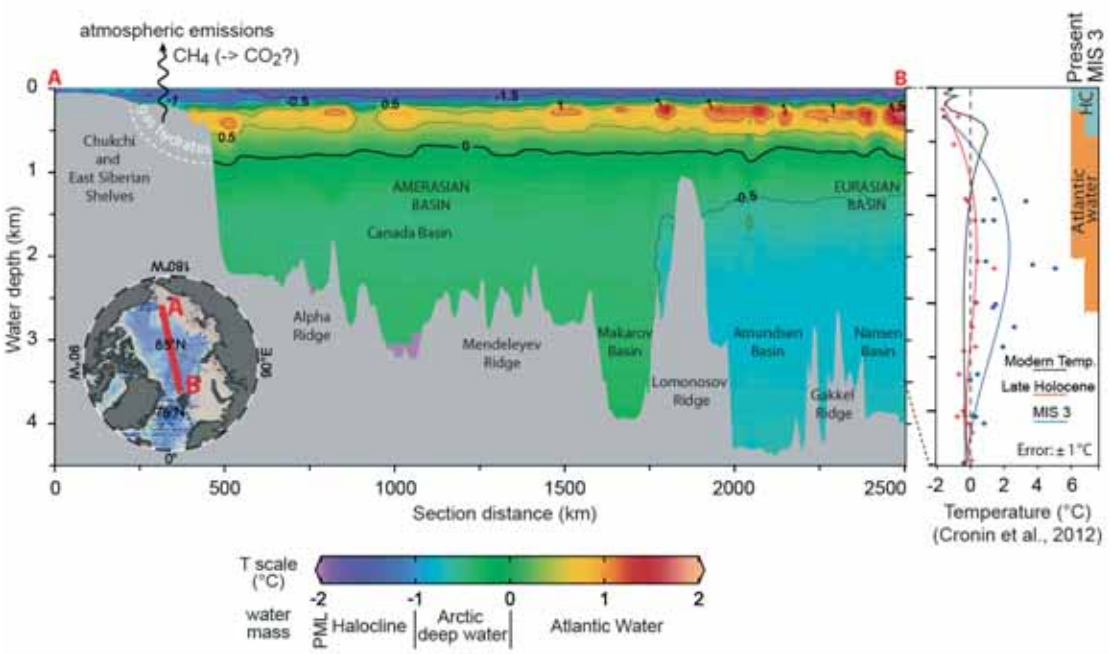

Figure 2. Arctic Ocean depth profile from a section drawn from the Bering Strait (A) to the Fram Strait (B). Color scale depicts modern temperatures derived from the World Ocean Atlas 2013 database (1955–2012) every 1° with a width of 200 km (Locarnini et al., 2013). The temperature scales show the range of the main Arctic water masses from surface to seafloor: i.e. the polar mixed layer (PML), halocline, Atlantic water and Arctic deep water. A simplified illustration of the main bathymetric features is colored in gray. Potential distribution of subsea gas hydrates between ~200-900 m water depths of the Arctic shelves and slopes are shown, acknowledging one of the Arctic climate-cryosphere-carbon (C3) system components addressed by the over-arching SWERUS-C3 2014 Expedition, although not directly tackled here. The rightmost panel shows reconstructed temperatures for the last glacial cycle using ostracod calcite Mg/Ca from sites reaching 3.5 km water depths (note vertical depth axis extension) after Cronin et al. (2012). Black line: modern temperature. Red and blue lines: third order polynomial fits of Mg/Ca-derived palaeotemperatures from Holocene (red) and Marine Isotope Stage 3 (blue). The authors interpreted higher MIS 3 temperatures and deepening in the halocline and Atlantic intermediate waters.

In the following section we outline the broad and specific aims for this thesis. Section 3 summarizes the oceanographic and palaeoclimate characteristics of the Arctic Ocean that are required to understand the objectives and interpret results. Section 4 provides an overview of the analytical methods applied throughout this thesis. A brief summary of the key results is presented for each paper in Section 5. Finally, remaining questions pointing towards future research paths are discussed in Section 6. The full manuscripts one in press, one in revision, and two awaiting submission are included after this kappa.

2. Thesis aims

The overarching aims of this thesis are (i) to evaluate the application of benthic foraminifera Mg/Ca-thermometry under the cold water conditions prevailing in the Arctic Ocean, and (ii) to evaluate the potential of Mg/Ca-thermometry for reconstructing late Quaternary Arctic Ocean BWT on the continental shelf, slopes and in the deep basin (Fig. 3). This resulted in four studies each with their own set of questions and goals:

Paper I The starting point was the to address the following questions:

- Is BWT the main control on Mg/Ca ratios in Arctic benthic foraminifera and is there sufficient sensitivity at the low temperatures found in the Arctic Ocean to capture small changes in water mass temperature useful for palaeoceanography?
- Can we apply the Arctic Mg/Ca–BWT calibrations in different regions of the Arctic Ocean using distinct benthic foraminifera species?

This was a large undertaking with the following specific steps and goals:
1. Assess the distribution of Arctic benthic foraminifera and find abundant species for trace metal analysis.
2. Field exploration/validation of the Arctic benthic foraminifera Mg/Ca method in six common Arctic benthic foraminifera species.
3. Determination of suitable benthic foraminifera species for Mg/Ca-BWT palaeoproxy application by testing both epi- and in-faunal ecologies (i.e. living at or below the sediment-water interface; respectively) and different shell microstructures hyaline (perforate) and porcelaneous (imperforate) taxa.
4. Contribute to a better understanding of the Mg/Ca palaeothermometry method at the cold end of the temperature spectrum by exploring the Mg/Ca relationship to other seawater chemical parameters such as the carbonate ion saturation state.
5. Compare and synthesize Arctic benthic foraminiferal Mg/Ca calibrations with calibrations established elsewhere to expand the cold end of the temperature spectrum in global Mg/Ca–BWT calibrations.

Paper II The second phase was to apply calibrations produced in Paper I to reconstruct BWT in the past and produce palaeoceanographic histories in the Arctic Ocean. In a case study, the question of how inflow of warmer Pacific water through Bering Strait has varied in the late Holocene was addressed. The specific goals here were:

1. To generate a time series of foraminiferal geochemical proxies (benthic foraminifera Mg/Ca and stable isotopes) on a high-resolution late Holocene record from the Herald Canyon (western Chukchi Sea) where Pacific water flows today.
2. Apply the Mg/Ca-temperature equation of the calibration obtained in Paper I to reconstruct palaeotemperature variations in the western Chukchi Sea.
3. Characterize Pacific water inflow variations from the Bering Strait into the Arctic Ocean and interpret their climatic driving mechanisms.

Paper III Having shown that Mg/Ca palaeothermometry worked in an Arctic shelf setting, the next step was to test this method in the central Arctic Ocean. This involved:

1. A regional survey of Mg/Ca ratios in benthic foraminifera from core-top sites (Lomonosov Ridge and Morris Jesup Rise) intermediate-to-deep water depths of the central Arctic Ocean that could be suitable for Mg/Ca palaeothermometry.
2. Radiocarbon-dating core-top sediments with the intention of identifying Holocene samples suitable to add to Paper I Mg/Ca–BWT calibration sets.
3. An exploration of the reasons for unexpectedly 'old' core-top ages and elevated trace metals in central Arctic Ocean foraminifera.

Paper IV As part of a follow up work to Paper II, it was discovered that foraminifera had been catastrophically lost to dissolution during core-storage. This motivated the final study, addressing the question, what is the driver of dissolution in sediments from the western Chukchi Sea? Here the specific aims were:

1. To investigate the modern oceanographic, lithological and in-sediment geochemical characteristics of a western Chukchi Sea sediment core.
2. Explain the geochemical phenomena driving foraminifera dissolution based on comparisons between shipboard and post-storage geochemical changes.

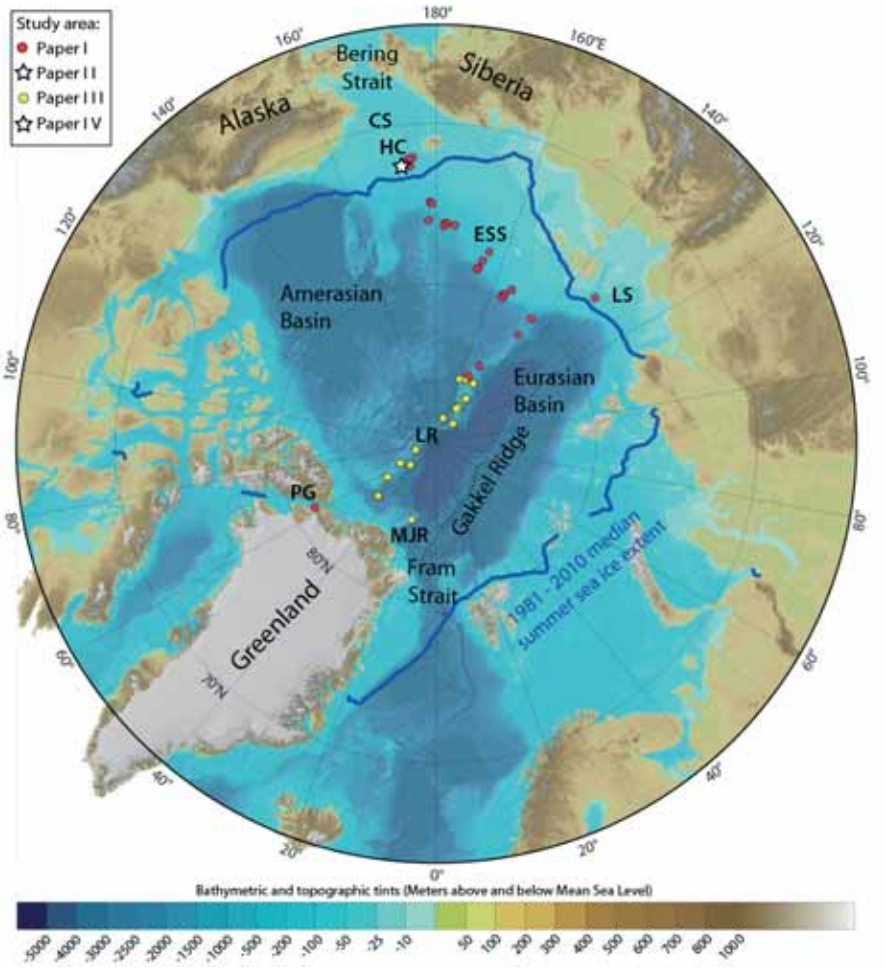

Figure 3. Arctic Ocean map showing the bathymetry and sites studied in the four papers included in this thesis. Relevant bathymetric features are: CS, Chukchi Shelf; HC, Herald Canyon; ESS, Eastern Siberian Shelf and slopes; LS, Laptev Shelf; LR, Lomonosov Ridge; MJR, Morris Jesup Rise; PG; Petermann Glacier (IBCAO 3D grid model after Jakobsson et al., 2012).

3. The Arctic Ocean

3.1 Bathymetry and physiography

In the 19th Century, it was common belief that the central Arctic Ocean was shallow containing scattered islands. This view changed following Nansen's *Fram* expedition (1893–1896), which revealed that the central Arctic Ocean consisted of a single deep basin (Nansen, 1902). This picture was elaborated on the increasing number of Arctic explorations that used icebreakers to reach more remote areas revealing that Arctic bathymetry is rather complex, containing several deep basins floored by abyssal plains and separated by huge underwater ridges (Weber, 1983). To date, the most detailed view of the Arctic Ocean seafloor is shown in the International Bathymetric Chart of the Arctic Ocean (IBCAO) (Jakobsson et al., 2012). All maps in this thesis are based on this chart (Fig. 3). The central Arctic Ocean occupies an area of nearly the same expanse as the Mediterranean Sea comprising only the ~4.3% of the global ocean area (Jakobsson, 2002). It is land-locked and enclosed by extensive continental shelves and slopes that are the widest and largest expanses in the world (~53% of the total Arctic Ocean area; Jakobsson, 2002). Analysis of benthic foraminiferal material from Arctic shelf settings is included in Papers I, II and IV. Arctic shelves cover a similar area to the deeper central Arctic basin leading to the shallowest mean water depths of 1201 m of the global oceans (Fig. 4) (Jakobsson, 2002).

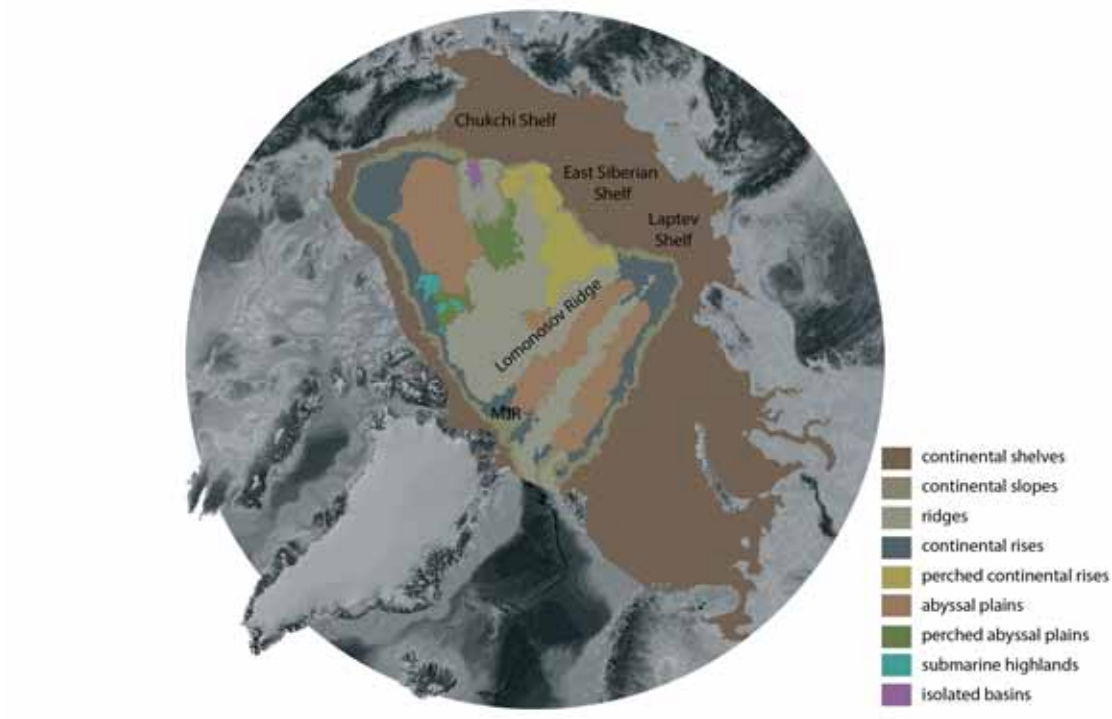

Figure 4. Arctic Ocean physiographic provinces modified after Jakobsson et al. (2003). Annotations identify the main regions/bathymetric features studied in this thesis. MJR: Morris Jesup Rise.

The deep central Arctic area contains two sub-basins (Amerasian and Eurasian) that are separated by a NE–SW trending underwater mountain chain, the Lomonosov Ridge, from which the material studied for Paper III derives (Fig. 3). This submerged ridge has heights of up to 3 km above the surrounding abyssal plains. At the summits water depths are shallowest (minimum ~600 m). Lomonosov Ridge is considered to be a continental fragment of continental crust that rifted from the Barents and Kara continental shelf ~56 Ma, during

spreading of the northern limb of the North Atlantic Mid-Ocean Ridge spreading system that continues into the Arctic Ocean (Wilson, 1963). This Arctic Ocean limb, is the ultraslow spreading Gakkel Ridge. Hydrothermal activity at the Gakkel Ridge might play a role in metal enrichment in the Arctic Ocean, especially in the Eurasian Basin (Middag et al., 2011; Klunder et al., 2012; Fitzsimmons et al., 2017).

The Arctic Ocean is connected to the Atlantic and Pacific oceans through the Fram and Bering Straits respectively. The Fram Strait shallowest point is at ~2500 m deep, whereas the Bering Strait is much shallower, ~53 m deep (Jakobsson et al., 2003; 2017). Altogether these bathymetric and geological features create unique oceanographic and palaeoceanographic environments when compared to the rest of the oceans. For instance, during glacial periods when sea level dropped by 120 m these shelves were entirely exposed, shrinking the areal size of the Arctic Ocean and shelf regions available for sedimentation (Jakobsson, 2002; Jakobsson et al., 2016). These processes may impart differences in sediment sources and accumulation rates, both on the shelves and in the basins, inducing geochemical changes in Arctic seafloor sediments (Papers III and IV).

3.2 Physical oceanography

One of the most distinctive oceanographic characteristics of the Arctic Ocean and its polar climate is that it is capped with a skin of sea ice, which in certain regions experience strong seasonal variations fluctuating from sea ice maxima in March and sea ice minima in September (Figs. 1 and 3). The main driver of sea ice drift in the Arctic Ocean is wind that forces two dominant surface currents to circulate, the Beaufort Gyre and the Transpolar drift. The latter was first described in 1897 as a result of the famous three year long '*Fram'* drift expedition (1893–1896), in which the Norwegian explorer Nansen intentionally froze his ship, the *Fram*, into Arctic pack ice to understand its movements (Nansen, 1902). These major surface currents export sea ice through the Fram Strait (Fig. 5a). Interestingly, wind-driven sea ice drift (Fig. 5a) is decoupled from the pattern of geostrophic circulation at deeper depths of the Arctic Ocean; subsurface water masses below the halocline flow counterclockwise as opposed to the surface (Fig. 5b) (Aagaard and Carmack, 1989). This occurs because atmospheric forcings are the main forcings to surface water and sea ice movements, whereas below the halocline Arctic Ocean layers are topographically steered (Rudels et al., 1994).

A thorough description of Arctic Ocean water masses and their properties follows since benthic foraminifera live in and extract the elements necessary for shell formation from these water masses where they intersect the benthic habitat. The study sites included in this thesis span water depths from 52–3814 m, from the shelf to deep abyssal plains, thus covering the main water masses in the Arctic Ocean (Fig. 5). An oceanographic transect from the Bering to the Fram Straits shows that the subsurface 0–200 m contains cold (-2–0°C) and fresher waters (~32.5–34.5 psu) derived from seasonal sea ice melt mixed together with riverine input (10% of the global river discharge) and Pacific and Atlantic inflow, namely the Arctic halocline layers where its upper part hosts Pacific origin waters and its lower part contains Atlantic origin waters (Fig. 5c) (Aagaard et al., 1981; Jones and Anderson, 1986; Jones et al., 1995; Rudels et al., 1996; Steele and Boyd, 1998; Serreze et al., 2006; Stein, 2008; Woodgate et al., 2012). Above the halocline sits the polar mixed layer (PML), the depth of which varies seasonally and spatially, being deeper (from ~25 to >50 m) in winter than summer (from ~5

to 30 m), and generally deeper in the eastern (regional mean ~20 m in summer, ~70 to >100 m in winter) compared to the western Arctic (~8 m in summer, 30 m in winter) (Rudels et al., 1991; 1996). None of our cores sampled this water mass directly, although the shallowest study site (52 m) might be seasonally influenced by the PML.

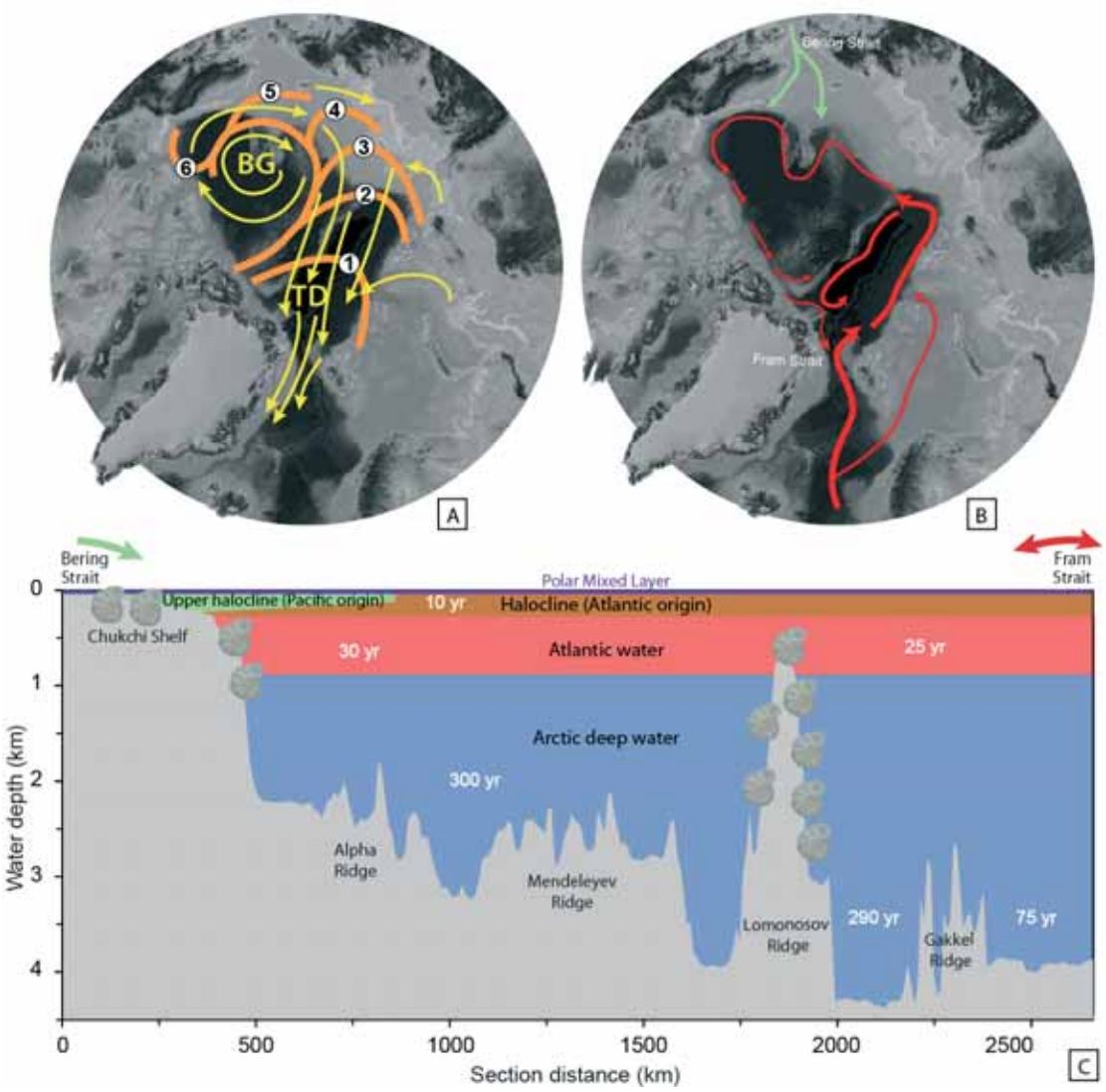

Figure 5. Arctic Ocean circulation from the surface-to-deep. (A) Yellow arrows, sea ice circulation patterns. Orange lines represent mean sea ice drift in years until its export to the Fram Strait (drawn after Bischof, 2000). TD: Transpolar Drift, BG: Beaufort Gyre. (B) Subsurface patterns of Arctic Ocean currents (drawn after Rudels et al., 1994). (C) Oceanic transect from the Bering to the Fram Strait showing the depth of the main Arctic water masses. Ages shown represent the approximate residence time for the different water masses in Arctic Ocean (Schlosser et al. 1994; Jones et al. 1995). Note the two main gateways that flow into the Arctic Ocean through continental gaps or gateways Pacific water through the Bering Strait (inflow) and Atlantic water through the Fram Strait (outflow and inflow). Benthic foraminifera cartoons illustrate the water depths, water masses and regions sampled in this thesis.

Beneath the halocline, sits Atlantic water sourced through Fram Strait that delivers heat (0–1°C) and salinity (~34.8 psu) to the intermediate depths of the Arctic Ocean (Coachman and Barnes, 1963). In the Arctic Ocean Atlantic water has a cyclonic and topographically driven circulation that flows between 200–900 m where it progressively densifies and deepens along its path around the Arctic Ocean (Fig. 5b, 5c) (Rudels et al., 1994). Changes in the properties of this Atlantic water mass have been reported over the last decades based on the instrumental

record showing increasing temperatures (Quadfasel et al., 1991; Carmack et al., 1995) and shoaling of the Atlantic layer in the Amundsen and Makarov Basins (Morison et al., 1998; Polyakov et al., 2017). This water mass is the primary component of the Arctic Ocean since it also contributes to the Arctic deep waters that fill the basin below 900 m. Arctic deep waters have a composition similar to the Atlantic water but slightly colder (< 0°C) and more homogenous (Rudels et al., 2009). For the past glacial-interglacial cycle, a 1–2°C warming of Atlantic water in the central Arctic Ocean has been inferred from ostracod Mg/Ca palaeothermometry (Cronin et al., 2012). Part of the motivation for this thesis, especially Paper III, was to obtain additional temperature records needed to test this idea.

Arctic Ocean layers are, thus, a mixture of imported waters from the Atlantic and Pacific. These different properties, together with large local seasonal freshwater imports, result in strong salinity-driven stratification, salinity being the dominant control on density considering the low temperature gradients that exist in the Arctic Ocean (from -2°C to 2°C) (Fig. 2) (Rudels et al., 2012). In fact, the Arctic Ocean has a 'reversed' vertical temperature gradient compared to global oceans, the surface ocean, which experiences the harsh polar winter, being colder than deeper flowing Atlantic waters. Hence, the halocline protects sea ice from the warmer Atlantic waters below (Aagaard et al., 1981; Rudels et al., 1996). Warming and shoaling of the Atlantic waters due to global warming, thus, may exacerbate sea ice decline.

The other important component of upper halocline waters is Pacific water that enters the Arctic Ocean through the Bering Strait. Pacific water in the Arctic is fresher and less dense than Atlantic waters, due to excess precipitation over evaporation occurring in the Pacific Ocean vs the Atlantic Ocean. It also has a high CO_2 and nutrient content reflecting ocean conditions in the North Pacific. It thus sits on top of Atlantic origin waters, and contributes to the Arctic halocline (Fig. 5c) (Jones et al., 1998). This water mass is thought to bring heat into the Arctic Ocean (Woodgate and Aagaard, 2005; Grebmeier, 2011), and therefore reconstructions of Pacific water past temperatures became the focus of study for Paper II.

Controls on Pacific water inflow into the Arctic are a not entirely clear and a subject of ongoing research, considering its potential to influence sea ice, stratification, carbonate chemistry and primary production in the western Arctic (Shimada et al., 2006; Woodgate et al., 2006; Harada, 2016). In the Chukchi Sea region, a northward flow of Pacific water since ~11000 cal yr BP, when the Bering Strait flooded following the last glacial period (Jakobsson et al., 2017), appears to be partly driven by lower sea level in the Arctic Ocean compared to the Bering Sea as well as wind stress patterns in the Bering Sea (Coachman and Aagaard, 1966; Danielson et al., 2014). Hence, it is becoming apparent that Pacific Ocean forcings may also be important.

Observations show that the inflow of Pacific waters and reconfiguration of Arctic Ocean water masses have varied significantly even over yearly time scales (Kinney et al., 1970; McLaughlin et al., 1996; 2002). Changes in the configuration of the halocline have in part been attributed to variations in the distribution of Pacific waters (Carmack et al., 1995; McLaughlin, et al., 1996). To explore this further, a late Holocene record of Pacific water inflow variability, using Arctic benthic Mg/Ca palaeothermometry, is presented in Paper II.

3.3 Chemical oceanography and sediment geochemistry: insights on early diagenesis

In addition to the Arctic physical oceanography, seawater geochemistry is of critical interest for the application of palaeoproxies that rely on chemical analyses. An understanding of sedimentary environments and sediment geochemistry is also crucial for foraminiferal palaeoproxy applications since any change in taphonomy will interfere with foraminiferal calcite preservation, potentially altering the original biogenic chemistry. These aspects turned out to be central to the research undertaken for this thesis and are the subjects of Papers III and IV.

The chemical signature of Arctic Ocean seawater is complex and reflects multiple processes and influences (Anderson, 1995). The oceanography of the Arctic Ocean and the preservation of biogenically precipitated calcite is a function of the chemical properties (mainly total carbonate and alkalinity) brought mainly by the distinct waters flowing through the Pacific-Atlantic gateways and the riverine inflow. Most of the Arctic floor lies above the lysocline for calcite (Jutterström and Anderson, 2005). However, compared with other ocean basins, mapping of calcium carbonate distribution in Arctic seafloor sediments is poor due to the challenges of sampling in this harsh and remote setting and further work on this aspect is needed. It is known from collected marine sediment cores that carbonate sediments are highly variable in their occurrence, with biogenic contributions from pelagic and benthic shells occurring during interglacial phases, but typically not glacials (Jakobsson et al., 2000; Backman et al., 2004; Cronin et al., 2008; O'Regan et al., 2008). Moreover, detrital carbonate eroded and transported by ice and fluvial processes can represent significant contributions to central Arctic sediments (Darby, 1971; Bischof et al., 1996).

The Arctic Ocean is subject to one of the lowest pH seawater values due to the higher gas solubility in colder waters (Anderson et al., 2017a). Arctic Ocean bottom water pH, measured during the SWERUS-C3 expedition in 2014 using Niskin bottles attached to CTD casts (Anderson et al., 2017a), show geographic and in-depth variations largely due to the respective inflows of Atlantic and Pacific waters. Seawater pH measured in the Eastern Siberian Arctic Ocean, slope, Chukchi Shelf and southern Lomonosov Ridge ranges from 7.5 to 8.2 (Fig. 6). Atlantic water has higher pH typically > 8 that is considered to have high buffering capacity, as shown by high carbonate content in seafloor sediments bathed by this water mass (Huber et al., 2000) (Fig. 6). In contrast, extending from the western Arctic, i.e. Eastern Siberian Sea/Chukchi Sea side, sits a pronounced tongue of lower seawater pH on the order of 7.7–7.9 (Fig. 6). These are regions of higher nutrient content and extensive biogeochemical transformation of organic matter, both of marine and terrestrial origins, which, together with brine production from sea ice formation results in a cold bottom water of relative high salinity and CO_2 content (Fig. 6) (Codispoti, 1979; Anderson and Dyrssen, 1989; Emerson and Hedges, 2008; Yu and Elderfield, 2007; Anderson et al., 2017a; 2017b).

A particular concern regarding Arctic biogenic carbonate preservation is the possibility of dissolution or alteration as a consequence of the harsh bottom conditions that result from variations in sea ice cover, and periodic, i.e. highly seasonal, interglacial-limited, surface production and export. Such issues have long been discussed (Herman, 1974; Huber et al., 2000; Steinsund and Hald, 1994). The samples analyzed in this thesis come from a wide variety of Arctic Ocean depths a fact that will lead to differences in foraminiferal test

preservation depending on their oceanographic setting. These concerns were realized, as reflected by the results presented in this thesis, documenting early diagenetic processes that add secondary calcite and metal oxides (Paper III) to severe calcite dissolution (Paper IV).

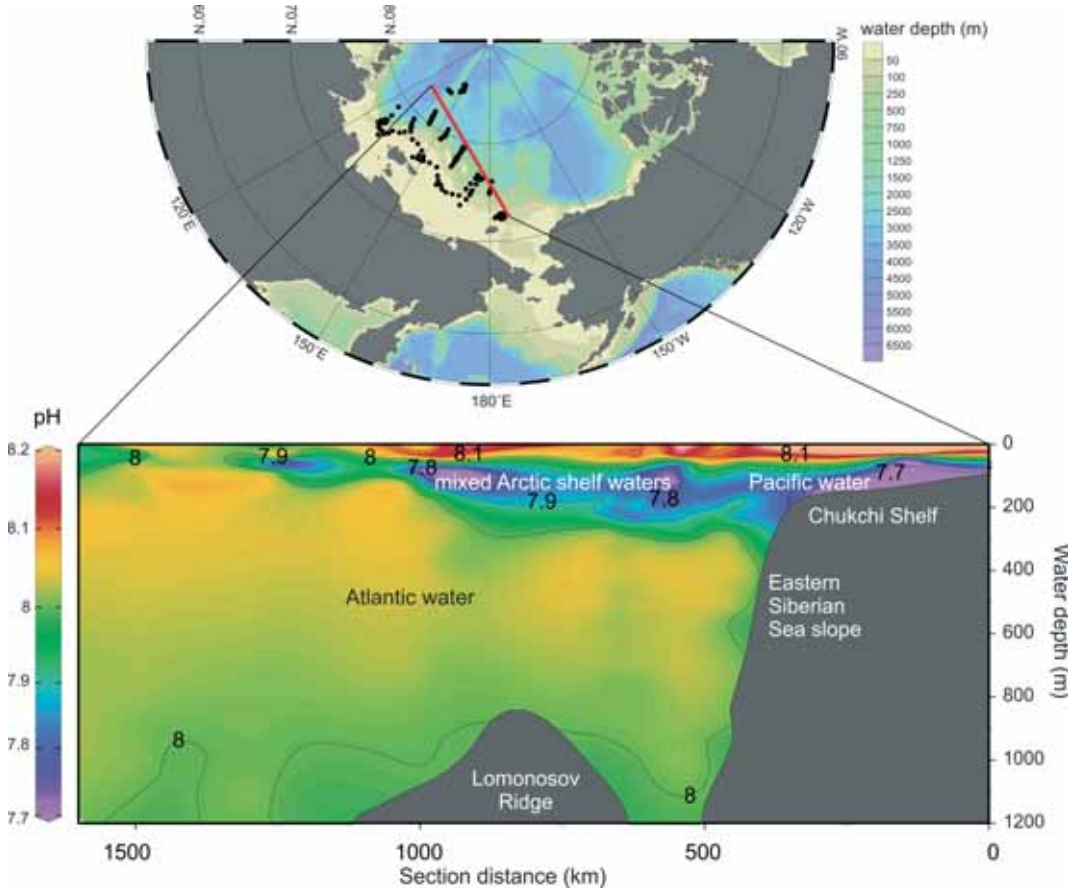

Figure 6. Arctic Ocean seawater pH values measured during Expedition SWERUS-C3 in 2014. Stations are depicted in the map as black dots and the red line highlights the area of the oceanographic pH transect. The map was drawn using Ocean Data View (Schlitzer, 2017).

Early diagenesis in marine sediments is known to be directly or indirectly linked to the degradation of organic matter (Huber et al., 2000; Steinsund and Hald, 1994). Organic carbon accumulation and preservation are generally higher on Arctic shelves where there is typically both higher production and overall higher sedimentation rates that can average ~200 cm/kyr on the western Chukchi Sea (Pearce et al., 2016). In the deeper perennially sea ice covered central Arctic Ocean, sedimentation rates are lower (from ~ 0.5 to 3 cm/kyr) and organic matter input is rather low (mainly highly seasonal), where ice rafting and melting provide significant sediment contributions (Backman et al., 2004; Stein and Macdonald, 2004; Rossel et al., 2016; Stein, 2008; Stein et al., 2010).

The differences in Arctic Ocean sedimentation regimes provide distinct dominant porewater geochemical zonations in sediments from the shelves to deeper settings due to the different pathways for organic matter degradation. These result in different in-situ geochemical burial environments in the central Arctic compared to the Arctic shelves, that impact foraminiferal preservation in various ways. These preservational aspects, in the context of Mg/Ca palaeothermometry, are the focus of Paper III (Mn and Fe reduction) and Paper IV (sulphate (SO_4^{2-}) reduction) (Fig. 7).

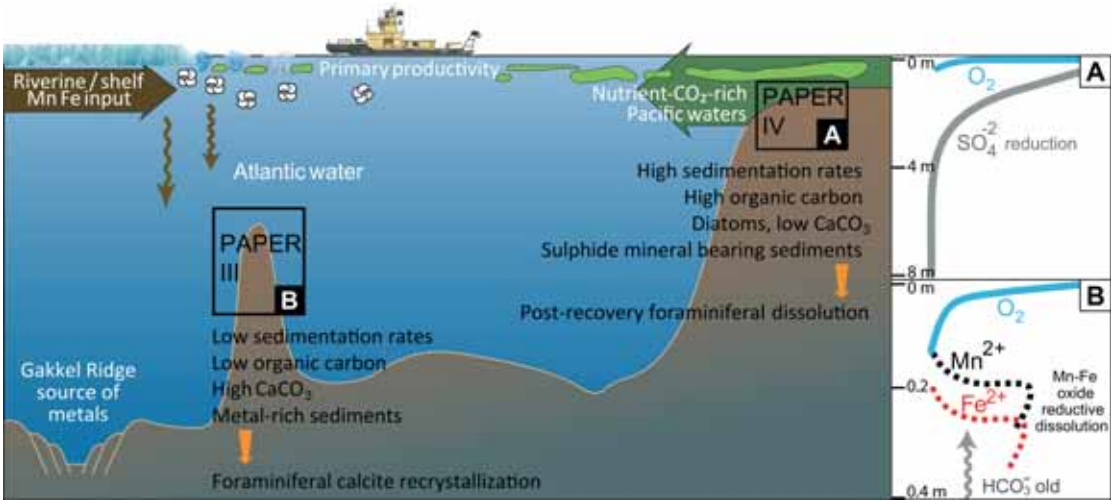

Figure 7. Sketch illustrating a water depth transect from the central Arctic Ocean (Lomonosov Ridge) to the Chukchi Shelf. It describes the distinct studied sedimentary settings, including water mass influences, during an interglacial scenario. Right hand boxes represent the main sediment porewater geochemical pathways on the Chukchi Shelf (A, Paper IV) and at the core-tops (B, Paper III). These mechanisms are leading to distinct foraminifera preservation issues through early diagenesis in each studied setting: Paper IV, post-recovery dissolution; Paper III recrystallization.

It is concluded that these key drivers are relative amounts of organic matter accumulation, subsurface oxygen penetration and consumption and availability of dissolved or particulate metals in porewater. At greater water depths where organic flux is lower, oxygen penetration into the seafloor sediment pile deepens and allows active oxidative/suboxic chemical processes to operate over the top decimeters, involving Mn and Fe oxidation and reduction further down. This has repercussions for foraminiferal tests that are exposed for long periods to the active redox processes (Paper III) (Schulz and Zabel, 2006). By contrast, in shelf sediments, the high organic flux and burial rates lead quickly to anoxic sediments already in the top few cm below the sediment surface, due to organic carbon being remineralized anaerobically by sulphate reducing bacteria (Paper IV) (Jørgensen, 1982; Jørgensen and Kasten, 2006; Bowles et al., 2014).

3.4 Late Quaternary palaeoclimatology and palaeoceanography and the sedimentary imprints

Atmosphere-ocean climate responses to periodic variations in the shape and orientation of Earth's orbit, known as Milankovitch cycles, is the overriding mechanism explaining the late Quaternary ~100 kyr glacial-interglacial cycles (Fig. 8) (Imbrie et al., 1984; Berger and Loutre, 2010). The multiple glacial-interglacial shifts of the past are recorded in marine sediments in distinct ways, including changes in sediment type, abundance, mineralogy and the oxygen stable isotope ($\delta^{18}O$) composition of foraminifera test calcite.

The repeated pattern of $\delta^{18}O$ increases and decreases, which reflects glacial and interglacial periods respectively through fractionation of ^{16}O into and out of ice sheets, provides the standard chemostratigraphic reference template known as the marine isotope stages (MIS), extending back several million years, to which other records can be compared (Lisiecki and Raymo, 2005). The MIS system becomes the main chronologic framework referred to

through this thesis for the Arctic Ocean records reaching back to late Quaternary timescales (Fig. 8). The multiple foraminiferal records spliced together to create the MIS framework (Lisiecki and Raymo, 2005), largely come from outside the Arctic Ocean, and in reality Arctic foraminiferal records themselves are too discontinuous to provide a direct $\delta^{18}O$ match. Thus, other sedimentary indicators, described in previous papers, have been used to identify the various MIS. This is detailed further below in section 4.2.

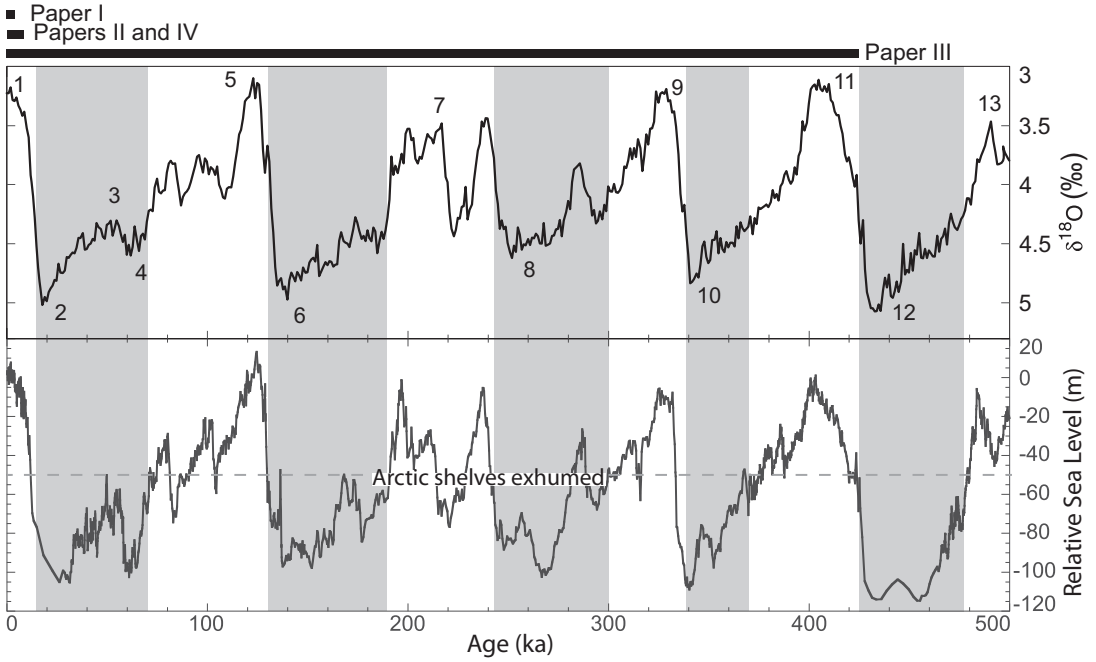

Figure 8. The global $\delta^{18}O$ stack after Lisiecki and Raymo, (2005). Bars at the top show the time periods that are covered in each study. Shaded in grey are the major glacial and interstadial periods. Global relative sea level reconstruction (3 point moving averages) after Rohling et al. (2010).

Different theories have arisen about the extent of ice in the Arctic Ocean during the late Quaternary. At first, Mercer (1970) proposed that during glacial periods, a vast ice shelf (i.e. sourced and maintained from land) extended across the entire Arctic Ocean, after making analogies with the ones present today in the Antarctic Southern Ocean. Later, Hughes et al., (1977) posited that a 1km thick floating ice shelf might have prevailed during the Last Glacial Maximum (LGM). This hypothesis was further tested through bathymetric survey, revealing marine glaciogenic landforms indicative of ice shelves, covering the entire Arctic Ocean at times during late Quaternary glacials, at least during the MIS 6 penultimate glaciation (Grosswald and Hughes, 1999; Jakobsson et al., 2016). Importantly, glacial-interglacial climate cycles induce large sea level fluctuations (Fig. 8). Taking the last glacial sea level lowering of 120 m as a benchmark (Mix and Ruddiman, 1984; Chappell and Shackleton, 1986), sea level fall of 120 m in the Arctic Ocean would uncover the massive extent of shelves across the Barents Sea, East Siberian Sea and Chukchi Sea, preventing shelf-sea oceanic transformations, and reducing coastal and shelf delivery of terrestrial erosional products to the central Arctic Ocean (Fig. 8) (Macdonald and Gobeil, 2012). Moreover, Pacific water inflow is blocked by the Bering land bridge during glacials (Jakobsson et al., 2017).

Concomitant with these glacial-interglacial intervals are drastic changes in foraminiferal recovery in central Arctic Ocean sediments, with both benthic and planktonic foraminifera being typically scarce during glacial clay-rich sediments and abundant during interglacial coarser-grained sediments (Herman, 1974; Jakobsson et al., 2000; Wollenburg et al., 2001; Backman et al., 2004; Cronin et al., 2008; O'Regan et al., 2008). Interestingly this is the opposite to foraminiferal preservation in other oceans, where clay-rich sediments tend to contain extremely well-preserved foraminifera even back tens of millions of years (Pearson and Burgess, 2008; Sexton and Wilson, 2009). Explanations for foraminifera absence during glacials remain speculative, ranging from a more nutrient limited and less productive central Arctic Ocean during glacials, with thick year-round sea ice and potentially ice-shelf cover (Jakobsson et al., 2016) resulting in decreased particle accumulation, to reduced Atlantic water inflow and increased corrosiveness of glacial bottom waters preventing calcareous shell preservation (Henrich et al., 1989; O'Regan et al., 2008; Cronin et al., 2008; Eynaud et al., 2009). With regards to the glacial units that contain foraminifera, the results of the central Arctic foraminifera study reveal widespread diagenesis that for now prevents the use of Mg/Ca palaeothermometry in this setting (Paper III). Additionally, it is possible that the larger sediment grain size played a role in enhancing benthic foraminiferal alteration through increasing sediment-porewater interactions (Sexton and Wilson, 2009). Hence, interglacial intervals, the only times when benthic foraminifera mainly occur in the studied cores, are the places where diagenesis could act more vigorous (Paper III).

Also intrinsic to the Arctic Ocean glacial-interglacial sedimentary regime are cyclic sedimentological layers varying in color from dark brown to medium brown that reflect concentration of Mn and Fe in sediments during interglacials (Ericson et al., 1964; Clark et al., 1980; Jakobsson et al., 2000; Darby et al., 2006). The origin of these metal-rich layers is still widely debated since these could be either climatic (produced from varying northern Siberia sources through an enhanced hydrological cycle) or diagenetic (from changing in-sediment redox and bottom water oxygen conditions) (Jakobsson et al., 2000; Löwemark et al., 2008; 2014; März et al., 2011; 2012; Meinhardt et al., 2016). Moreover, hydrothermal sources of Mn and Fe from Gakkel Ridge could be play a role in modifying these and other element supplies to deep water in the restricted basin (Middag et al., 2011; Klunder et al., 2012; Fitzsimmons et al., 2017; Hein et al., 2017).

In late Quaternary glacial periods, palaeoceanographic evidence suggests that there has been a reduction in warm Atlantic water inflow (Cronin et al., 1995; Hebbeln and Wefer, 1997; Matthiessen et al., 2001; Nørgaard-Pedersen et al., 2003). A ~1°C colder and fresher Atlantic water has been inferred from studies of ostracod assemblages of the last glacial period (Cronin et al., 1995). On the other hand, during MIS 3 a deepening in the Atlantic water layer together with a 1–2°C warming has been found by using ostracod Mg/Ca (Cronin et al., 2012). In this thesis, these interglacial metal-rich layers where foraminifera are found preserved have been observed to coincide with diagenetic Mg enrichment in benthic foraminifera shells, implying that other taphonomic changes that concentrate metals occur. Hence, Paper III investigates the mechanisms for early diagenesis found in the central Arctic Ocean (Fig. 7).

During the last glacial, the Arctic Ocean was cut off on its Pacific side but during the Holocene, at ~11 cal ka BP, the Bering Strait is thought to have re-flooded allowing Bering Sea water into the Arctic Ocean (Jakobsson et al., 2017). This Holocene Pacific-Arctic

reconnection is thought to influence the post-glacial climate evolution since inflowing Pacific waters into the Arctic Ocean bring heat and freshwater with associated controls on Arctic sea ice extent (Shaffer and Bendtsen, 1994; Hu et al., 2012; Ortiz et al., 2012; Woodgate et al., 2012). The effect of Pacific inflow variations through time is thus a critical component in Arctic Ocean palaeoceanography and palaeoclimate and therefore become the focus of Paper II. A question in this respect is the role of North Pacific-Arctic teleconnections through atmospheric forcings, such as the Aleutian Low, as a possible driving mechanism directing Pacific water inflow into the Arctic Ocean through the Bering Strait (Paper II).

3.5 Foraminifera calcification and test Mg content

Foraminifera (d'Orbigny, 1826), Latin for 'hole bearers', are micrometer-scale single-celled protists that inhabit all the oceans on Earth. Benthic forms (i.e. living on or within the upper few cm of the sediment) appeared in the fossil record in the early Cambrian (~570 Ma), whereas the planktonic varieties (floating in the upper hundred meters of the water column) came later, in the Middle Jurassic (~174 Ma).

Foraminifera can build organic, agglutinated (by cementing particles) or calcareous shells, also known as tests. Different types of calcareous tests occur, hyaline (perforate, low Mg/Ca (decimals or units of mmol/mol)) and porcelaneous (imperforate, high Mg/Ca (tens of mmol/mol)), as a function of their distinct biomineralization pathways (de Nooijer et al., 2009). These shells get preserved after death in the marine sedimentary record above the carbonate compensation depth. In turn, their shell chemistry preserves a signature of the physical, biological and chemical conditions of their seawater habitat at the time of shell formation, which can be used to decode past oceanographic and environmental conditions over all Cenozoic timescales.

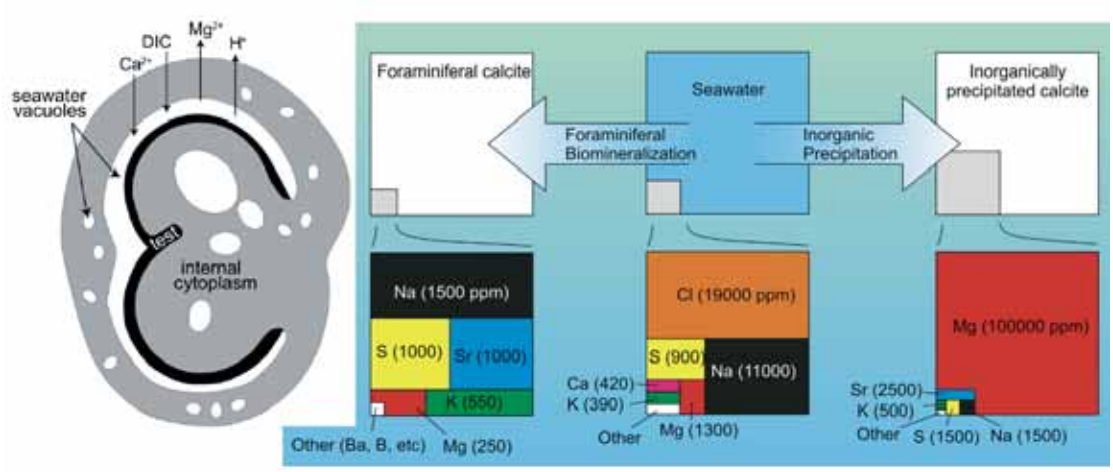

Figure 9. Modifications of seawater elemental composition (including Mg) for foraminiferal calcite biomineralization (left hand side) versus inorganic calcite precipitated from seawater (right hand side). Images modified after Erez (2003) and de Nooijer et al. (2014). DIC = Dissolved inorganic carbon.

Foraminifers calcify their $CaCO_3$ tests out of seawater. Many other metals besides Ca, occur as traces in seawater. Foraminifera have been found to have the ability to discriminate against Mg uptake during test biomineralization since Mg inhibits calcification, as shown by culture

and field studies at known temperature (Fig. 9) (Chave, 1954; Izuka, 1988; Davis et al., 2000; Erez, 2003). This is further reflected by the fact that modern seawater Mg/Ca content is 5.5 mol/mol while a foraminifera tests encloses 1000–3000 times lower Mg/Ca than the ambient seawater concentration (Lea, 1999). Moreover, it is found that foraminifera tend to elevate their intracellular water pH in order to promote calcification (Fig. 9) (de Nooijer et al., 2009).

Geochemical palaeoceanographic proxies require the use of single species to remove potential offsets introduced by different biomineralization pathways and vital effects such as different calcification depths or different growing seasons (Bentov and Erez, 2005; de Nooijer et al., 2009). Rigorous taxonomy is thus crucial to ensure that appropriate taxa are selected prior to geochemical analysis. Early studies of Arctic foraminifera taxonomies may appear in the rather inaccessible Russian literature. Pioneering non-Russian Arctic foraminifera studies were initiated by Loeblich and Tappan (1953), Green (1960), Ericson et al. (1964) and Herman (1964). The only true polar species of planktonic foraminifera is *Neogloboquadrina pachyderma* (Ravelo and Hillaire-Marcel, 2007), although species of *Turborotalita* appear well suited to the Arctic both in modern times and the late Quaternary (Cronin et al., 2008; Husum and Hald, 2013; Manno and Pavlov, 2014).

For benthic foraminifera the diversity is higher, influenced by seafloor physiography and food supply (Lagoe, 1977; Scott et al., 1989; Vilks, 1989; Wollenburg, 1992; Bergsten, 1994; Wollenburg and Mackensen, 1998; Osterman et al., 1999). This is further examined in this thesis as part of the search for modern benthic foraminifera appropriate for testing Mg/Ca-thermometry in the Arctic Ocean (Paper I). From all studied surface sediments, 6 species were found to occur in sufficient abundance and spanning the full range of water depths of interest in order to be potentially useful geochemical signal carriers. These are *Elphidium clavatum, Nonionella labradorica, Cassidulina neoteretis, Quinqueloculina arctica, Oridorsalis tener* and *Cibicidoides wuellerstorfi* (Fig. 10).

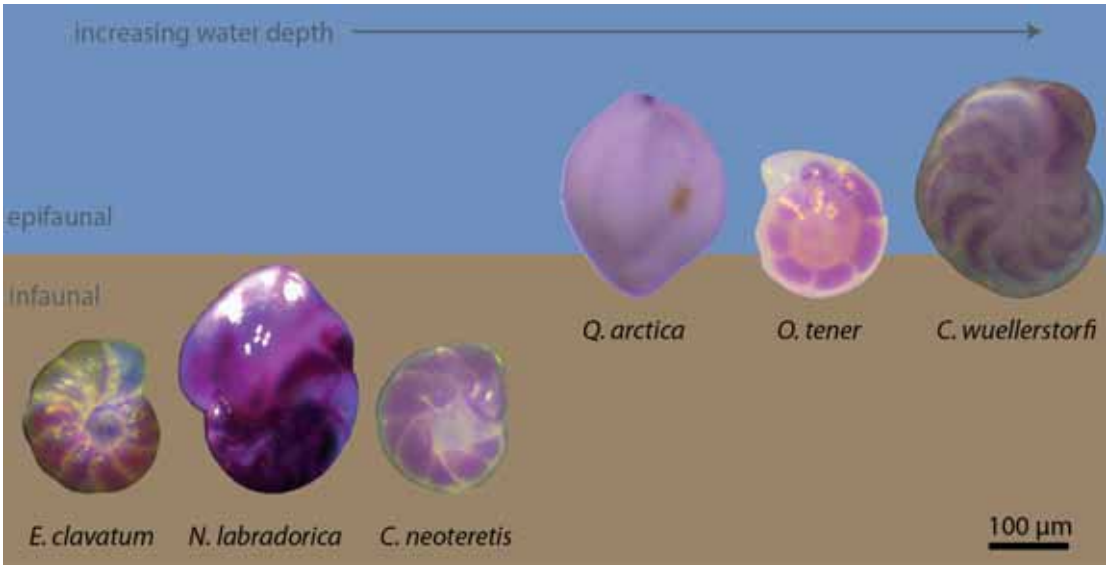

Figure 10. Multicore Rose Bengal stained benthic foraminifera studied throughout this thesis showing their preferred water depth and seafloor habitat (*E: Elphidium*, *N: Nonionella*, *C: Cassidulina*, *O: Oridorsalis*, *C: Cibicidoides* and *Q: Quinqueloculina*).

4. Materials and background to methods

4.1 Expedition SWERUS-C3 fieldwork: coring, water sampling and initial sediment handling

The SWERUS-C3 Leg 2 expedition in July–October 2014, crossed the Arctic Ocean onboard icebreaker Oden along the Siberian continental margin from Pt. Barrow (Alaska) to Tromsø (Norway). Participation in this expedition was part of my Ph.D. project. This expedition recovered sediments and collected oceanographic data from a previously un-cored area on the Chukchi Shelf, East Siberian Shelf and slopes as well as from the Lomonosov Ridge part closest to the East Siberian Sea. My main shipboard duties were: take responsibility for the material recovered by multicoring operations on deck; piston and gravity core splitting; sediment core sampling (every 8 cm by using 10 cc plastic scoops); sample washing/sieving for separation of sand size/micropaleontology size particles; microscope microfossil examination to establish foraminiferal abundances and attempt biostratigraphy; microfossil identification and separation of biogenic calcite for radiocarbon dating; sediment pH measurements and writing up results from microscope investigations for the cruise-report.

Sediment coring during the SWERUS-C3 Leg 2 expedition used both a multicorer device to recover the best possible copies of the sediment-water interface (optimal for benthic-proxy field calibrations), and a piston corer for obtaining longer sediment sequences. The multicorer was an Oktopus GmbH, comprising eight polycarbonate liners of 60 cm long and 10 cm diameter (Fig. 11). Oceanographic data was collected using a SeaBird 911 conductivity temperature depth (CTD) system (with certified stability of 0.001 °C) during which seawater was also sampled in Niskin bottles that opened and closed at specified depths, including a couple of dm from the seafloor to capture bottom water properties. The paired multicore material and matching oceanographic data suites were critical to building modern Arctic benthic foraminifera Mg/Ca–BWT field calibrations (Paper I). The methods used to retrieve longer cores involved trigger weight, piston and gravity coring devices that recover 10 cm diameter sediment cores in a plastic core liner. The devices were built by Stockholm University. Piston core SWERUS-C3-L2-2PC1 recovered from Herald Canyon, Chukchi Sea, turned out to contain an exceptionally high resolution late Holocene record that became the focus of Paper II where the new Arctic Ocean Mg/Ca–BWT calibration for *E. clavatum* was successfully applied in order to reconstruct past seawater temperatures (Paper II). Additionally, sediment porewaters were extracted using rhizon sampling and their chemical composition analyzed during the SWERUS-C3 expedition. These data were used in Paper IV in order to explore the causes of foraminiferal dissolution post-recovery.

Additional foraminifera material presented in this thesis was recovered from Arctic Ocean sediment cores collected during several Swedish icebreaker *Oden* expeditions in 1996, 2007, 2009 and 2012: Arctic Ocean ’96 and Lomonosov Ridge off Greenland (LOMROG I-II and III) retrieved by trigger weight, piston and gravity coring devices. These cores were stored at the Stockholm University Department of Geological Sciences (IGV). The cores were selected based on the different water depths and geographic locations of the central Arctic Ocean Lomonosov Ridge to originally expand the Arctic Ocean Mg/Ca-temperature calibrations into deeper water settings (Paper III).

Figure 11. Multicorer used for sampling seafloor sediments (left) and CTD Cast with 24 Niskin bottles (right) used to sample seawater at specified depths during the SWERUS-C3 expedition. The materials and data were used in the construction of modern benthic foraminifera Mg/Ca–BWT calibrations.

4.2 Dating Arctic Ocean sediments

Knowing the age of the foraminiferal samples found in core-top samples is paramount to building modern calibrations and two main methods have been applied for age determinations; Rose Bengal staining (Paper I) and radiocarbon dating (Papers II, III, IV).

Rose Bengal is a protein die that stains the foraminifer protoplasm, and other organic matter, in a vivid pink (Fig. 10) (Walton, 1952). This was used to identify living benthic foraminifera in the newly recovered SWERUS-C3 multi-core samples as part of Paper I; the goal was to measure Mg/Ca in Rose Bengal stained (RBS) 'modern' specimens with the assumption that these should best reflect the sampled, prevailing field BWT constraints. RB staining was not possible for samples taken from archived cores recovered several years ago or more.

The most widely used technique for dating late Quaternary interglacial Arctic sediments is radiocarbon (^{14}C) dating. ^{14}C, which is a radioactive (unstable) isotope of carbon, is produced by the interaction between cosmic radiation and atmospheric nitrogen (^{14}N). ^{14}C enters into the global carbon cycle as $^{14}CO_2$ that can either be incorporated into organic matter of dissolve in the oceans. Radioactive decay of ^{14}C to ^{12}C provides the 'clock' (Libby, 1952), since ^{14}C has a half life of 5730 years, allowing dating back to ~40,000 years. In the marine realm, $^{14}CO_2$ dissolves in seawater to become ^{14}C-DIC that is incorporated into the biogenic calcite. The assumption is that no more calcite carrying ^{14}C will be incorporated post death, thereafter the shell ^{14}C starts decaying in a predictable way. Biogenic calcite produced by a range of marine calcifiers, including foraminifera, can be dated in this way.

An important step in calculating ^{14}C ages form marine materials is that the results must be corrected for the global marine reservoir effect (R). This effect originates from the fact that it

can take several hundred years for atmospheric CO_2 to equilibrate throughout the ocean water column, which shows important differences in terms of DIC content and CO_2 exchange in the surface compared to the deep ocean. For instance, organisms living in seawater that has been in less contact with the atmosphere will result in older ^{14}C ages than they really are. Furthermore, the R value varies through time and region. Today the modern R value averages ~ 400 yr in the global oceans but this can vary even for closely related geographical locations, due to factors such as upwelling, leading to incomplete or heterogeneous mixing. Therefore, local marine local reservoir effects (ΔR) are needed. For the central Arctic Ocean we have applied a ΔR correction of 300 yr (Paper III) based on the value calculated in Hanslik et al. (2010), whereas for the western part of the Arctic Ocean (on the shallow Chukchi Shelf) a ΔR of 400 yr has been established by Pearce et al. (2017) and used in the age model of Paper II.

In the central Arctic Ocean radiocarbon dates were measured on the core-top occurrences of the planktic foraminifera *N. pachyderma*, with a focus on the 4-chambered morphotype to minimize biological or chronological biases (Healy-Williams, 1992). Nevertheless, the resulting ^{14}C ages in 16 sites in the central Arctic are rather old (up to 12 thousand years) for core-top samples, suggesting that other factors, besides sediment mixing, are influencing the foraminiferal ^{14}C chronometer. As suggested previously in Atlantic records (Barker et al., 2007; Wycech et al., 2016), these old ^{14}C dates may derive from a diagenetic mechanism influencing central Arctic foraminifera calcite that has not previously been identified in the central Arctic Ocean. This aspect is discussed in Paper III where it is found that benthic foraminifera with high Mg/Ca ratios coincide with core-top samples with surprisingly high ^{14}C dates that moreover appear to be positively correlated. The paper posits that diagenetic additions of secondary calcite using HCO_3^{2-} from older (deeper) sources lead to elevated Mg concentrations and old core-top ages into the suboxic zone where early diagenesis was occurring (Fig. 7).

Dating downcore records in central Arctic marine sediments is generally challenging. Firstly, biostratigraphy is limited due to the discontinuous occurrence of calcareous microfossils, appearing mainly during interglacials (Cronin et al., 2008). Resulting foraminiferal $\delta^{18}O$ curves that could be matched to the MIS framework are thus also discontinuous. Moreover, the potential for $\delta^{18}O$ chemostratigraphy is complicated because large riverine discharge and melt water pulses that associated with deglaciations, swamp any global ice volume signal $\delta^{18}O$ making difficult to resolve the typical patterns (Fig. 8) (Spielhagen et al., 2004). Even palaeomagnetic-stratigraphy in Arctic sediments is complicated since it shows many excursions of long duration. Instead dating capitalizes on a variety of other relative dating approaches, such as Mn-Fe cycle stratigraphy (Jakobsson et al., 2000; Löwemark et al., 2014) and the occurrence of calcareous microfossils, those features themselves allowing distinction between glacials and interglacials, tied together with sparse biostratigraphic datums (Backman et al., 2009) and geochemical methods, including ^{14}C-dating, calcium intensity cycles, and aminoacid racemization. Adding to this the effects of diagenesis, leads to uncertainties in accurately dating Arctic sediments. The age models used for the downcore records in Paper III are no exception. These have been produced as part of previous work and were not part of this thesis.

For Paper II and IV, age models were built on the basis of 14 radiocarbon dated mollusk shells, for which I collected the material, and the 3.6 ka Aniakchak tephra identification (Pearce et al., 2017). The age model for this core (Herald Canyon, late Holocene core 2-PC1)

is extremely well populated with geochemical dates and is considered robust. For Paper III, downcore age constraints for cores 96/12-pc1, LOMROG07-PC04 on the Lomonosov Ridge and core LOMROG07-PC08 on the Morris Jesup Rise derive from foraminifera radiocarbon dates, nannofossil and foraminiferal biostratigraphy, foraminiferal abundance patterns, benthic foraminiferal marker events, calcium intensity peaks and aminoacid racemization (Jakobsson et al., 2000; Hanslik, 2011). There could be alternative interpretations of the MIS stratigraphy (M. O'Regan, *pers. comm.*), however, the age models have not been critically analyzed as part of this thesis.

4.3 Benthic foraminifera geochemical analysis

4.3.1 Trace metals (Papers I, II and III)

Chemical reactions occur faster at higher temperatures since more molecules engage in reactions and form bonds as they move and collide faster (Arrhenius, 1889). Incorporation of Mg into the calcite lattice occurs following an endothermic process, therefore, more Mg incorporation arises in warmer waters. A century ago, the first instance of temperature having an effect on the biogenic carbonate trace metal content was reported by Wigglesworth-Clarke and Wheeler (1917). This thermodynamic effect was further explored in planktonic foraminifera with the advances in mass spectrometry (Savin and Douglas, 1973) and more than a decade later, in benthic foraminifera of the *Cassidulina* genus (Izuka, 1988). Extensive subsequent work into Mg/Ca temperature sensitivity has been carried out since the mid 90s (Nürnberg et al., 1996; Rosenthal et al., 1997; Hastings et al 1998; Elderfield and Ganssen, 2000; Lear et al., 2000; Barker et al., 2003; Evans et al., 2016).

Many dissolved metal ions, including Mg^{2+} and Ca^{2+}, are present in seawater and these move through Earth reservoirs via geochemical cycles that link the atmosphere, oceans, rivers, sediments and rocks. These processes determine the residence time of a substance in seawater. Importantly for the Mg/Ca palaeothermometry, Mg and Ca have long residence times in seawater, thought to be on the order of approximately 1 Myr for Mg and 10 Myr for Ca (Broecker and Peng, 1982).

This Mg/Ca palaeotemperature proxy relies on the fact that, in the crystal lattice, Mg is incorporated during shell formation as an impurity, and the amount is intimately linked to seawater temperature based on inorganic thermodynamics, where higher Mg is incorporated in warmer waters during foraminiferal calcification (Lea, 1999). Mg/Ca ratios in benthic foraminiferal calcite are a commonly used proxy for reconstructing past bottom water temperatures. There have been Arctic benthic foraminifera Mg/Ca studies from northern Greenland and Svalbard environments (Kristjánsdóttir et al., 2007; Quillmann et al., 2012; Skirbekk et al., 2016), but the method is still underexplored in the Arctic Ocean.

All the trace metal data presented in this thesis were analysed using solution-based Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at Cardiff University, where whole specimens were dissolved in acid and the resulting solution analyzed. Sample preparation and analysis were entirely carried out at Cardiff University ICP-MS facility, in collaboration with Prof. Carrie Lear. The initial survey for Mg/Ca–BWT proxy application using SWERUS-C3 multicores showed that the most abundant species in halocline waters were *E. clavatum* and *N. labradorica*, in Atlantic waters *C. neoteretis* and *Q. arctica* and in

Arctic deep waters *O. tener* and *C. wuellerstorfi* (Fig. 9) (Paper I). These are all hyaline taxa with the exception of *Q. arctica* being porcelaneous (imperforate, high Mg concentration). Trace metal samples consisted of 3–40 foraminiferal tests (depending on species size and abundance) extracted from prepared sand-fraction samples. The shells were first crushed into 10–50 µm-sized fragments by hand between glass slides. These fragments were then placed in polypropylene acid cleaned (10% HCl) Eppendorf safe lock tubes (0.5 ml) that were then brought to Cardiff University trace metal clean laboratory. The multi-specimen samples comprising at least several specimens produces a more reliable homogenized average signal.

Sample preparation for foraminiferal trace metal ICP-MS analyses requires rigorous pre-cleaning steps to try and remove surficial remaining organic matter, clays and diagenetic precipitates from both internal and external surfaces (Boyle, 1983; Boyle and Keigwin, 1985; Boyle and Rosenthal, 1996; Barker et al., 2003). The samples were randomly placed in polypropylene racks. In this thesis the cleaning protocol of Boyle and Keigwin (1985) was followed, which consists of the following (Fig. 12):

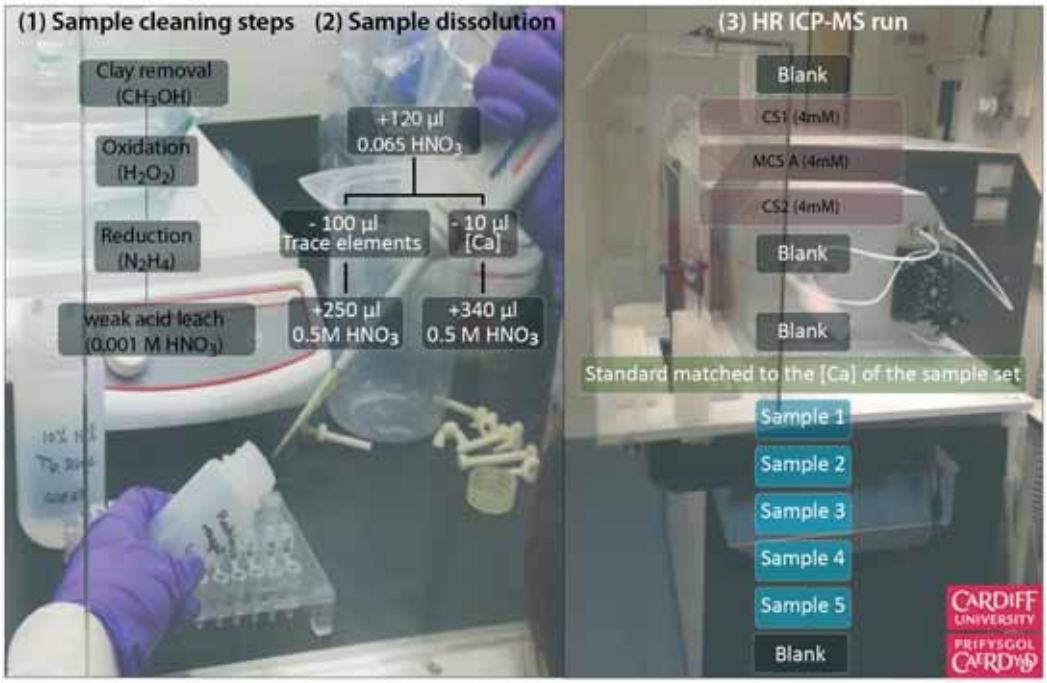

Figure 12. Workflow for the foraminifera trace metal analysis. Foraminiferal sample cleaning steps and sample dissolution and dilution (left), and HR ICP-MS sequence run of the foraminiferal samples (blue rectangles).

(i) three clay removal steps by ultrasonically cleaning the tests in methanol (CH_3OH)/deionized-water solution, since remaining clays have the greatest effects on modifying original Mg/Ca ratios (Barker et al. 2003);

(ii) an oxidizing step using alkali-buffered hydrogen peroxide (H_2O_2), in order to remove adhered organic matter;

(iii) a reductive step using diluted hydrazine hydrate (N_2H_4), a strong reducing agent, which is necessary because sediments deposited in active redox environments with low sedimentation rates, as found in the central Arctic Ocean (Paper III), can result in increased tendency for formation of diagenetic Mn- and Fe-rich oxides (Barker et al. 2003);

(iv) a weak acid leach using 0.001 M HNO_3, to remove any adsorbed contaminant during the cleaning procedure.

Attempts were made to carry out this pre-cleaning routine at Stockholm University IGV, however it was discovered that hydrazine hydrate is a highly restricted chemical substance in Sweden, thus cleaning was only conducted at Cardiff University.

The clean benthic foraminifera samples were then dissolved by adding 120 µl of trace metal free 0.065 M nitric acid (HNO_3) per sample tube (Fig. 12), vortex stirred for a few seconds and centrifuged for three minutes. To promote dissolution, the tubes were refrigerated for at least 12 h (5°C). Once fully dissolved, two aliquots for analyses were pipetted off from the tubes: a 10 µl aliquot for Ca analysis and a 100 µl aliquot for element/Ca. Multiple trace metals can be analyzed at the same time, giving additional insights into bottom water and porewater environments, and post burial processes. Thus Al, Fe, Mn, Li, Sr, Cd, U, B, Nd, Ba, were measured together with Mg. Trace metal aliquots were diluted by adding 250 µl of trace metal pure 0.5 M Optima HNO_3 in the trace metal aliquot, and 340 µl for the Ca aliquot (Fig. 12). Samples of a final volume of 350 µl were measured on a Thermo Element XR high-resolution inductively coupled plasma mass spectrometer (HR ICP-MS) (Rosenthal et al., 1999; Lear et al., 2002). This ICP-MS instrument works by injecting the sample liquids through capillaries into a nebulizer where they were the sample is transformed into a spray that reaches a plasma torch at ~ 7700 °C. Once there, the sample gets ionized, i.e. separated into ions grouped by mass-to-charge ratios.

The analysis started by running in-house consistency standards (CS1, CS2, MCS A) mixed and maintained at Cardiff University at a concentration of 4 mM in order to determine analytical drift, quality and long-term precision. Samples were run in blocks of five, separated by a blank composed of 0.5M Optima HNO_3 and a standard matching the Ca concentration of the samples to determine accuracy of the results (Fig. 12). The analyses finished with the same 3 consistency standards run at the beginning and two blanks. Initial ICP-MS raw data is reported as intensity counts per second (cps). Then, these intensities are translated to molarity units by comparing the cps to the standards of known Ca composition.

Establishing whether the resulting foraminifera trace metal signals reflect original biogenic calcite or have been altered is a crucial step before attempts to reconstruct BWT can be made. A first step is to consider the absolute Mg/Ca values. In the Arctic Ocean trace metal set, if Mg/Ca is > 2mmol/mol (as the values mainly obtained in Paper III), it is considered to include some contamination phase. Another perspective comes from examining relationships between Mg/Ca and other trace metal/Ca ratios. Positive relationships, e.g. between Mg/Ca and Fe/Ca implies some form of diagenetic contamination. The trace metal data derived from core-top and downcore samples from the Lomonosov Ridge (Paper III) showed clear correlations between Mg/Ca and, e.g. U/Ca, Al/Ca and Fe/Ca. Principal component analysis was used to further investigate which elements Mg clustered with, in an attempt to identify the source of calcite contamination. In contrast, benthic foraminiferal trace metal data derived from RBS modern taxa and the late Holocene downcore record from the Chukchi Sea easily passed all the screening tests. These Mg/Ca data, thus, were used in Paper I to establish empirical Mg/Ca and temperature relationships (calibrations) on the basis of the field studies, whereas in Paper II, a calibration was applied to the downcore Herald Canyon Mg/Ca record to produce a late Holocene BWT history of Pacific Water inflow (Paper II).

4.3.2 Oxygen isotopes (Paper II)

Traditionally, oxygen isotopes have been applied to interpret past seawater temperatures since the discovery of Urey's palaeothermometer (1947). He showed that the fractionation (i.e. discrimination) of the heavy ^{18}O isotope and the light ^{16}O isotope from solution to biogenic calcite shell is temperature dependent and established the $\delta^{18}O$ per mil (‰) notation based on the ^{18}O / ^{16}O ratio (R):

$$\delta^{18}O\ (‰) = [(R_{sample} - R_{standard}] \times 1000 \quad (1)$$

This $\delta^{18}O$ per mil notation facilitated the use and comparison of oxygen isotope values due to the low $^{18}O/^{16}O$ ratio in calcite that further needed to be compared to a standard of known $^{18}O/^{16}O$ composition. Equation 1 shows that a positive value signals that the sample is enriched in the heavy isotope with respect to the reference standard.

Pioneering work by Emiliani (1954) using $\delta^{18}O$ values from foraminifera shells found in deep-sea cores from the Swedish deep-sea expedition Albatross (1947–8) was interpreted as variations in Pleistocene ocean temperatures on glacial-interglacial timescales and was the first to propose the system of MIS back to stage 22 (Emiliani, 1955). According to the $\delta^{18}O$-temperature relationships relatively higher $\delta^{18}O$ is linked to lower calcification temperatures and vice versa. Subsequent work demonstrated that, although the $^{18}O/^{16}O$ ratio fractionates as a function of seawater temperature, the foraminifera shell calcite $\delta^{18}O$ values also reflect the prevailing global seawater isotopic composition, which itself varies as a function of terrestrial ice volume (Shackleton and Opdyke, 1973). Furthermore, Shackleton and Opdyke (1973) calibrated the Pleistocene deep-sea $\delta^{18}O$ record to palaeomagnetic data, thus strengthening the MIS stage system as a chronological tool. It is now well known that the $\delta^{18}O$ on glacial time scales is reflecting fractionation produced by the hydrological cycle due to the Rayleigh fractionation (Fig. 13). This is explained by the fact that heavy oxygen isotope in the water molecule ($H_2{}^{18}O$) tends to condensate more easily and will preferentially precipitate in lower latitudes while ^{16}O is contained in vapor phase ($H_2{}^{16}O$) reaching higher latitudes (Fig. 13). Hence, the ^{16}O water content in the cloud droplets progressively increases while moving from the warm equator to the cold waters, regulated by a Rayleigh distillation processes. As a result, from the tropical rains to the polar snows the $\delta^{18}O$ values will be decreasing. For ice core $\delta^{18}O$ the fractionation follows this same concept.

For this thesis, benthic foraminifera $\delta^{18}O$ was measured using a Gasbench II coupled to a Thermo Scientific MAT 253 mass spectrometer. Approximately 0.2 mg of foraminifera per sample was flushed with helium gas in a septum-seal glass vial. 100µl of 99% H_3PO_4 was added to each sample for reacting to CO_2. Based on these measurements the reproducibility was calculated to be better than 0.15‰. Standards used were Carm-1 and CaCO Merck that were calibrated to international standards NBS18, IAEA-CO-1 and IAEA-CO-8, all reported in ‰ relative to Pee Dee Belemnite (PDB). Foraminiferal PDB values were corrected to Standard Mean Ocean Water (SMOW) to derive $\delta^{18}O$ of seawater (Pearson, 2012).

In the seasonally dynamic upper layers of the Arctic Ocean, the $\delta^{18}O$ proxy is known to be complicated due to melting or formation of sea ice (Anderson and Dyrssen, 1989; Spielhagen et al., 2004). This is because in the surface ocean sea ice has shown to preferentially incorporate ^{18}O (Craig and Gordon, 1965; Pfirman et al., 2004). Reported values for $\delta^{18}O$ in the Arctic Ocean sector bathed by bottom Pacific halocline waters are -2‰ for shelf waters,

-1‰ for Pacific sourced water, and 0‰ for sea ice melt water (Melling and Moore, 1995; Yamamoto-Kawai and Tanaka, 2005). Knowing this, in this thesis paired foraminiferal Mg/Ca and $\delta^{18}O$ measurements were made to try and disentangle these signals in the dynamic Herald Canyon region, Chukchi Sea (Paper II). This approach revealed remarkable relationships between an ice cores $\delta^{18}O$ and Pacific halocline Mg/Ca-derived palaeotemperatures, and suggesting external forcing, potentially Pacific Ocean teleconnections influencing Arctic warming.

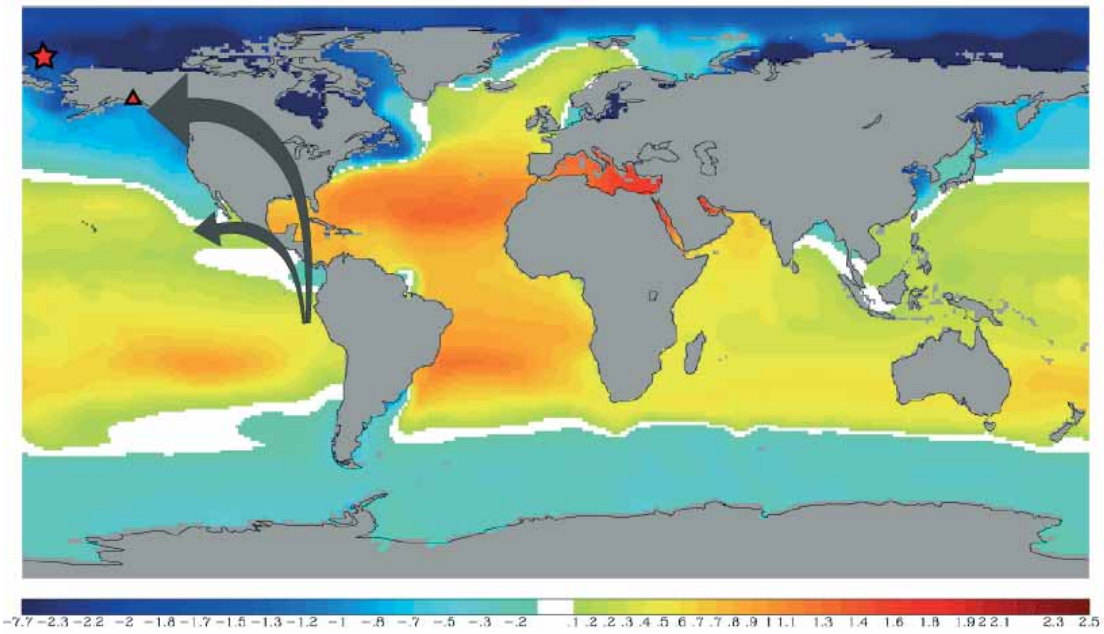

Figure 13. Surface $\delta^{18}O$ seawater map of LeGrande and Schmidt (2006). Arrows show the latitude effect on water isotope fractionation (decreasing $\delta^{18}O$ with increasing latitude) by Rayleigh distillation. Red star and triangle identify the location of $\delta^{18}O$ records discussed in Paper III. Star corresponds to Herald Canyon core 2-PC1, in which benthic foraminifera $\delta^{18}O$ and Mg/Ca records were generated, and the triangle identifies an ice core $\delta^{18}O$ record (Mount Logan; Fisher et al., 2004) used for comparison (Paper II).

4.4 Evaluation of foraminiferal test preservation

In this thesis one of the key goals was to reconstruct BWT in the Arctic Ocean. Discovery of widespread foraminiferal calcite Mg enrichment across central Arctic Ocean cores, and later, total dissolution of Herald Canyon foraminifera when attempts were made to resample the core in 2015, showed this was not going to be quite so simple. Therefore, while the initial Chukchi shelf BWT reconstruction was a success, it became clear that before the method could be pushed forward, attention should be turned to the diagenetic mechanisms driving these changes. This is the focus of Papers III and IV. These studies show that preservation between 'pristine' (modern tests from shelf, slopes and ridges; and fossil tests from the Chukchi Shelf; Papers I and II) and diagenetic (fossil tests from the Lomonosov Ridge and Morris Jesup Rise; Paper III) can differ spatially and temporally.

Post-mortem foraminiferal diagenetic effects may affect original test geochemistry and thus compromise the interpretation of geochemical proxies (Branson et al., 2015). Neomorphic recrystallization (i.e. same mineral but different crystal form) is the replacement of biogenic calcite by cementation as overgrowths or infilling the chambers of a secondary mineral, for instance inorganic calcite overgrowths. Since the Mg concentration in hyaline foraminifera is

so small, this may lead to an enrichment of the original Mg introduced in the formation of the calcite test. This can be further explained by the partition coefficient of Mg^{2+} in inorganic calcite being higher than in biogenic calcite (Fig. 9), tested through laboratory experiments (Katz, 1973). Foraminiferal diagenesis in the Arctic Ocean is poorly studied and carbonate preservation is known to be extremely limited and variable (Bergsten, 1994; Feely et al., 2002; Jutterström and Anderson, 2005). Across the wide expanses of Arctic shelf seas, which are occupied by colder (< 0 °C) and fresher waters of the Arctic mixed layer and underlying halocline waters (Rudels et al., 2004), very different hydrographic conditions prevail and even more limited and variable occurrences of foraminifera-containing calcareous sediments (Steinsund and Hald, 1994; Hald and Steinsund, 1996). In the Arctic Ocean, even post-recovery dissolution of using foraminiferal calcite has been encountered (L. Polyak and M. Hald, *pers. comm.*).

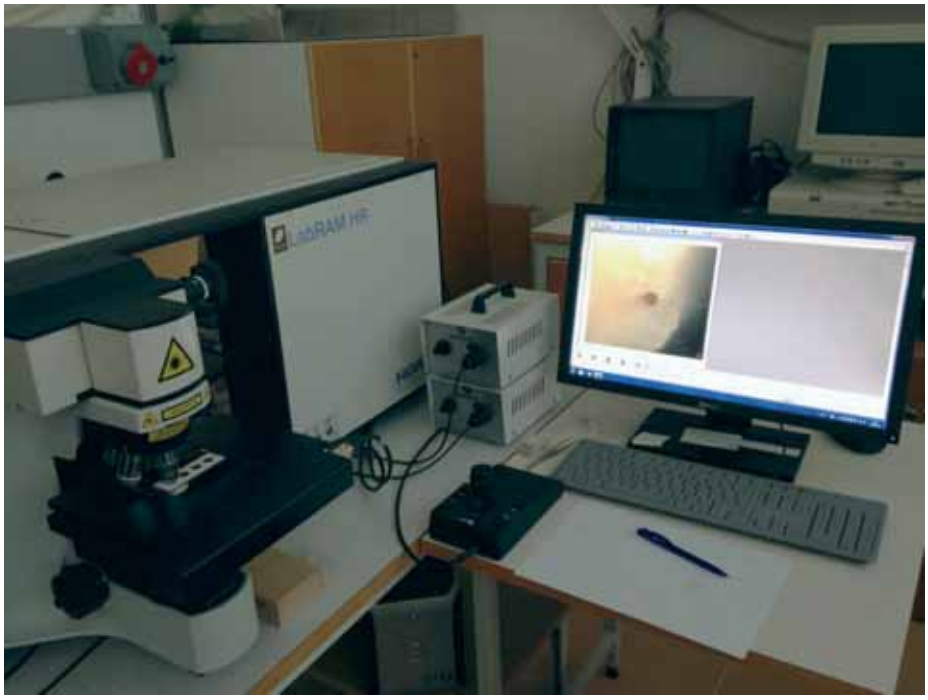

Figure 14. Raman instrument showing on the computer screen (right) a brownish spot growing on foraminiferal test calcite.

A variety of analytical instruments housed at Stockholm University IGV were used to investigate and document the diagenetic alteration. In paper III, visual 3D determination of the grain shapes and qualitative elemental determination of any present diagenetic phases was performed by using Scanning Electron Microscopy (SEM) coupled with an Energy-Dispersive Spectroscopy (EDS) device. EDS was conducted using an Oxford instrument X-Max 80 detector and the elemental spectra was calculated by photon counting normalized to 100% with a ± 1% 2σ detection limit. Raman spectroscopy was used in an attempt to identify specific mineral phases in pristine and altered foraminifera. This is a vibrational spectroscopic technique that works by adding energy to the chemical bonds between atoms and can determine mineral composition through differences in the crystal structure even in mineral polymorphs (Roberts and Murray, 1995) with help of reference spectra (the RRUFF database; Lafuente et al., 2015). Raman spectra were collected using a confocal laser Raman microspectrometer Horiba instrument LabRAM HR 800 (Fig. 14). Excitation was provided by an Ar-ion laser (λ=514nm) source with a low laser power (below 1mW) to reduce laser

penetration depth, minimize mineral transformation and avoid shell breakage. A possible limitation of this method could derive from the laser penetration depth (5–10μm). In this respect, for a 3μm-thick diagenetic coating, the Raman may provide a mixed signal of the original and diagenetic foraminiferal test material.

Another case of poor foraminiferal preservation investigated in this thesis is large scale dissolution of foraminifera and other biogenic calcite from Chukchi Shelf core 2-PC1, during core storage. Microscope observations show how foraminifera tests progressively dissolved and lost their complete microstructure within months after core retrieval (Paper IV). Here downcore X-ray fluorescence (XRF) data indirectly supported chemical evidence for dissolution by post-recovery porewater acidification of the core. XRF works by exciting with X-rays the marine sediments, then these emit a secondary fluorescence or radiation that has a recognized wavelength as a function of known atomic number. Archive halves were run on Itrax core scanner housed at Stockholm University IGV. Interestingly, the ability for the XRF to detect Ca diminishes with storage time (Paper IV). The post storage XRF runs showed a dramatic drop in Ca counts in parallel with test dissolution. Ca cannot not disappear from the core, thus the signal was interpreted to reflect a shift in Ca from solid phase (biogenic calcite) into solution. This finding complicates approaches were XRF Ca is used to identify foraminiferal levels, as used previously (Rothwell et al., 2016).

An additional finding in this diagenesis investigation is that trace metal ratios can serve as a way of identifying the nature of post-depositional test alteration. This is relevant to interpreting and understanding the rather old core-top ^{14}C ages in the central Arctic Ocean. As suggested previously in a study of Atlantic Quaternary sediments (Wycech et al., 2016), positive correlation between Mg/Ca and ^{14}C suggests the ages themselves can be explained by diagenetic processes. Moreover, throughout this thesis the Mg/Ca have been validated by cross-comparing the entire trace element dataset where linear correlations between Mg/Ca and trace element/Ca exist, thus suggesting addition of non biogenic Mg (Paper III). Particularly, Paper III core-top and downcore late Quaternary foraminifera have shown that calcite diagenetic processes (Fig. 7) alter original biogenic calcite Mg/Ca ratios, thus comprising their use as Mg/Ca palaeothermometers.

5. Summary of key results

5.1 Paper I

Arctic Ocean benthic foraminifera Mg/Ca ratios and global Mg/Ca-temperature calibrations: New constraints at low temperatures.

The paper explores the relationship between Mg/Ca and BWT in the Arctic Ocean. This paper has been accepted for publication in the journal *Geochimica et Cosmochimica Acta*. The main objective of this study was to test the idea that the Mg content of benthic foraminifera shells is systematically related to BWT even at the low temperatures found in the Arctic Ocean and on the shelf compared with the central basin where different water masses exist. The study adds important data at the cold end of the global BWT spectrum, where previous studies show low Mg/Ca temperature sensitivity, and suggests that benthic foraminifera can be useful

palaeothermometers in the Arctic Ocean. The field calibration suites include samples form 27 sites, spanning water depths of 52–1157 m and BWT of -1.8 to 0.9 °C from new Arctic Ocean regions: Arctic shelves, slopes and Lomonosov Ridge (Fig. 1). The different sites intersect all three of the principal Arctic water masses, i.e. the halocline, and Pacific water, Atlantic water and Arctic deep water (Fig. 5).

A survey of the most abundant and recurrent Rose Bengal stained ('living') benthic foraminifera species in these water masses identified 6 species as potential candidates for Mg/Ca palaeothermometry; *E. clavatum* and *N. labradorica* (halocline); *C. neoteretis* and *Q. arctica* (Atlantic water); *O. tener* and *C. wuellerstorfi* (Arctic deep water). These species have either epifaunal or infaunal habitats and all form hyaline tests with exception of *Q. arctica* that builds porcelaneous (imperforate) tests. This variety allows testing whether habitat or biomineralization pathway plays a role in Mg/Ca temperature sensitivity. Based on these investigations, the Mg/Ca ratios in the five studied hyaline species show concentrations consistent with expected values in Mg/Ca–BWT calibrations at the 'cold end'. These values range from 0.52 to 1.06 mmol/mol in *E. clavatum*, 1.11 to 1.31 mmol/mol in *N. labradorica*, 0.84 to 1.20 mmol/mol in *C. neoteretis*, 1.43 to 1.78 mmol/mol in *O. tener* and 1.15 to 1.48 mmol/mol in *C. wuellerstorfi*. In contrast, Mg/Ca ratios of the porcelaneous species *Q. arctica,* which are naturally considerably higher than in the hyaline species (18.89 to 75.08 mmol/mol), appear to vary more as a function of bottom water $\Delta[CO_3^{2-}]$ than temperature in cold Arctic bottom waters, implying this taxon is not suitable for reconstructing temperatures in this setting.

The new Arctic data are compared with similar monospecific/or monogeneric data from outside of the Arctic Ocean to help validate the results and synthesize the large sample set to improve Mg/Ca–BWT relationships. The new data allows a refinement of Mg/Ca–BWT calibrations at the cold end of the BWT spectrum and are as follows: *Nonionella labradorica* Mg/Ca = 1.325±0.01 × e^(0.065±0.01 × BWT), r^2=0.9, *Cassidulina neoteretis* Mg/Ca = 1.009±0.02 × e^(0.042±0.01 × BWT), r^2=0.6, *O. tener* / *umbonatus* Mg/Ca = 1.317 ± 0.03 × e^(0.102±0.01 BWT), r^2=0.7, *C. wuellerstorfi* Mg/Ca = 1.043 ± 0.03 × e^(0.118±0.1 BWT), r^2=0.4. A calibration for *Elphidium clavatum* is also presented, Mg/Ca = 0.816±0.06 + 0.125±0.05 × BWT, r^2=0.4. This is based only on the new Arctic Mg/Ca constraints since no previous data exists for this species.

5.2 Paper II

Late Holocene variability in Arctic Ocean Pacific Water inflow through the Bering Strait.

In this paper a high-resolution palaeoclimate and palaeoceanographic record is presented from the Herald Canyon (western Chukchi Sea). This was submitted as a manuscript to the journal *Geology*. It was sent out to review, we only recently received a set of positive reviews with an invitation to resubmit pending revised (ongoing). Previous studies have investigated the inflow of Pacific waters but not from the Arctic western Chukchi Sea side or in this degree of detail. The site is located at 57 m water depth in the Herald Canyon and the seafloor, thus benthic foraminifera, sits in the modern path of Pacific waters flowing into the Arctic Ocean (Figs. 3 and 5).

The new core, collected during SWERUS-C3 expedition, has excellent age control based on 14 mollusk radiocarbon dates and identification of the Aniakchak tephra at 3.6 ka (Pearce et al., 2017) that lead to exceptionally high accumulation rates giving unprecedented detail of the late Holocene back ~ 4000 years. The major and most recurrent benthic foraminifera species is *E. clavatum* and thus the new Mg/Ca–BWT *E. clavatum* calibration equation from Paper I is applied to estimate late Holocene BWT. $\delta^{18}O$ data, also measured on *E. clavatum* is used to disentangle BWT and seawater oxygen stable isotope signals ($\delta^{18}O_{sw}$) converted to SMOW.

The measured *E. clavatum* Mg/Ca ratios vary from 0.51 to 0.93 mmol/mol, the derived BWT range from -2.4 to 1°C and reconstructed ($\delta^{18}O_{sw}$) from -1.2 to -0.16 ‰. These fluctuations are interpreted as relative indicators of changes in upper halocline water sources and properties and used to disentangle influences of Pacific vs Arctic shelf waters. Despite the late Holocene being regarded as having a relatively stable climate, the geochemical records (Mg/Ca and $\delta^{18}O$ in benthic foraminifera) capture temperature oscillations in the bottom waters of the Herald Canyon on the order of 3.5°C. This is interpreted from the *E. clavatum* Mg/Ca values that show millennial to centennial Mg/Ca variability. The Herald Canyon records suggest that a cooling trend brought by reduced Pacific water inflow prevailed over the past ~1000 yr. The records are detailed enough to resolve centennial scale changes and suggest that the last century was characterized by bottom water warming, decreased sea ice and more intense Bering Strait through-flow.

An important finding is the similarity between the Herald Canyon Arctic Mg/Ca record and Mount Logan ice core $\delta^{18}O$ from the Canadian-Pacific margin, which has been previously interpreted to record changes in precipitation source (Fisher et al., 2004). Confidence in the ability of Mg/Ca bottom water palaeothermometry to capture temperature variations on the Chukchi shelf results from this correspondence and from correlations with solar minima. Hence, it has been inferred that a common climatic forcing mechanism links these atmospheric and marine records. It is proposed that changes in the intensity and position of the Aleutian Low pressure system are intimately connected to wider Pacific climate variability and Pacific water inflow properties to the Arctic; Aleutian Low variability can produce both a switch in precipitation source from equatorial Pacific to north Pacific source that can be detected in the Mount Logan ice core $\delta^{18}O$, and act to enhance or block flow through the Bering Strait.

Thus, the variability in Herald Canyon benthic geochemical proxies is interpreted as providing an index of the strength of Pacific/Bering Sea water inflow to the Chukchi Sea over the last 4000 yr. It should be possible, therefore, using Arctic Mg/Ca palaeothermometry, to separate the Pacific water exchange and freshwater input on the western Chukchi Sea part of the Arctic Ocean.

5.3 Paper III

Mg/Ca ratios in late Quaternary benthic foraminifera from the central Arctic Ocean.

Previous studies applying Mg/Ca palaeothermometry from the central Arctic Ocean using another group of marine calcifying microfossils, i.e. ostracods, has allowed reconstructions of

variability in intermediate water temperatures on glacial-interglacial time scales (Cronin et al., 2012). Paper II of this thesis demonstrates that benthic foraminifera Mg/Ca palaeothermometry can be used to reconstruct past BWT in an Arctic shelf setting. Paper I provides evidence, in the form of realistic Mg/Ca-temperature calibrations based on modern (RBS) benthic foraminifera, that in theory the method should work in the central Arctic Ocean. Paper III pushes the work forward by exploring the palaeo application in the central Arctic Ocean using the species *C. neoteretis*, *O. tener* and *C. wuellerstorfi*. The study is based on core material retrieved from deeper water settings on Lomonosov Ridge and Morris Jesup Rise (Fig. 3). Seafloor depths at these stations intersect the subsurface water masses of the Arctic, i.e. Atlantic water and Arctic deep water (Fig. 5). The samples comprise 16 ^{14}C dated core-tops and three downcore sequences that contain several interglacial-glacial cycles (Fig. 8).

The first anomaly was that many of the *N. pachyderma* ^{14}C dates for the central Arctic core-tops are surprisingly old, i.e. between 1262–11733 cal yr BP. The measured benthic calcite Mg/Ca ratios in these core-top samples also show unexpectedly high Mg/Ca compared to RBS modern equivalents from a Lomonosov Ridge multicore sample (Paper I) (up to on average 7 times higher). Other trace metal ratios, including U/Ca, Cd/Ca, Fe/Ca, Nd/Ca, Al/Ca, Ba/Ca and Mn/Ca are also high compared to the RBS calibration set. Importantly, in many instances Mg/Ca co-varies with the other metal/Ca ratios suggesting that the original calcite trace metal compositions have been modified due to early diagenetic effects. Mg/Ca values higher than 2 mmol/mol, that is the majority of the dataset, are thus likely contaminated. The picture is the same for the downcore records in three different regions of the central Arctic Ocean. From this grows the main premise of this paper stating that core-top and downcore fossil Mg/Ca as well as core-top ^{14}C results from central Arctic settings are affected by early diagenetic processes and that this is a widespread phenomenon.

Complications in the use of foraminiferal trace metal analysis in the central Arctic Ocean have been alluded before by the scientific community, but never properly documented. This paper provides the first systematic evidence for plausible mechanisms driving foraminiferal diagenesis in this setting. Test preservation was examined through Raman spectroscopy (Fig.14) and EDS techniques, both showing that secondary coatings and fillings are common on central Arctic foraminifera fossils. We suggest this is caused by a combination of high metal content in central Arctic sediments, combined with low sedimentation rates in the Arctic that leave benthic foraminifera tests within the shallow redox-active suboxic burial zone sufficiently long for the addition of metal-rich carbonate coatings (Fig. 7). The processes resulting in widespread Mn-Fe oxide precipitation (producing Mn-sedimentary layer cycles) is suggested to play a role here. High Mn and Fe transport from the vast Arctic shelves results in wide scale precipitation of Mn and Fe oxides (Löwemark et al., 2014), which in the process scavenge other metals, including Mg (Fig. 7). Mn and Fe are subsequently reduced in the suboxic zone at burial depths of ~15-30 cm where metal rich carbonate coatings can also precipitate.

Interestingly, there is a pulse of better preservation, and realistic unaltered benthic Mg/Ca ratios (< 2 mmol/mol) in the deepest studied downcore, interpreted as being older than MIS 7. Here, only the common Atlantic water species *C. neoteretis* occurs, suggesting that the improved preservation/lack of diagenetic coatings is likely due to a change in palaeoceanography at this time.

Diagenesis may also explain the 'old' core-top ^{14}C ages (up to 12 kyr). Carbonate is generally limited to interglacial periods, thus somewhat scarce in central Arctic cores. When existing buried carbonate dissolves at deeper depths due to sulphate reduction, old dissolved HCO_3^{2-} diffusing upwards may deliver an older ^{14}C imprint incorporated as diagenetic coatings close to the seafloor (Fig. 7). This is not a new idea (e.g. Wycech et al., 2016), but it is the first time it has been suggested for the Arctic Ocean. Overall the study concludes that central Arctic benthic foraminifera have been exposed close to the seafloor for longer time periods compared to fossils in shelf settings, where high sediment flux affords rapid test protection and preservation of 'original' trace metal ratios (Paper II).

5.4 Paper IV

Post-recovery dissolution of calcareous microfossils in sediments from a highly productive Arctic marine environment.

Foraminiferal tests are present in the sedimentary record after many decades of core storage (as shown for instance with the material used for Paper III). Moreover, it is considered that clay rich sediments, favor the retention of original microstructure and geochemistry (Wilson and Opdyke, 1996; Pearson et al., 2001). However, this is not the case for the clay-rich sediments of the western Chukchi Shelf after observing whole-scale dissolution during one year in cold storage. Paper IV documents and explores the mechanism for post coring calcite dissolution in Herald Canyon core 2-PC1, using oceanographic and pore water chemistry constraints, microscopy and downcore XRF elemental mapping.

Resident bottom waters on the Chukchi Self already show a lower bottom water pH when compared to the central Arctic Ocean waters (Fig. 6), yet well-preserved foraminifera were extracted from core-tops and the downcore sequence 24 hours after core retrieval. These proved to be a rich archive for reconstructing variability in Pacific water inflow during the late Holocene (Paper II). However, when we returned to resample 2-PC1 the foraminifera tests had largely dissolved. Dissolution was anticipated before the cruise, based on previous anecdotal stories about coring on the Arctic shelves, and systematic core pH measurements were taken accordingly, shipboard (48 hours post coring), and after 1 yr of storage in the Stockholm University IGV core repository. However, the severity and speed of the dissolution was beyond anything expected. SEM micrographs document the dissolution that ranges from deep test corrosion to total dissolution leaving only organic linings. Core acidification was revealed by a drop in pH over time, and lowering of Ca and Sr in successive XRF scans with increasing storage time. This paper provides the first thorough documentation of post-coring foraminifera dissolution.

The key porewater chemical measurements provided insights into the likely driving mechanism of the dissolution. Importantly, downcore shipboard porewater alkalinity and sulphate profiles, and sediment total organic carbon and nitrogen show that these sediments are organic rich with high rates of sulphate reduction possibly due to the presence of abundant sulphides created under high sedimentation rate anoxic burial conditions (Fig. 7). Core retrieval and subsequent laboratory handling (core splitting and sampling) contributed significantly to oxidize the sulphides, with concomitant acid release. Sediments of the Chukchi Sea are thus primed for calcite dissolution. The background bottom waters contain

Pacific derived CO_2 and nutrient rich waters such that they are already undersaturated waters with respect to $CaCO_3$. Carbonate rain is also minimal, lacking coccolith or planktonic foraminifera contributions, thus the sediment buffering capacity is low. Sulphide mineral oxidation in this, and other similar settings, can thus explain the observed biogenic dissolution.

6. Discussion: unresolved questions and further considerations

The main breakthroughs of this thesis have been:

(i) Mg/Ca palaeothermometry works in principal in the Arctic Ocean; even the small temperature gradients occurring in the new field-calibration set were captured in the analyzed modern foraminifera (Paper I).

(ii) Mg/Ca palaeothermometry can be successfully applied, at least in an Arctic shelf setting, to reconstruct past Arctic Ocean palaeotemperatures (Paper II).

(iii) Application of the method is hindered in the central Arctic Ocean due to the effects of widespread early diagenesis that adds Mg to benthic foraminifera test surfaces, likely in the form of carbonate coatings post burial (Paper III).

(iv) Mechanisms driving the central Arctic Ocean foraminiferal diagenesis have been proposed that link the new observations of high foraminiferal trace metal compositions with existing knowledge of intense Mn-Fe recycling occurring in the isolated Arctic Ocean (Paper III). Moreover, it is suggested that diagenesis could also be the reason for problematic (old) core-top radiocarbon dates observed here.

(v) Dramatic dissolution of foraminiferal calcite (Paper IV) in the Chukchi Sea has been explained by the high sedimentation rates, high organic matter, low carbonate, corrosive-bottom water ocean and burial setting that results in ‘in-situ’ sulphide formation and ‘ex-situ’ (i.e. post-recovery) sulphide oxidation, which releases sulphuric acid to the pore waters.

The major goal that was not realized in this thesis was to reconstruct central Arctic Ocean BWT. In Paper III, SEM, EDS and Raman analysis have revealed that although the central Arctic foraminifera have secondary coatings, as seen by calcite overgrowths leading to high Mg compositions, the internal intra-test calcite did not contain high Mg. A natural way forward to overcome this is to use Laser ablation ICP-MS to target this apparently ‘original’ calcite preserved within the test interior (de Nooijer et al., 2014).

The case of core-storage dissolution of calcite (Paper IV) needs to be further investigated in other Arctic Ocean sediments. It appears that the foraminifera have also disappeared from an adjacent core, 4-PC1 recovered from slightly deeper water in the Chukchi Sea. Monitoring post-storage changes in other sediment cores retrieved in 2016 from the central Arctic Ocean through time is ongoing and the data need to be synthesized. In any case, this account serves as a caution to future drilling planned in similar shallow, high accumulation and highly productive shelf seas.

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References

Aagaard, K., Coachman, L.K., Carmack, E.C., 1981. On the halocline of the Arctic Ocean. Deep Sea Res., 28, 529–545.

Aagaard, K. and Carmack, E. C., 1989. The role of sea ice and other fresh water in the Arctic Circulation. J. Geophys. Res., 94, 14485–14498.

Anderson, L., Dyrssen, D., 1989. Chemical oceanography of the Arctic Ocean. In: The Arctic seas: climatology, oceanography, geology and biology, (ed. Y. Herman). New York, Van Nostrand., 93–114.

Anderson, L.G., 1995. Chemical Oceanography of the Arctic and its Shelf Seas. In: Arctic Oceanography: Marginal Ice Zones and Continental Shelves, (eds. W.O. Smith and J.M. Grebmeir), American Geophysical Union, Washington D.C., doi: 10.1029/CE049p0183.

Anderson, L.G., Ek, J., Ericson, Y., Humborg, C., Semiletov, I., Sundbom, M., Ulfsbo, A., 2017a. Export of calcium carbonate corrosive waters from the East Siberian Sea. Biogeosciences, 14, 1811–1823.

Anderson, L.G., Björk, G., Holby, O., Jutterström, S., Magnus Mörth, C., O'Regan, M., Pearce, C., Semiletov, I., Stranne, C., Stöven, T., Tanhua, T., Ulfsbo, A., Jakobsson, M., 2017b. Shelf-Basin interaction along the East Siberian Sea. Ocean Sci., 13, 349–363.

Arrhenius, S., 1896. On the influence of carbonic acid in the air upon the temperature of the ground. Philos. Mag. J. Sci., 5, 237–276.

Arrhenius, S., 1889. Uber die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren. Z. Phys. Chem., 4, 226–248.

Backman, J., Jakobsson, M., Løvlie, R., Polyak, L., Febo, L.A., 2004. Is the central Arctic Ocean a sediment starved basin? Quat. Sci. Rev., 23, 1435–1454.

Backman, J., Fornaciari, E., Rio, D., 2009. Biochronology and paleoceanography of late Pleistocene and Holocene calcareous nannofossil abundances across the Arctic Basin. Marine Micropaleontology, 72, 86–98.

Barker, S., Greaves, M., Elderfield, H., 2003. A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry. Geochemistry Geophisics Geosystems, 4, 1–20.

Barker, S., Broecker, W., Clark, E., and Hajdas, I., 2007. Radiocarbon age offsets of foraminifera resulting from differential dissolution and fragmentation within the sedimentary bioturbated zone. Paleoceanography, 22, PA2205.

Bentov, S., Erez, J., 2005. Novel observations on biomineralization processes in foraminifera and implications for Mg/Ca ratio in the shells. Geology, 33, 841–844.

Berger, A., Loutre, M-F., 2010. Modeling the 100-kyr glacial–interglacial cycles. Global and Planetary Change., 72, 275–281, doi: 10.1016/j.gloplacha.2010.01.003.

Bergsten, H., 1994. Recent Benthic Foraminifera of a Transect From the North-Pole to the Yermak Plateau, Eastern Central Arctic-Ocean. Mar. Geol., 119, 251–267.

Bischof, J., Clark, D., Vincent, J., 1996. Pleistocene paleoceanography of the central Arctic Ocean: the sources of ice rafted debris and the compressed sedimentary record. Paleoceanography, 11, 743–756.

Bischof, J., 2000. Ice drift, ocean circulation and climate change. Praxis Publishing Ltd, Chichester, 215 pp.

Bowles, M.W., Mogollón, J.M., Kasten, S., Zabel, M. and Hinrichs, K.-U., 2014. Global rates of marine sulfate reduction and implications for sub-seafloor metabolic activities.

Science, 344, 889–891.

Boyle, E., 1983. Manganese carbonate overgrowths on foraminifera tests. Geochim. Cosmochim. Acta, 47, 1815–1819.

Boyle, E.A., Keigwin, L. D., 1985. Comparison of Atlantic and Pacific paleochemical records for the Last 215.000 years: Changes in deep ocean circulation and chemical inventories. Earth and Planetary Science Letters, 76, 135–150.

Boyle, E.A., Rosenthal, Y., 1996. Chemical hydrography of the South Atlantic during the last glacial maximum: d13C vs. Cd. In: The South Atlantic: Present and Past Circulation, eds. G. Wefer, W. H. Berger, G. Siedler and D. Webb. Berlin, Springer-Verlag, 423-443.

Branson, O., Read, E., Redfern, S. A. T., Rau, C., Elderfield, H., 2015. Revisiting diagenesis on the Ontong Java Plateau: Evidence for authigenic crust precipitation in *Globorotalia tumida*. Paleoceanography, 30, 1490–1502, doi:10.1002/2014PA002759.

Broecker, W. S., Peng, T. H. and Beng, Z., 1982. Tracers in the Sea. Lamont-Doherty Geological Observatory, Columbia University.

Carmack, E.C., Macdonald. R.W., Perkin, R.G., McLaughlin, F.A., Pearson R.J., 1995. Evidence for warming of Atlantic water in the Southern Canadian Basin of the Arctic Ocean: Results from the Larsen-93 Expedition. Geophys. Res. Lett., 22, 1061–1064.

Chappell, J., Shackleton, N.J., 1986. Oxygen isotopes and sea level. Nature, 324,137–140.

Chave, K.E., 1954. Aspects of the biochemistry of magnesium: 1. Calcareous marine organisms. Journal of Geology, 62, 266–283.

Clark, D.L., Whitman, R.R., Morgan, K.A., Mackay, S.D.. 1980. Stratigraphy and glacial-marine sediments of the Amerasian Basin, central Arctic Ocean. Geol. Soc. Am. Spec. Pap., 181, 57 pp.

Coachman, L.K., Aagaard, K., 1966. On the water exchange through Bering Strait. Limnol. Oceanogr., 11, 44–59.

Codispoti, L.A., 1979. Arctic Ocean processes in relation to the dissolved silicon content of the Atlantic: Mar. Sci. Commun., 5, 361–381.

Craig, H., Gordon, L.I., 1965. Deuterium and oxygen 18 variations in the ocean and the marine atmosphere, in: E Tongiori (Ed.), Stable Isotopes in Oceanographic Studies and Paleotemperatures. Consiglio nazionale delle richerche, Laboratorio de geologia nucleare, Pisa CNR, 9–130.

Cronin, T.M., Holtz, T.R., Jr., Stein, R., Spielhagen, R., Futterer, D., Wollenberg, J. 1995. Late Quaternary paleoceanography of the Eurasian Basin, Arctic Ocean. Paleoceanography, 10, 259-281.

Cronin, T.M., Smith, S.A., Eynaud, F., O'Regan, M., King, J., 2008. Quaternary paleoceanography of the central Arctic based on Integrated Ocean Drilling Program Arctic Coring Expedition 302 foraminiferal assemblages. Paleoceanography, 23, PA1S18.

Cronin T.M., Dwyer, G.S., Farmer, J., Bauch H., Spielhagen, R.F., Jakobsson, M., Nilsson, J., Briggs, W.M., Stepanova, A., 2012. Deep Arctic Ocean warming during the last glacial cycle. Nat. Geosci., 5, 631–634.

Danielson, S.L., Weingartner, T.J., Hedstrom, K.S., Aagaard, K., Woodgate, R., Curchitser, E., Stabeno, P.J., 2014. Coupled wind-forced controls of the Bering-Chukchi shelf circulation and the Bering Strait throughflow: Ekman transport, continental shelf waves, and variations of the Pacific-Arctic sea surface height gradient: Prog. Oceanogr., 125,

40–61.

Darby, D.A., 1971. Carbonate cycles and clay mineralogy of Arctic Ocean sediment cores. Ph.D. Thesis, Univ. Wisconsin-Madison, 43 pp.

Darby, D.A., Polyak, L., Bauch, H.A., 2006. Past glacial and interglacial conditions in the Arctic Ocean and marginal seas – a review. Progress in Oceanography, 71, 129–144.

Davis, K.J., Dove, P.M., De Yoreo, J.J., 2000. The role of Mg2+ as an impurity in calcite growth. Science, 290, 1134–1137.

De Nooijer, L.J., Toyofuku, T., Kitazato, H., 2009. Foraminifera promote calcification by elevating their intracellular ph. PNAS, 106, 15374–15378.

De Nooijer, L.J., Hathorne, E. C., Reichart, G. J., Langer, G., and Bijma, J., 2014. Variability in calcitic Mg/Ca and Sr/Ca ratios in clones of the benthic foraminifer *Ammonia tepida*. Marine Micropaleontology, v. 107, p. 32P43.

Ding, Q., Schweiger, A., L'Heureux, M., Battisti, D.S., Po-Chedley, S., Johnson, N.C., Blanchard-Wrigglesworth E., Harnos K., Zhang Q., Eastman R. and Steig E. J., 2017. Influence of high-latitude atmospheric circulation changes on summertime Arctic sea ice. Nat. Clim. Chang., 7, 289–295.

Dmitrenko, I.A., Polyakov, I.V., Kirillov, S.A., Timokhov, L.A., Frolov, I.E., Sokolov, V.T., Simmons, H.L., Ivanov, V.V., Walsh, D., 2008. Toward a warmer Arctic Ocean: spreading of the early 21st century Atlantic Water warm anomaly along the Eurasian Basin margins, J. Geophys. Res.-Oceans, 113, 1–13.

d'Orbigny, A.D., 1826. Tableau methodique de la classes des cephalopod. Annals des Sciences Naturelles, 7, 245–314.

Elderfield, H., Ganssen, G., 2000. Past temperature and delta-18O of surface ocean waters inferred from foraminiferal Mg/Ca ratios. Nature, 405, 442–445.

Elderfield, H., Yu, J., Anand, P., Kiefer, T., Nyland, B., 2006. Calibrations for benthic foraminiferal Mg/Ca paleothermometry and the carbonate ion hypothesis. Earth Planet. Sci. Lett., 250, 633–649.

Emerson, S., Hedges, J., 2008. Chemical Oceanography and the Marine Carbon Cycle. Cambridge University Press.

Emiliani, C., 1954. Depth habitats of some species of pelagic foraminifera as indicated by oxygen isotope ratios. American Journal of Science, 252, 149–158.

Emiliani, C., 1955. Pleistocene temperatures. Journal of Geology, 63, 538–578.

Erez, J., 2003. The source of ions for biomineralization in foraminifera and their implications for paleoceanographic proxies. Rev. Mineral. Geochem., 54, 115–149.

Ericson, D.B., Ewing, M., Wollin, G., 1964. Sediment cores from the Arctic and subarctic seas. Science, 144, 1183–1192.

Evans, D., Wade, B.S., Henehan, M., Erez, J., Müller, W., 2016. Revisiting carbonate chemistry controls on planktic foraminifera Mg/Ca: implications for sea surface temperature and hydrology shifts over the Paleocene–Eocene Thermal Maximum and Eocene–Oligocene transition: Clim. Past, 12, 819–835.

Eynaud, F., Cronin, T. M., Smith, S., Zaragozi, S., Mavel, J., Mary, Y., Mas, V., Pujol, C., 2009. Morphological variability of the planktonic foraminifer *Neogloboquadrina pachyderma* from ACEX cores : Implications for Late Pleistocene circulation in the Arctic Ocean. Micropaleontology, 55, 101–116.

Farmer, J.R., Cronin, T.M., de Vernal, A., Dwyer, G.S., Keigwin, L.D., Thunell, R.C., 2011.

Western Arctic Ocean temperature variability during the last 8000 years. Geophys. Res. Lett., 38, L24602, https://doi.org/10.1029/2011GL049714, 2011.

Farmer, J.R., Cronin, T.M., Dwyer, G.S., 2012. Ostracode Mg/Ca paleothermometry in the North Atlantic and Arctic oceans: Evaluation of a carbonate ion effect. Paleoceanography, 27, PA2212, doi:10.1029/2012PA002305.

Francis, J.A., Hunter, E., Key, J.R., Wang X., 2005. Clues to variability in Arctic minimum sea ice extent. Geophys. Res. Lett., 32, L21501.

Feely, R.A., Sabine, C.L., Lee, K., Millero, F.J., Lamb, M.F., Greeley, D., Bullister, J.L., Key, R.M., Peng, T., Kozyr, A., Ono, T., Wong, C.S., 2002. In situ calcium carbonate dissolution in the Pacific Ocean. Global Biogeochem. Cycles 16, 1–12. https://doi.org/10.1029/2002GB001866Green, K.E., 1960. Ecology of some Arctic foraminifera. Micropaleontology, 6, 57–78.

Fisher, D., Wake, C., Kreutz, K., Yalcin, K., Steig, E., Mayewski, P., Anderson, L., Zheng, J., Zdanowicz, C., Demuth, M., Waszkiewicz, M., Koerner, R.M., Sekerka, J., Osterberg, E., Abbott, M.B., Finney B.P., Burns, S.J., 2004. Stable Isotope Records From Mount Logan, Eclipse Ice Cores and Nearby Jellybean Lake. Water Cycle of the North Pacific Over 2000 Years and Over Five Vertical Kilometres: Sudden Shifts and Tropical Connections. Géographie Phys. Quat., 58, 337–352.

Fitzsimmons, J.N., John, S.G., Marsay, C.M., Hoffman, C.L., Nicholas, S.L., Toner, B.M., German, C.R., Sherrell, R.M., 2017. Iron persistence in a distal hydrothermal plume supported by dissolved–particulate exchange. Nature Geoscience, 10, 162–163, doi:10.1038/ngeo2908.

Grebmeier, J.M., 2011. Shifting Patterns of Life in the Pacific Arctic and Sub-Arctic Seas. Ann. Rev. Mar. Sci., 4, 63–78.

Grosswald, M.G., Hughes, T.J., 1999. The case for an ice shelf in the Pleistocene Arctic Ocean. Polar Geography, 23, 23–54.

Hald, M., Steinsund, P.I., 1996. Benthic foraminifera and carbonate dissolution in the surface sediments of the Barents and Kara seas. In: Surface-Sediment Composition and Sedimentary Processes in the Central Arctic Ocean and along the Eurasian Continental Margin. Stein, R., Ivanov, G.I., Levitan, M.A., Fahl, K. (eds.), d 285–307.

Hanslik, D., Jakobsson, M., Backman, J., Björck, S., Sellén, E., O'Regan, M., Fornaciari, E., Skog, G., 2010. Quaternary Arctic Ocean sea ice variations and radiocarbon reservoir age corrections. Quat. Sci. Rev., 29, 3430–3441.

Hanslik, D., 2011. Late Quaternary Biostratigraphy and Paleoceanography of the central Arctic Ocean. Doctoral thesis. Department of Geological Sciences, Stockholm University.

Harada N., 2016. Review: Potential catastrophic reduction of sea ice in the western Arctic Ocean: Its impact on biogeochemical cycles and marine ecosystems. Glob. Planet. Change, 136, 1–17.

Hartmann D. L., Tank, M. G. K., Rusticucci M., 2013. IPCC Fifth Assessment Report, Climate Change 2013: The Physical Science Basis.

Hastings, D.W., Russell, A.D., Emerson, S.R., 1998. Foraminiferal magnesium in *Globigerinoides sacculifer* as a paleotemperature proxy. Paleoceanography, 13, 161–169.

Healy-Williams, N., 1992. Stable isotope differences among morphotypes of *Neogloboquadrina pachyderma* (Ehrenberg): implications for high-latitude palaeoceanographic studies. Terra Nova, 4, 693–700.

Hebbeln, D., Wefer, G., 1997. Late Quaternary paleoceanography in the Fram Strait. Paleoceanography, 12, 65–78.

Henrich, R., Kassens, H., Vogelsang, E., Thiede, J., 1989. Sedimentary facies of glacial-interglacial cycles in the Norwegian Sea during the last 350 ka. Mar. Geol., 86, 283–319.

Herman, Y., 1964. Temperate Water Planktonic Foraminifera in Quaternary Sediments of Arctic Ocean. Nature, 201, 386–387.

Herman Y., 1974. The Arctic Seas, Climatology, Oceanography, Geology and Biology. (ed. Y. Herman). Springer Verlag, New York. 888 pp.

Huber, R., Meggers, H., Baumann, K., Henrich, R., 2000. Recent and Pleistocene carbonate dissolution in sediments of the Norwegian – Greenland Sea. Mar. Geol., 165, 123–136.

Hughes, T.J., Denton, G.H., Grosswald, M.G., 1977. Was there a late-Würm Arctic ice sheet? Nature, 266, 596–602.

Husum, K., Hald, M., 2013. Arctic planktic foraminiferal assemblages: Implications for subsurface temperature reconstructions. Marine Micropaleontology, 99, 8–17.

Imbrie, J., Hays, J.D., Martinson, D.G., McIntyre, A., Mix, A.C.,. Morley, J.J, Pisias, N.G., Prell, W.L., Shackleton, N.J., 1984. The orbital theory of Pleistocene climate: Support from a revised chronology, of the marine $\delta^{18}O$ record, in Milankovitch and Climate, Part 1, edited by A. Berger, Springer, New York, 269–305.

Izuka, S., 1988. Relationship of magnesium and other minor elements in tests of Cassidulina subglobosa and *C. oriangulata* to physical oceanic properties. J. Foraminiferal Res., 18, 151–157.

Jakobsson, M., Lovlie, R., Al-Hanbali, H., Arnold, E., Backman, J., Mörth, M., 2000. Manganese and colour cycles in Arctic Ocean sediments constrain Pleistocene chronology. Geology, 28, 23–26.

Jakobsson, M., Løvlie, R., Arnold, E. M., Backman, J., Polyak, L., Knutsen, J. O. and Musatov, E., 2001. Pleistocene stratigraphy and paleoenvironmental variation from Lomonosov Ridge sediments, central Arctic Ocean. Glob. Planet. Change, 31, 1–22.

Jakobsson, M., 2002. Hypsometry and volume of the Arctic Ocean and its constituent seas, Geochem. Geophys. Geosyst., 3, 5, 10.1029/2001GC000302.

Jakobsson, M., Mayer, L. A., Coakley, B., Dowdeswell, J. A., Forbes, S., Fridman, B., Hodnesdal H., Noormets, R., Pedersen, R., Rebesco, M., Schenke, H.-W., Zarayskaya Y., Accettella, D., Armstrong, A., Anderson, R. M., Bienhoff, P., Camerlenghi, A., Church, I., Edwards, M., Gardner, J.V., Hall, J.K., Hell, B., Hestvik, O. B., Kristoffersen, Y., Marcussen, C., Mohammad, R., Mosher, D., Nghiem, S.V., Pedrosa, M. T., Travaglini, P.G., Weatherall, P., 2012. The International Bathymetric Chart of the Arctic Ocean (IBCAO) Version 3.0, Geophysical Research Letters 39, L12609, doi: 10.1029/2012GL052219.

Jakobsson, M., Nilsson, J., Anderson, L.G., Backman, J., Bjork, G., Cronin, T.M., Kirchner, N., Koshurnikov, A., Mayer, L., Noormets, R., O'Regan, M., Stranne, C., Ananiev, R., Barrientos Macho, N., Cherniykh, D., Coxall, H., Eriksson, B., Floden, T., Gemery, L., Gustafsson, O., Jerram, K., Johansson, C., Khortov, A., Mohammad, R., and Semiletov, I., 2016. Evidence for an ice shelf covering the central Arctic Ocean during the penultimate glaciation, Nature Communications, 7, 10365.

Jakobsson, M., Pearce, C., Cronin, T.M., Backman, J., Anderson, L.G., Barrientos, N., Björk, G., Coxall, H., De Boer, A., Mayer, L.A., Mörth, C.M., Nilsson, J., Rattray, J.E., Stranne, C., Semiletov, I., O'Regan, M., 2017. Post-glacial flooding of the Bering Land

Bridge dated to 11 cal ka BP based on new geophysical and sediment records. Clim. Past, 13, 991–1005.

Jones E.P. and Anderson L.G., 1986. On the origin of the chemical properties of the Arctic Ocean halocline. Journal of Geophysical Research, 91, C9, 10759–10767.

Jones, E.P., Rudels, B. and Anderson, L.G., 1995. Deep waters of the Arctic Ocean: origins and circulation. Deep-Sea Research,-Part I, 42, 737-760.

Jones, E.P., Anderson, L.G., Swift, J.H., 1998. Distribution of Atlantic and Pacific waters in the upper Arctic Ocean: implications for circulation. Geophys. Res. Lett., 25, 765–768.

Jørgensen, B.B., 1982. Mineralization of organic matter in the sea bed - The role of sulphate reduction. Nature, 296, 643-645.

Jørgensen B.B., Kasten S., 2006. Sulphur cycling and methane oxidation, in Marine Geochemistry (eds Schulz H. D., Zabel M., editors. (Heidelberg: Springer), 271–309.

Jutterström, S., Anderson, L.G., 2005. The saturation of calcite and aragonite in the Arctic Ocean. Mar. Chem., 94, 101–110.

Katz, A., 1973. The interaction of magnesium with calcite during crystal growth at 25–90°C and one atmosphere. Geochimica et Cosmochimica Acta, 37, 1563–1586.

Kinney, P., Arhelger, M.E, Burrell, D.C., 1970. Chemical characteristics of water masses in the Amerasian basin of the Arctic Ocean. J. Geophys. Res., 75, 4097–4104.

Klunder, M.B., Laan, P., Middag, R., de Baar H.J.W., Bakker, K., 2012. Dissolved iron in the Arctic Ocean: Important role of hydrothermal sources, shelf input and scavenging removal. Journal of Geophysical Research: Oceans, 117, C04014.

Kristjánsdóttir, G.B., Lea, D.W., Jennings, A.E., Pak, D.K., Belanger, C., 2007. New spatial Mg/Ca-temperature calibrations for three Arctic, benthic foraminifera and reconstruction of north Iceland shelf temperature for the past 4000 years. Geochemistry Geophys. Geosystems, 8, QO3P21.

Lafuente, B., Downs, R. T., Yang, H., Stone N., 2015. The power of databases: the RRUFF project. In: Highlights in Mineralogical Crystallography (eds. T. Armbruster and R. M. Danisi). W. De Gruyter, Berlin, Germany, 1–30.

Lagoe, M.B., 1977. Recent benthic foraminifera from the Central Arctic Ocean. J. Foraminiferal Res., 7, 106–129.

Lea, D., 1999. Trace elements in foraminiferal calcite. In Modern Foraminifera (ed. B. K. S. Gupta). Kluwer Academic Publishers.

Lear, C.H., Elderfield, H., Wilson, P.A., 2000. Cenozoic Deep-Sea Temperatures and Global Ice Volumes from Mg/Ca in Benthic Foraminiferal Calcite. Science, 287, 269–272.

Lear, C.H., Rosenthal, Y., Slowey N., 2002. Benthic foraminiferal Mg/Ca-paleothermometry: a revised core top calibration, Geochimica et Cosmochimica Acta, 66, 3375–3387.

Leduc, T.B., 2007. Sila dialogues on climate change: Inuit wisdom for a cross-cultural interdisciplinarity. Climate Change, 85, 237–250.

LeGrande, A.N., and G.A. Schmidt, 2006. Global gridded data set of the oxygen isotopic composition in seawater. Geophys. Res. Lett., 33, L12604, doi:10.1029/2006GL026011.

Libby, W.F., 1952. Radiocarbon dating, University of Chicago Press.

Lisiecki, L.E., Raymo, M.E., 2005. A Pliocene-Pleistocene stack of 57 globally distributed benthic $\delta^{18}O$ records. Paleoceanography, 20, PA1003, doi:10.1029/2004PA001071.

Locarnini, R.A., Mishonov, A.V., Antonov, J.I., Boyer, T.P., Garcia, H.E., Baranova, O.K.,

Zweng, M.M, Paver, C.R., Reagan, J.R., Johnson, D.R., Hamilton, M., Seidov, D., 2013. World Ocean Atlas 2013, Volume 1: Temperature. S. Levitus, Ed., A. Mishonov Technical Ed.; NOAA Atlas NESDIS 73, 40 pp.

Loeblich, A.R., Tappan, H. 1953. Studies of Arctic Foraminifera. Smithsonian Miscellaneous Collections, 121, 1–150.

Löwemark, L., Jakobsson, M., Mörth, M., Backman J., 2008. Arctic Ocean manganese contents and sediment colour cycles, Polar Research, 27, 105–113, doi: 10.1111/j.1751-8369.2008.00055.x.

Löwemark, L., März, C., O'Regan, M., Gyllencreutz, R., 2014. Arctic Ocean Mn-stratigraphy: Genesis, synthesis and inter-basin correlation. Quat. Sci. Rev., 92, 97–111.

Manno, C., Pavlov, A.K., 2014. Living planktonic foraminifera in the Fram Strait (Arctic): Absence of diel vertical migration during the midnight sun. Hydrobiologia, 721, 285–295.

Martin, P.A., Lea, D.W., Rosenthal, Y., Shackleton, N.J., Sarnthein, M., Papenfuss T., 2002. Quaternary deep sea temperature histories derived from benthic foraminiferal Mg/Ca. Earth Planet. Sci. Lett., 198, 193–209.

Matthiessen, J., Knies, J., Nowaczyk, N.R., Stein, R., 2001. Late Quaternary dinoflagellate cyst stratigraphy at the Eurasian continental margin, Arctic Ocean: Indications for Atlantic water inflow in the past 150,000 years. Global and Planetary Change, 31, 65–86.

McLaughlin, F.A., Carmack, E.C., Macdonald, R.W., Bishop, J.K.B., 1996. Physical and geochemical properties across the Atlantic/Pacific water mass boundary in the southern Canada Basin. J. Geophys Res., 101, 1183–1197.

McLaughlin, F.A., Carmack, E.C., Macdonald, R.W., Weaver, A.J., Smith, J., 2002. The Canada Basin 1989–1995: upstream events and far-field effects of the Barents Sea branch. J. Geophys. Res., 107. doi:1029/2001JC000904.

März, C., Stratmann, A., Matthiessen, J., Meinhardt, A. K., Eckert, S., Schnetger, B., Vogt, C., Stein, R., Brumsack, H. J., 2011. Manganese-rich brown layers in Arctic Ocean sediments: Composition, formation mechanisms and diagenetic overprint. Geochim. Cosmochim. Acta, 75, 7668–7687.

März, C., Poulton, S. W., Brumsack, H., Wagner, T., 2012. Climate-controlled variability of iron deposition in the Central Arctic Ocean (southern Mendeleev Ridge) over the last 130,000 years. Chem. Geol., 330-331, 116–126.

Meinhardt, A.K., März, C., Schuth, S., Lettmann, K.A., Schnetger, B., Wolff, J. O., Brumsack, H.J., 2016. Diagenetic regimes in Arctic Ocean sediments: Implications for sediment geochemistry and core correlation: Geochimica et Cosmochimica Acta, 188, 125–146.

Melling, H., Moore, R., 1995. Modification of halocline source waters during freezing on the Beauford Sea shelf: Evidence from oxygen isotopes and dissolved nutrients. Cont. Shelf Res., 15, 89–113.

Mercer, J.H., 1970. A former ice sheet in the Arctic Ocean? Palaeogeogr. Palaeoclimatol. Palaeoecol., 8, 19–27.

Middag, R., de Baar, H. J. W., Laan, P. and Klunder, M. B., 2011. Fluvial and hydrothermal input of manganese into the Arctic Ocean. Geochim. Cosmochim. Acta, 75, 2393–2408.

Mix, A.C., Ruddiman, W.F., 1984. Oxygen-isotope analyses and Pleistocene ice volumes. Quaternary Res., 21, 1–20.

Morison, J.H., Steele, M., Anderson, R., 1998. Hydrography of the upper Arctic Ocean measured form the nuclear submarine USS Pargo. Deep Sea Res I, 45, 15–38.

Nansen, F. 1902. Oceanography of the North Polar Basin. The Norwegian North polar expedition 1893–1896. Sci. Res., 9, 427 pp.

Nørgaard-Pedersen, N., Spielhagen, R.F., Erlenkeuser, H., Grootes, P.M., Heinemeier, J., Knies, J., 2003. Arctic Ocean during the Last Glacial Maximum: Atlantic and polar domains of surface watermass distribution and ice cover. Paleoceanography, 18, 1063.

Nürnberg, D., Bijma, J., Hemleben C., 1996. Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures. Geochim. Cosmochim. Acta, 60, 803–814.

O'Regan, M., King, J., Backman, J., Jakobsson, M., Pa, H., Moran, K., Heil, C., Sakamoto, T., Cronin, T.M., Jordan R.W., 2008. Constraints on the Pleistocene chronology of sediments from the Lomonosov Ridge. Paleoceanography, 23, PA1S19.

Ortiz, J.D., Nof, D., Polyak, L., St-Onge, G., Lisé-Pronovost, A., Naidu, S., Darby, D., Brachfeld, S., 2012. The late Quaternary flow through the Bering Strait has been forced by the Southern Ocean winds. J. Phys. Oceanogr., 42, 2014–2029.

Osterman, L.E., Poore, R.Z., and Foley, K.M., 1999. Distribution of benthic foraminifers (>125 μm) in the surface sediments of the Arctic Ocean: United States Geological Survey Bulletin, 2164, 1–28.

Pearce, C., Varhelyi, A., Wastegård, S., Muschitiello, F., Barrientos, N., O'Regan, M., Cronin T.M., Gemery, L., Semiletov, I., Backman, J., Jakobsson, M., 2017. The 3.6ka Aniakchak tephra in the Arctic Ocean: A constraint on the Holocene radiocarbon reservoir age in the Chukchi Sea. Clim. Past 13, 303–316.

Pearson, P., Ditchfield, P., Singano, J., 2001. Warm tropical sea surface temperatures in the Late Cretaceous and Eocene epochs. Nature, 413, 401–407.

Pearson, P.N., Burgess, C.E., 2008. Foraminifer shell preservation and diagenesis: comparison of high latitude Eocene sites. Geological Society, London, Special Publications, 303, 59–72.

Pearson, P.N., 2012. Oxygen Isotopes in Foraminifera: Overview and Historical Review. Paleontol. Soc. Pap., 18, 1–38.

Peterson, B. J., Holmes, R.M., McClelland, J.W., Vorosmarty, C.J., Lammers, R.B., Shiklomanov, A.I., Shiklomanov, I.A., Rahmstorf, S., 2009. Increasing river discharge to the Arctic Ocean. Science, 298, 2171–2173.

Pfirman, S.,W. Haxby, H. Eicken, M. Jeffries, Bauch, D., 2004. Drifting Arctic sea ice archives changes in ocean surface conditions, Geophys. Res. Lett., 31, L19401, doi:10.1029/2004GL020666.

Polyakov, I., et al., 2007. Observational program tracks Arctic Ocean transition to a warmer state, Eos Trans. AGU, 88, 398–399, doi:10.1029/2007EO400002.

Polyakov, I.V., Pnyushkov, A.V., and Timokhov, L.A., 2012. Warming of the Intermediate Atlantic Water of the Arctic Ocean in the 2000s. J. Climate, 25, 8362–8370.

Polyakov, I.V., Pnyushkov, A.V., Alkire, M., Ashik, I.M., Baumann, T., Carmack, E.C., Goszczko, I., Guthrie, J., Ivanov, V.V., Kanzow, T., Krishfield, R., Kwok, R., Sundfjord, A., Morison, J., Rember, R., Yulin, A., 2017. Greater role for Atlantic inflows on sea-ice loss in the Eurasian Basin of the Arctic Ocean. Science, 356, 285–289, doi:10.1126/science.aai8204.

Quadfasel, D., Sy, A., Wells, D., Tunik A., 1991. Warming in the Arctic. Nature, 350, 385.

Quillmann, U., Marchitto, T., Jennings, A., Andrews, J.T., Friestad, B.F., 2012. Cooling and freshening at 8.2 ka on the NW Iceland Shelf recorded in paired δ18O and Mg/Ca measurements of the benthic foraminifer *Cibicides lobatulus*. Quaternary Research, 78, 528–539.

Ravelo, A.C., Hillaire-Marcel, C., 2007. The use of oxygen and carbon isotopes of foraminifera in paleoceanography. In: Hillaire-Marcel, C., de Vernal, A. (Eds.), Proxies in Late Cenozoic Paleoceanography. Elsevier, 735–764.

Reagan, M.T., Moridis, G.J., 2007. Oceanic gas hydrate instability and dissociation under climate change scenarios, Geophys. Res. Lett., 34, L22709, doi:10.1029/2007GL031671.

Roberts, S. and Murray, J.W., 1995. Characterization of cement mineralogy in agglutinated foraminifera (Protista) by Raman spectroscopy. Journal of the Geological Society 1995, 152, 7–9, doi: 10.1144/gsjgs.152.1.0007.

Rohling, E.J., 2010. Continuous 520,000-year sea-level record in 250-year timesteps, on an independent radiometrically calibrated chronology. Geochim Cosmochim Acta 74, 12, A878–A878.

Romanovskii, N.N, Hubberten, H.W., Gavrilov, A.V., Eliseeva, A.A., Tipenko, G.S., 2005. Offshore permafrost and gas hydrate stability zone on the shelf of East Siberian Seas. Geo Mar. Lett., 25, 167–182, doi:10.1007/s00367-004-0198-6.

Rosenthal, Y., Boyle, E.A., Slowey, N., 1997. Temperature control on the incorporation of magnesium, strontium, fluorine, and cadmium into benthic foraminiferal shells from Little Bahama Bank: Prospects for thermocline paleoceanography. Geochimica et Cosmochimica Acta, 61, 3633–3643.

Rosenthal, Y., Field, M.P., Sherrell, R.M., 1999. Precise determination of element/calcium ratios in calcareous samples using sector field inductively coupled plasma mass spectrometry. Anal. Chem., 71, 3248–3253.

Rossel, P.E., Bienhold, C., Boetius, A., and Dittmar, T., 2016. Dissolved organic matter in pore water of Arctic Ocean sediments: Environmental influence on molecular composition. Org. Geochem., 97, 41–52.

Rothwell, R.G., Hoogakker, B., Thomson, J., Croudace, I.W., Frenz, M., 2006. Turbidite emplacement on the southern Balearic Abyssal Plain (western Mediterranean Sea) during Marine Isotope Stages 1–3: an application of ITRAX XRF scanning of sediment cores to lithostratigraphic analysis. In: New Techniques in Sediment Core Analysis. Rothwell, R.G. (ed). Geol. Soc. Spec. Publ., 267, 79–98, doi:10.1144/ GSL.SP.2006.267.01.06.

Rudels, B., Larsson, A.-M., Sehlstedt, P.I., 1991. Stratification and water mass formation in the Arctic Ocean: some implications for the nutrient distribution. Polar Research, 10, 19–32, doi: 10.3402/polar.v10i1.6724.

Rudels, B., Jones, E.P., Anderson, L.G., Kattner G., 1994. On the Intermediate Depth Waters of the Arctic Ocean. Polar Oceans and Their Role is Shaping the Global Environment, Geophysical Monograph, 85, 33–46.

Rudels, B., Anderson, L.G., Jones, E.P., 1996. Formation and evolution of the surface mixed layer and halocline of the Arctic Ocean. Journal of Geophysical Research: Oceans, 101, 8807–8821.

Rudels, B., Jones, E.P., Schauer, U., Eriksson, P., 2004. Atlantic sources of the Arctic Ocean surface and halocline waters. Polar Res., 23, 181–208.

Rudels, B., Anderson, L., Eriksson, P. , Fahrbach, E., Jakobsson, M., Jones, E. P., Melling,

H., Prinsenberg, S., Schauer, U., Yao, T., 2012. Observations in the Ocean, in Lemke, P., ed., Arctic Climate Change: The ACSYS Decade and Beyond, Volume 43, Springer, 117–198.

Savin, S.M., Douglas, R.G., 1973. Stable isotope and magnesium geochemistry of recent planktonic foraminifera from the South Pacific. Bulletin of the Geological Society of America, 84, 2327.

Shackleton, N.J., Opdyke, N.D., 1973.Oxygen isotope and Palaeomagnetic stratigraphy of equatorial pacific core V28-238: oxygen isotope temperatures and ice volumes on a 105 year and 106 year scale. Quat. Res., 3, 39–55.

Shaffer, G., Bendtsen, J., 1994. Role of the Being Strait in controlling North Atlantic Ocean circulation and climate. Nature 367, 354–357. http://dx.doi.org/10.1038/ 367354a0.

Schlitzer, R. Ocean Data View, available at: http://odv.awi.de, last access: December 2017.

Schlosser, P., Kromer, B., Östlund, H.G., Ekwurzel, B., Bönisch, G., Loosli, H.H., and Purtschert, R., 1994. On the 14C and 39Ar distribution in the central Arctic Ocean: implications for deep water formation. Radiocarbon, 36, 327–343.

Schulz, H.D., Zabel, M., 2006. Marine Geochemistry. 2nd ed., 574 pp., Springer, New York.

Scott, D. B., Mudie, P. J., Baki, V., MacKinnon, K. E., Cole, F. E., 1989. Biostratigraphy and late Cenozoic paleoceanography of the Arctic Ocean: foraminiferal, lithostratigraphic, and isotopic evidence. Geol. Soc. Am. Bull. 101, 260–277.

Semiletov, I., Makshtas, O.A., Akasofu, S.I., and Andreas, E.L., 2004. Atmospheric CO_2 balance: the role of Arctic sea ice. Geophys. Res. Lett., 31, 1–4.

Serreze, M.C., Walsh, J.E., Chapin III, F.S., Osterkamp, T., Dyurgerov, M., Romanovsky, V., Oechel, W.C., Morison, J., Zhang T., Barry, R.B., 2000. Observational evidence of recent change in the northern high-latitude environment, Climatic Change, 46, 159–207.

Serreze, M.C., Barrett, A.P., Slater, A.G., Woodgate, R.A., Aagaard, K., Lammers, R.B., Steele, M., Moritz, R., Meredith, M., Lee, C.M., 2006. The large-scale freshwater cycle of the Arctic, J. Geophys. Res., 111, C11010.

Serreze, M.C., Barrett, A.P., Stroeve, J.C., Kindig, D.N., Holland, M.M., 2009. The emergence of surface-based Arctic amplification. The Cryosphere, 3, 11-19.

Serreze, M. and Barry, R., 2011. Processes and impacts of Arctic Amplification. Global and Planetary Change, 77, 85–96.

Sexton, P.F., Wilson, P.A., 2009. Preservation of benthic foraminifera and reliability of deep-sea temperature records: Importance of sedimentation rates, lithology, and the need to examine test wall structure. Paleoceanography, 24, 1–14.

Shimada, K., Kamoshida, T., Itoh, M., Nishino, S., Carmack, E., McLaughlin, F., Zimmermann, S., Proshutinsky, A., 2006. Pacific Ocean inflow: Influence on catastrophic reduction of sea ice cover in the Arctic Ocean. Geophys. Res. Lett., 33, 3–6.

Skirbekk, K., Hald, M., Marchitto, T.M., Junttila, J., Klitgaard Kristensen D., Aagaard Sørensen, S., 2016. Benthic foraminiferal growth seasons implied from Mg/Ca-temperature correlations for three Arctic species. Geochem. Geophys. Geosyst., 17, 1–21.

Spielhagen, R.F., Baumann, K.-H., Erlenkeuser, H., Novaczyk, N.R., Nørgaard-Pedersen, N., Vogt, C., Wesel, D., 2004. Arctic Ocean deep-sea record of northern Eurasian ice sheet history. Quaternary Science Reviews, 23, 1455–1483.

Spielhagen, R.F., Werner, K., Sorensen, S.A., et al., 2011. Enhanced modern heat transfer to the Arctic by warm Atlantic water. Science, 311, 450–453.

Steele, M., Boyd, T., 1998. Retreat of the cold halocline layer in the Arctic Ocean. J. Geophys. Res., 103, 10419–10435.

Steele, M., Ermold, W. & Zhang, J. Arctic Ocean surface warming trends over the past 100 years, 2008. Geophys. Res. Lett., 35, 244–255.

Stein, R., 2008. Arctic Ocean Sediments: Processes, Proxies, and Paleoenvironment. Developments in Marine Geology 2 (ed. Stein R.), 1–592. ISBN: 978-0-444-52018-0.

Stein, R., Macdonald, R.W. (eds.), 2004. The organic carbon cycle in the Arctic Ocean. Springer, Berlin.

Steinsund, P.I., Hald, M., 1994. Recent calcium carbonate dissolution in the Barents Sea: Paleoceanographic applications. Mar. Geol., 117, 303–316.

Stranne, C., O'Regan, M., Dickens, G.R., Crill, P., Miller, C., Preto, P., and Jakobsson, M., 2016. Dynamic simulations of potential methane release from East Siberian continental slope sediments, Geochem. Geophy. Geosy., 17, 872–886.

Thatcher, K.E., Westbrook, G.K., Sarkar, S., Minshull, T.A., 2013. Methane release from warming-induced hydrate dissociation in the West Svalbard continental margin: Timing, rates, and geological controls. J. Geophys. Res. Solid Earth, 118, 22–38, doi:10.1029/2012JB009605.

Urey, H., 1947. The thermodynamics of isotopic substances. J. Chem. Soc., 562–581.

Vilks, G., 1989. Ecology of recent foraminifera on the Canadian Continental shelf of the Arctic Ocean. In: Y. Herman (Ed.), The Arctic Seas, climatology, oceanography, geology and biology. New York: Van Nostrand Reinhold, 497–569

Walton, W.R., 1952. Techniques for Recognition of Living Foraminifera. Contrib. Cushman Found. Foraminifer. Res. 3, 56–60.

Weber, J.R., 1983. Maps of the Arctic Basin Sea Floor: A History of Bathymetry and its Interpretation. Arctic, 36, 2, 121–142.

Wigglesworth-Clarke, F., Wheeler, W. C., 1917. The inorganic constituents of marine invertebrates. Washington. 56 p.

Wilson, J.T., 1963. Hypothesis of Earth's behavior. Nature, 198, 925–929.

Wilson, P.A., Opdyke, B.N., 1996. Equatorial sea-surface temperatures for the Maastrichtian revealed through remarkable preservation of metastable carbonate. Geology, 24, 555–558.

Wollenburg, J., 1992. Zur Taxonomie von rezenten benthischen Foraminiferen aus dem Nansen-Becken, Arktischer Ozean = Taxonomic notes on recent benthic Foraminifera from Nansen Basin, Arctic Ocean, 112, 137 pp.

Wollenburg, J.E., Kuhnt, W., Mackensen, A., 2001. Changes in Arctic Ocean paleoproductivity and hydrography during the last 145 kyr: The benthic foraminiferal record. Paleoceanography, 16, 65–77.

Wollenburg, J.E., Mackensen, A., 1998. Living benthic foraminifers from the central Arctic Ocean: faunal composition, standing stock and diversity. Marine Micropaleontology 34, 153–185.

Woodgate, R.A., Aagaard, K., 2005. Revising the Bering Strait freshwater flux into the Arctic Ocean. Geophys. Res. Lett., 32, L02602.

Woodgate, R.A., Aagaard K., Weingartner, T.J., 2006. Interannual changes in the Bering Strait fluxes of volume, heat and freshwater between 1991 and 2004. Geophys. Res. Lett., 33, 2–6.

Woodgate, R.A., Weingartner, T.J., Lindsay, R., 2012. Observed increases in Bering Strait oceanic uxes from the Paci c to the Arctic from 2001 to 2011 and their impacts on the Arctic Ocean water column. Geophysical Research Letters, 39, L24603.

Wycech, J., Kelly, D. C., and Marcott, S. A. (2016) Effects of seafloor diagenesis on planktic foraminiferal radiocarbon ages. Geology, 44, 551–554.

Yamamoto-Kawai, M., Tanaka, N., 2005. Freshwater and brine behaviors in the Arctic Ocean deduced from historical data of d18O and alkalinity (1929 – 2002 A.D.). J. Geophys. Res., 110, 1–16.

Yu, J., Elderfield, H., 2007. Benthic foraminiferal B/Ca ratios reflect deep water carbonate saturation state. Earth Planet. Sci. Lett., 258, 73–86.