Tracing marine hypoxic conditions during warm periods using a microanalytical approach

Ni, Sha

2020

LUND UNIVERSITY

PO Box 117
221 00 Lund
+46 46-222 00 00

Tracing marine hypoxic conditions during warm periods using a microanalytical approach

SHA NI
ENVIRONMENTAL SCIENCE | CEC | FACULTY OF SCIENCE | LUND UNIVERSITY

Printed by Media-Tryck, Lund 2020 NORDIC SWAN ECOLABEL 3041 0903

LUND UNIVERSITY

Lund University
Faculty of Science
Centre for Environmental and Climate Research (CEC)
Department of Geology

ISBN 978-91-7895-698-2

Tracing marine hypoxic conditions during warm periods using a microanalytical approach

Tracing marine hypoxic conditions during warm periods using a microanalytical approach

Sha Ni

DOCTORAL DISSERTATION

by due permission of the Faculty of Science, Lund University, Sweden.
To be defended at Pangea, Geocentrum II, Sölvegatan 12, Lund.
Thursday 10 December 2020, 09:00

Faculty opponent
Helen Coxall
Stockholm University

Organization	Document name
LUND UNIVERSITY Centre for Environmental and Climate Research (CEC) Department of Geology	**Doctoral dissertation**
	Date of issue **2020-12-10**
Author: Sha Ni	Sponsoring organization

Title and subtitle

Tracing marine hypoxic conditions during warm periods using a microanalytical approach

Abstract

Deoxygenation, i.e. loss of oxygen from the oceans, often considerably influences the aquatic organisms and the whole ecosystem and changes biogeochemical cycles. It results in increasing bottom areas of hypoxia (<2 mg/l dissolved oxygen), which has been primarily attributed to global warming and increased eutrophication. It is vital to study the present-day anthropogenically-induced environmental changes in coastal settings such as hypoxia and their outcomes. The Baltic Sea is highly sensitive to hypoxia, which has occurred during several warm periods in the past. The studies of comparable hypoxic events during the warm periods in the past can help us better understand the cause, severity, and potential outcomes of environmental changes in the present day.

In this thesis, I reconstructed the past environmental conditions, i.e. water temperature, salinity, and oxygen concentrations from eight sites in the Baltic Sea using a multi-method approach including synchrotron X-ray spectroscopy and plasma analytical methods. I used trace elements and stable isotopes analyses on benthic foraminifera from two warm periods in the past, the Eemian (130 – 115 thousand years before present AD 1950, ka BP) and the Holocene (11.5 ka BP to present) to study how the extent and severity of hypoxia and other environmental factors have varied in the Baltic Sea over time.

During the Eemian period, the bottom water in the southern and western Baltic Sea show larger seasonal variations. There was a rapid salinity increase in the early Eemian due to a wider and deeper passage from the North Sea to the Baltic Sea. The temperature differences between cold and warm seasons were increasing in the first half of the Eemian period. During the mid- and late-Eemian, the bottom water became more stagnant with lower oxygen content. The trends agree with the simulation results, indicating influences from North Atlantic Oscillation and precipitation-evaporation balance. During the Holocene period, the bottom water salinity increased dramatically ~7,700–7,500 years ago and decreased ~4,100–2,500 years ago, coinciding with the variations in bottom water oxygen content and temperature. The reconstructions were based on species-specific calibration and the geochemistry of 'clean' foraminiferal calcite without contamination from authigenic minerals. The diagenetic coatings on foraminifera formed under extremely low oxygen conditions in the deepest basin in the Baltic Sea were highly enriched in multiple elements, which could significantly alter the foraminiferal geochemistry. The study can be used as guidance for interpreting foraminiferal trace element analyses from extreme environmental conditions. The calibration study from the low oxygen basin, the Santa Barbara Basin, shows the importance of species-specific calibrations under a restricted oxygen environment and improved the application of oxygen proxy using trace elements, i.e. manganese incorporation in foraminiferal calcite.

Key words

environmental changes; hypoxia; foraminifera; Eemian; Holocene; trace elements; stable isotopes; LA-ICP-MS; synchrotron-based µXRF

Classification system and/or index terms (if any)		
Supplementary bibliographical information		**Language: English**
ISSN and key title		**ISBN:** 978-91-7895-698-2
Recipient's notes	**Number of pages: 205**	Price
	Security classification	

Signature Ni Sha Date 2020-10-30

Tracing marine hypoxic conditions during warm periods using a microanalytical approach

Sha Ni

LUND
UNIVERSITY

Cover photos by Sha Ni

Faculty of Science
Centre for Environmental and Climate Research
Department of Geology

ISBN 978-91-7895-698-2 (print)
ISBN 978-91-7895-699-9 (pdf)

Printed in Sweden by Media-Tryck, Lund University
Lund 2020

Media-Tryck is a Nordic Swan Ecolabel certified provider of printed material. Read more about our environmental work at www.mediatryck.lu.se

Printed matter 3041 0903

MADE IN SWEDEN

知止而后有定，定而后能静，

静而后能安，安而后能虑，虑而后能得。

《大学》

The point where to rest being known, the object of pursuit is then determined; and, that being determined, a calm unperturbedness may be attained to. To that calmness there will succeed a tranquil repose. In that repose there may be careful deliberation, and that deliberation will be followed by the attainment of the desired end.

THE GREAT LEARNING (*Daxue*) in Confucianism

translated by James Legge

Contents

List of papers

This thesis consists of four papers listed below, which have been attached to the thesis. Paper I and IV are manuscripts. Paper II and III have been published in journals and are reprinted under the permission of the respective publishers.

Paper I

Ni, S., Quintana Krupinski, N. B., Chonewicz, J., Lu, Z., Zhang, Q., Groeneveld, J., Knudsen, K. L., Seidenkrantz, M. S., Filipsson, H. L. **Proxy-based reconstructions and model simulations of seasonal Eemian climate in the Baltic Sea**. Manuscript.

Paper II

Ni, S., Quintana Krupinski, N.B., Groeneveld, J., Fanget, A.S., Böttcher, M.E., Liu, B., Lipka, M., Knudsen, K.L., Naeraa, T., Seidenkrantz, M.S. and Filipsson, H.L., 2020. **Holocene hydrographic variations from the Baltic-North Sea transitional area (IODP site M0059)**. *Paleoceanography and Paleoclimatology*, 35(2), p.e2019PA003722.

Paper III

Ni, S., Quintana Krupinski, N.B., Groeneveld, J., Persson, P., Somogyi, A., Brinkmann, I., Knudsen, K.L., Seidenkrantz, M.S. and Filipsson, H.L., 2020. **Early diagenesis of foraminiferal calcite under anoxic conditions: A case study from the Landsort Deep, Baltic Sea (IODP Site M0063)**. *Chemical Geology*, p.119871.

Paper IV

Brinkmann I., Ni S., Schweizer M., Oldham V., Quintana Krupinski N.B., Medjoubi K., Somogyi A., Whitehouse M., Hansel C., Barras C., Bernhard J.M., Filipsson H. L. **Foraminiferal Mn/Ca as a bottom-water hypoxia-proxy: an assessment of *Nonionella stella* in the Santa Barbara Basin, USA**. Manuscript.

Author contributions

	Paper I	Paper II	Paper III	Paper IV
Concept and study design	S. Ni H.L. Filipsson N.B. Quintana Krupinski	S. Ni H.L. Filipsson N.B. Quintana Krupinski	S. Ni H.L. Filipsson	I. Brinkmann S. Ni H.L. Filipsson
Fieldwork	K.L. Knudsen, M.S. Seidenkrantz	N.B. Quintana Krupinski J. Groeneveld	N.B. Quintana Krupinski J. Groeneveld	S. Ni J.M. Bernhard H.L. Filipsson V. Oldham N.B. Quintana Krupinski C. Hansel
LA-ICP-MS		S. Ni N.B. Quintana Krupinski T. Naeraa	S. Ni	
ICP-OES	S. Ni J. Groeneveld J. Chonewicz			
µXRF			S. Ni I. Brinkmann H.L. Filipsson A. Somogyi	I. Brinkmann S. Ni H.L. Filipsson A. Somogyi C. Barras
Raman			S. Ni P. Persson	
SEM and/or EDS	S. Ni J. Chonewicz	S. Ni	S. Ni	I. Brinkmann S. Ni
Statistics	S. Ni	S. Ni	S. Ni	I. Brinkmann S. Ni
Stable Isotopes	J. Groeneveld S. Ni	M.E. Böttcher M. Lipka		
Modeling	Z. Lu Q. Zhang	B. Liu		
Foraminifera faunal analysis/rDNA		A.S. Fanget K. L. Knudsen, M.S. Seidenkrantz		M. Schweizer
Data interpretation and discussion	S. Ni H.L. Filipsson J. Chonewicz N.B. Quintana Krupinski K. L. Knudsen, M.S. Seidenkrantz	S. Ni N.B. Quintana Krupinski H.L. Filipsson J. Groeneveld K. L. Knudsen, M.S. Seidenkrantz M.E. Böttcher B. Liu	S. Ni H.L. Filipsson N.B. Quintana Krupinski K. L. Knudsen, M.S. Seidenkrantz A. Somogyi	I. Brinkmann S. Ni H.L. Filipsson J.M. Bernhard V. Oldham C. Barras A. Somogyi K. Medjoubi M. Schweizer M.Whitehouse
writing	S. Ni	S. Ni	S. Ni	I. Brinkmann
Comments on manuscript	all co-authors	all co-authors	all co-authors	all co-authors

Acknowledgments

The PhD position was funded by the Centre for Environmental and Climate Research (CEC), the Department of Geology, and the VR-funded Linnaeus centre of excellence “Lund University Centre for studies of Carbon Cycle and Climate Interactions (LUCCI)”, all at Lund University. I am grateful for additional financial support provided by Crafoord Foundation, Kungliga Fysiografiska Sällskapet i Lund and the Faculty of Science, Lund University.

I wish to thank IODP and ESSAC for funding and organizing Expedition 347, the crew and Exp. 347 scientific party for their work during the cruise and the following subsampling. I would also like to thank the crew of R/V Robert Gordon Sproul, for two unforgettable sampling cruises in the Santa Barbara Basin, USA. The synchrotron-based experiments were supported by the project CALIPSOplus from the EU Framework Programme for Research and Innovation HORIZON 2020.

I am so grateful to have been accompanied by so many wonderful people through this PhD journey.

First, I want to thank warmly my main supervisor Helena Filipsson, for having given me this great opportunity to do my PhD in Lund and guiding me to the field of Paleoceanography and the world of foraminifera. Thank you for being always encouraging and helpful during this four-year journey, and thank you for caring and supporting me going through those tough days. You were always providing me constructive and fast feedback and suggestions and helped me learn a lot.

My co-supervisor, Nadine, you were always patiently answering my questions and guiding me to all kinds of practical work, thank you for always offering good advice and insights, contributing your knowledge and giving a different perspective. Thank you for the wonderful time and also with Kai.

I also want to thank my co-supervisor, Per, for the good opportunity of doing micro XRF work and giving me constructive insights and support with Raman Spectroscopy.

My examiner, Charlotta Turner, I am very appreciative of the encouraging and supportive words and advice you have given over the years.

My sincere thanks go to my co-authors, Helena Filipsson, Nadine Quintana Krupinski, Inda Brinkmann, Jeroen Groeneveld, Marit-Solveig Seidenkrantz, Karen Luise Knudsen, Michael Böttcher, Julia Chonewicz, Zhengyao Lu, Qiong Zhang, Anne-Sophie Fanget, Bo Liu, Marko Lipka, Tomas Naeraa, Per Persson, Andrea Somogyi, Joan Bernhard, Magali Schweizer, Christine Barras, Colleen Hansel, Martin Whitehouse, Veronique Oldham, Kadda Medjoubi, for sharing your knowledge, expertise and inspiring ideas. Thank you Sylvain, Leif, Jesper, Carl and Chiara for discussing and helping me with mineralogy and model questions. Thank you Dirk for the amazing microCT work and the trip to Japan. The work would not have been possible without contributions from you all.

I am very grateful to the entire Department of Geology and CEC, thank you all fellow and former colleagues for all the good times. I am so lucky to have you in the same group, always providing help and support – Laurie, Inda, Nadine, Karl, Petra, Julia, Ezgi and Wenxin. Thank you Zhouling and Bingjie for being wonderful roommates in the first two years, the nice parties and the moments we had together. Thank you who welcomed me so warmly in Lund when I first started and for all the activities – Minjie, Guigui, Billy, Anton, Petra, Ashley… Thank you Roro, Tintin and Carla for sharing and listening to me and comforting me during the tough time, and Ingrid, Cindy, Megan, Andreas, Sofia, Franzi, Maria… it was always nice spending time with you guys after work and at parties. Thank you, Gert, Per-Erik, Åsa, and members of the Kansli for helping me with all different kinds of issues, also the rest of you, thank you for being so nice the whole time, and making the department such a pleasant workplace.

Special thanks to all the people from CEC, Pål-Axel, Åsa-Katrin, Natascha, Ylva, Adrian, Tian, Maria, Julia, Micaela, Ivette, Cecilia, and all others for providing such a challenging interdisciplinary group and such a nice working environment, organizing many nice workshops, trips and PhD meetings, also for sharing your views from different perspectives.

Many thanks go to my friends Peng, Mousong, Zhendong, Zhengyao, Yi, Yanzi, Yixin, Weiming, Yuhao, Wenxin and all the others who brought my life lots of laughter and made it more colourful. Thank you so much Minjie, Haorui and Zhao taking care of my cat when I was away.

To all of you who made these past four years a wonderful journey of a lifetime!

Lastly, I would like to thank my family, for always supporting me, loving me through these years.

感谢我的爸爸妈妈对我的养育，关爱，理解和支持，感谢我的家人们，谢谢爷爷奶奶姥姥姥爷一直以来的无限爱护。感谢您们一直以来做我的坚强后盾，我爱你们！

Popular Science Summary

Deoxygenation is recognized with growing concern in coastal and open regions of the ocean and has been primarily attributed to global warming and enhanced nutrient input in the coastal region. The marine ecosystems are controlled by different environmental stressors, such as temperature, salinity, oxygen concentration and pH. It is important to study the present-day human-induced environmental changes such as warming, deoxygenation and acidification and their impact on the coastal habitats, nutrient biogeochemical processes, and fisheries, etc. The studies of ocean environmental conditions during comparable climate stages in the past can help us better understand the processes happening today and potential outcomes in the future. We applied a multi-microanalytical approach, using the chemistry of marine sediments and microfossils to reconstruct the water conditions.

Foraminifera are unicellular organisms with calcareous shells which are widely used for paleoclimate studies. Trace elements incorporated into foraminiferal calcite can be altered by different environmental conditions such as dissolved oxygen concentration. Therefore, the information recorded in foraminifera fossils in marine sediments can help us understand the past climate variations.

In this thesis, I studied low oxygen conditions in the Baltic Sea during two warm periods in the past, the Last Interglacial Eemian period (130-115 thousand years before present; ka BP) and the Holocene (8 ka BP-present). Trace element and stable isotopes geochemistry of foraminifera were used to reconstruct past marine conditions (e.g. temperature, salinity and oxygenation). I analyzed the trace elemental concentration (Mg/Ca, Mn/Ca, Ba/Ca) in calcite shells of low-oxygen tolerant foraminifera species sampled from eight sites southwest Baltic Sea. In particular, I use Mn/Ca in calcite as a potential proxy for low oxygen conditions, as Mn is a redox-sensitive element, and its concentration in the bottom- and pore waters increases in hypoxic conditions. The results show an increasing seasonality during Eemian in the southern and western Baltic Sea and the oxygen content of bottom water became lower in the Straits area. During the Holocene period, in the Straits, the bottom water oxygen concentration and temperature varied with salinity, the conditions were relatively warmer, more saline and stagnant during 7.5 – 4.1 ka BP.

There are some challenges while using foraminifera geochemistry for reconstructions: diagenesis contamination on primary shells, and the demand of species-specific calibrations. We discovered different kinds of secondary minerals formed under extreme conditions attached to foraminiferal shells in the deepest basin in the Baltic Sea and their chemical components. We studied Mn concentration and distribution in shells of low-oxygen tolerant benthic foraminifera from modern Santa Barbara Basin, NE Pacific Ocean, using synchrotron micro-X-ray fluorescence mapping. The approach allows us to better understand

biomineralization processes in foraminifera and to study the correlation between Mn incorporation and environmental conditions, and further investigate the use of Mn/Ca in foraminiferal calcite as an indicator for low-oxygen conditions in past seawater.

Introduction

Ocean system variations, i.e. warming, acidification and deoxygenation, are global problems and potential risks to marine biodiversity, ecosystems, and human society. Dissolved oxygen (DO) is one of the environmental variables that has changed drastically in a short period of time. Deoxygenation, i.e. loss of DO from the oceans, is recognized with growing concern in coastal and open regions of the oceans. Low DO concentrations are known as hypoxic conditions, defined as <2 mg/l DO (Diaz & Rosenberg 2008). Below this level, the respiration of many benthic invertebrates appears to be affected (Rosenberg et al., 1991). Hypoxia often causes mortality of aquatic organisms and changes of species composition and variability. It also influences the whole ecosystem and changes biogeochemical cycles. There are over 40 systems in global oceans that experience hypoxic conditions with documented benthic community effects and recovery data since 1905, including the Baltic Sea, Black Sea, Gulf of Aden, Arabian Sea, Bay of Bengal, Philippine region, northwest Pacific margin, eastern Pacific, Norwegian region and southwest African region (Kamykowski & Zentara 1990; Diaz & Rosenberg 1995; Diaz 2001; Zhang et al., 2010).

Oxygen from the atmosphere and phytoplankton photosynthesis dissolves in the water and provides the respiration needs of all animals in the system (Diaz 2001). The DO in surface waters mixes down into the water column by diffusion and vertical mixing and further to bottom waters. Vertical mixing can be forced by the wind, tides or currents on large scale. Water masses at the surface of the ocean are transported to depth via downwelling when the surface ocean is cold or rarely, more saline, and form deep water masses. In contrast, upwelling happens when winds and surface currents draw the surface water away from the coast, and cooler, usually nutrient-rich and oxygen-depleted water moves upward to the ocean surface. In the deeper part of the water column and sediments, heterotrophic metabolisms (e.g. respiration), degradation of organic matter (OM), re-oxidation of reduced constituents (RC) such as sulfide, methane, etc., as well as chemoautotrophy (e.g. oxidation of ammonium) consume DO through a variety of pathways and, when the consumption exceeds DO supply, hypoxia can develop (Zhang et al., 2010)

The expansion of hypoxia has been primarily attributed to global warming and increased coastal eutrophication (i.e. the effect of nutrient enrichment) (Carstensen et al., 2014a). Climate change (i.e. increased temperature, sea level rise, enhanced hydrological cycles, and shifts in wind patterns) and increased anthropogenic nutrient loading result in more susceptible marine ecosystems (Conley et al., 2009a, 2011; Ning et al., 2018; Breitburg, 2002, Fig. 1). Bottom water hypoxia is developed through enhanced stratification and respiration rates, decreased oxygen solubility, increased metabolism and remineralization rates, and increased production of OM (Rabalais et al., 2009).

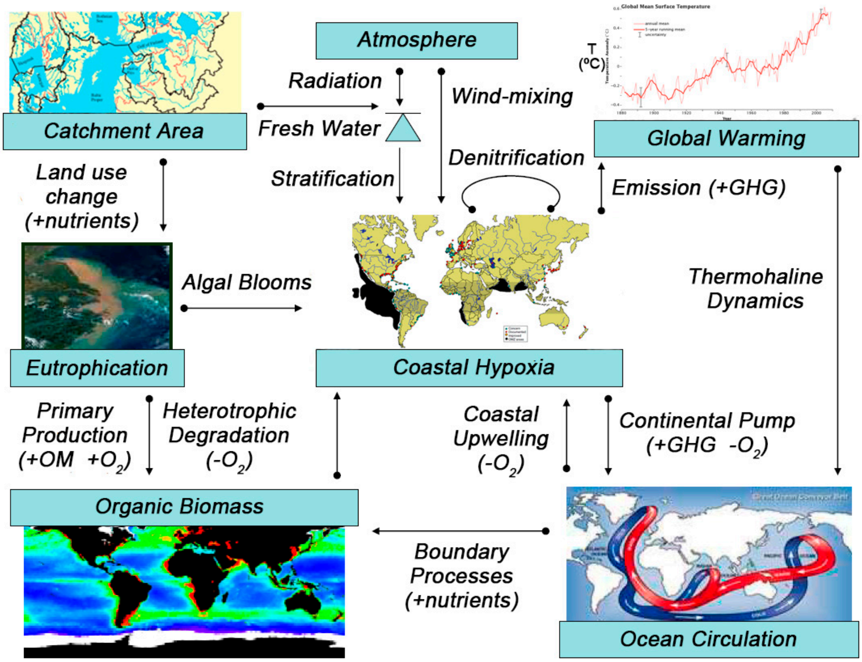

Figure 1. Schema of hypoxia in the global coastal ocean. Major mechanisms related to hypoxia are shown, including the availability of nutrients, marine primary productivity, the effect of climate change, and ocean circulation, etc. (modified after Zhang et al., 2010).

Global warming has the potential to strengthen vertical stratification and reduce the surface salinity due to enhanced precipitation rate and river input. Subsequently, it may result in less dissolved O_2 in bottom waters due to decreased solubility and less mixing and diffusion of O_2 from the upper to lower part of the water column. In addition, the increasing temperature may also influence the rates of biological processes such as photosynthesis and respiration (Rabalais et al., 2009).

Both stratification and decomposition of OM must occur for hypoxia to develop and persist (Diaz 2001). Stratification occurs as the bottom water becomes isolated from the exchange with oxygen-rich surface water due to density (temperature and/or salinity) differences of water bodies and decreased ventilation due to geographical isolation. Excess nutrients from land runoff and oceanic upwelling, hydrologic changes and biological interactions (e.g. reduced grazing, population growth) can lead to increased coastal production of organic matter or eutrophication (Nixon, 1995; Rabalais et al., 2009; Meier et al., 2018). Eutrophication may result in increasing the rate of production and biomass of the phytoplankton community (e.g. algal blooms) (Fig. 1). When increased primary production exceeds the available oxygen in a system, the balance of the system will be interrupted. Subsequently, it will result in more organic matter burial on the sea floor and oxygen depletion due to its decomposition.

Seasonal hypoxia and periodic hypoxia are the most common forms of low dissolved oxygen events recorded around the globe (Diaz & Rosenberg, 1995; Diaz & Breitburg, 2009). Seasonal hypoxia normally occurs during summer or early autumn while periodic hypoxia occurs several to many times per year. The frequency and duration of hypoxic events normally depend on the type of systems, nutrient loads and organic accumulation rate, which vary over time. Once hypoxia is developed in a system, it can quickly become an annual event (Diaz & Breitburg, 2009) and then lead to an increase in further hypoxia (Conley et al., 2007). Moreover, persistent hypoxia may develop to anoxic events, meaning zero dissolved O_2 in the environment. Hypoxia is often associated with upwelling areas and oceanic oxygen minimum zones (OMZ), which are the largest low-oxygen areas on earth. Seasonal hypoxia often causes mortality of benthic organisms and changes species composition, which are important in the ecosystem.

The area of hypoxia in the Baltic Sea has expanded sixfold, from less than 10,000 km^2 before 1950 to more than 60,000 km^2 since 2000 (Carstensen et al., 2014a, Fig. 2). Since the 20th century, anthropogenic eutrophication has become widespread and of great concern for the countries along the Baltic coastal region due to a large amount of urban and agricultural nutrient input, which stimulates phytoplankton bloom (Wulff et al., 2007, Helcom, 2018). Widespread oxygen deficiency has severely reduced benthic communities in the Baltic Sea over the last decades (Laine, 2003) and produced benthic "ecological deserts" that annually cover over 30% of the Baltic seafloor (Karlson et al., 2002).

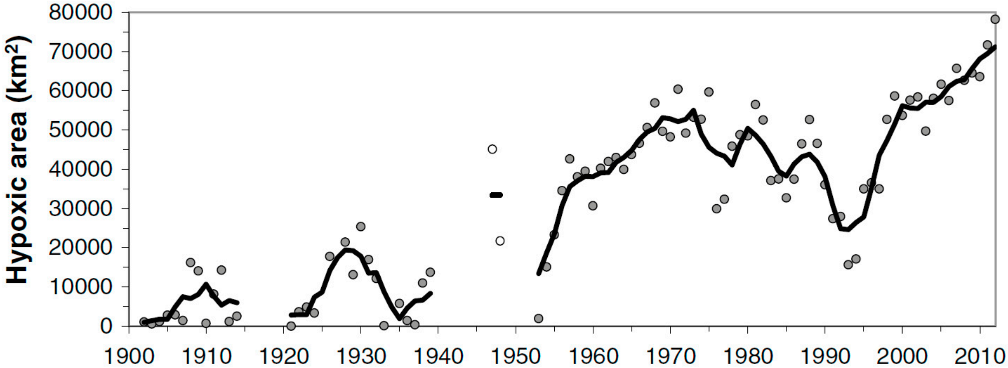

Figure 2. Long-term variations of the bottom area with hypoxic conditions in the Baltic Sea (modified after Carstensen et al., 2014b). The solid line indicates 5-year moving average.

Hypoxia has not only occurred in the present, but also occurred intermittently in the geological history, and often associated with large temperature and salinity variations. There is extensive literature on Baltic paleoenvironmental records of past oxygen-indicating environment facies (e.g. Tyson & Pearson 1991; Jillbert & Slomp, 2013; Kabel et a., 2012; van Helmond et al., 2017; van Wirdum et al., 2019). Sediment records in the Baltic Sea with laminated sediment deposition indicated hypoxia during three major periods in the Holocene, i.e. between ca. 8000-4000, 2000-800 thousand years before present (ka BP) and during the last ca. 100 years (Zillén et al., 2008). Preservation of laminated sediment indicates past bottom water hypoxia due to the absence of bioturbation of the benthic fauna. Hypoxia and eutrophication have become major scientific challenges, especially in the Baltic region. However, compared to the hypoxia in relatively deeper basins, long-term hypoxic events on the coastal area of the Baltic Sea need to be further investigated in order to obtain a solid understanding of past variability in hypoxia and the development of hypoxia at present and the future.

Scope of the thesis

In this thesis, the following questions are addressed:

How did the bottom water temperature, salinity and oxygen concentration vary during the Last Interglacial period (Eemian) in the Baltic Sea and how were the changes linked to larger scale climate variability?

How the extent and severity of hypoxia as well as associated ecosystem changes in the Baltic region have varied over the Holocene from 7.5 ka BP to the present?

What are the challenges of using trace elements in foraminiferal tests as proxies for reconstructing past environmental conditions?

How does the Mn/Ca in benthic foraminifera respond to the sedimentary redox conditions and low bottom water dissolved oxygen concentrations?

The history of the Baltic Sea

The present Baltic Sea

The Baltic Sea is one of the world’s largest semi-enclosed brackish water basins (412,560 km^2) and central to North European nations. With nine coastal countries, 8,000 km of coastline, more than 85 million people living in its drainage basin, it is one of the most actively and systematically investigated seas in the world (Leppäranta & Myrberg 2009). It has enormous economic, recreational and societal value. In the Baltic Sea, the brackish living conditions create unique habitats supporting specific biodiversity with well-adapted organisms (Helcom 2013; Pyhälä et al., 2014).

It has a mean depth of 52 m and the greatest depth of 459 m in Landsort Deep in the western Gotland Basin (Fig. 3). There is a considerable inflow of freshwater from land, but only a restricted inflow of oceanic water from the North Sea through the Skagerrak, Kattegat, and the narrow Danish Straits (Little Belt, Great Belt and the Sound, Fig. 3), resulting in a permanent halocline that separates an upper layer of brackish water from more saline bottom waters. The restricted opening of the Baltic Sea to the ocean and high freshwater inflow creates a gradient of decreasing salinity in a south-to-north direction (Villns & Norkko 2011, Fig. 3). The mean salinity of the Baltic Sea is about 7, whereas the salinity of the Danish Straits is about 25 (Leppäranta & Myrberg 2009).

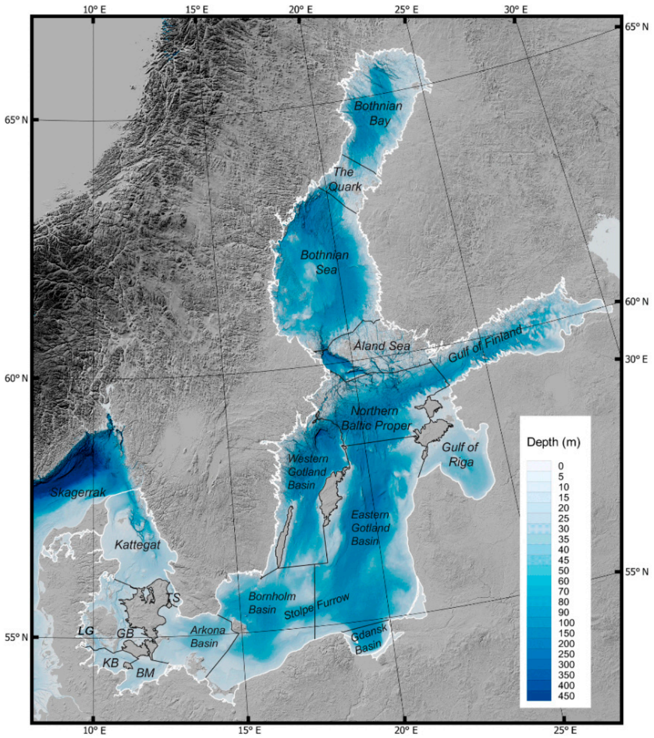

Figure 3. Bathymetric map of the Baltic Sea (modified after Jakobsson et al., 2019). Sub-basins are shown with black lines. BM: is Bay of Mecklenburg; LB: Little Belt; GB: Great Belt; TS: the Sound; KB: Kiel Basin.

The Holocene Baltic

Geological records show that the Baltic Sea is a dynamic ecosystem that has undergone many environmental changes over the last 16 thousand years (ka) (Björck, 2008; Andrén et al., 2011). Following the decay of Fennoscandian Ice Sheet and the subsequent land-uplift since ~ 21 thousand years before present (ka BP), the Baltic Sea went through five phases (both lacustrine and saline) until reaching the modern Baltic Sea stage: The Baltic Ice Lake (16-11.7 ka BP), Yoldia Sea (11.7-10.7 ka BP), Ancylus Lake (10.7-9.8 ka BP), Initial Littorina Sea (9.8-8.5 ka BP) and Littorina Sea (8.5 ka BP to ~3 ka), and finally present-day Baltic thereafter. By ca. 10 ka BP the entire Baltic basin was deglaciated and reached fully brackish marine conditions at ca. 8 ka BP. It then reached a Holocene maximum salinity between 6 and 4 ka BP (Gustafsson and Westman 2002; Andrén et al., 2011). Since 4 ka BP, the salinity of the Baltic Sea has decreased and the sea level dropped continually to the present level. The Littorina Sea is characterized by a very distinct increase in organic matter content and an increasing abundance of brackish marine phytoplankton. Enrichment of trace elements barium (Ba) and vanadium (V) observed in sediments during the Littorina Sea is linked to the cycling of organic carbon and implies that increased productivity in the basin caused the rise in organic carbon content (Sternbeck et al. 2000).

Due to its relative isolation from the global ocean and large freshwater influx, the Baltic Sea is salinity stratified and hence more naturally vulnerable to hypoxia. Hypoxia during the Holocene was strongly influenced by the postglacial history characterized by a complex interaction between changing sea levels, irregular land-uplift, and variable climate (Conley et al., 2009a). The modern hypoxic conditions in the Baltic Sea represent the third major hypoxic interval since the transition from the Ancylus freshwater phase to the Littorina marine phase; hypoxia also existed during the Holocene Thermal Maximum (HTM), ca. 9–4 ka and the Medieval Warm Period (MWP), ca. 1200–750 yr ago (Zillén et al., 2008). The marine inflow into the Baltic Sea at the beginning of HTM probably caused the release of phosphorus from sediments (Dijkstra et al., 2016; 2018), and result in enhancing the growth of algae and cyanobacteria. The salinity stratification together with increasing temperature and primary production initiated and strengthened hypoxia in the Baltic basin. The oxygen conditions improved significantly after ca. 4 ka BP due to salinity decreases and increasing wind stress in a more humid and cold climate (Gustafsson and Westman 2002; Conley et al., 2002). There is a strong correlation between stratification and North Atlantic Oscillation (NAO), which is one of the most important phenomena of climate fluctuations in North Atlantic and Europe. It impacts sea levels over the northwest European continental shelf and increases water temperatures and precipitation, and decreases salinities (e.g. Wakelin et al., 2003; Möllmann et al., 2005). It has a strong influence on the regime of the westerly winds across the North Atlantic resulting in changes in winter temperatures on the Atlantic and nutrient availability and river run-off (Lindahl et al. 1998). Besides

NAO-related stratification and warming, increased anthropogenic eutrophication cannot be neglected. The late Littorina Sea record of hypoxia in the Baltic Sea may thus be due to multiple stressors, where both climate and human impacts may have interacted (Andrén et al., 2011).

The Last Interglacial Baltic

The last major warm period (interglacial), the Eemian Stage (ca. 130–115 ka; marine isotope stage (MIS) 5e), was characterized at high northern latitudes by rapid changes in the polar front movement, ocean circulation, and oceanic heat fluxes. It was a period of generally higher global sea level (e.g. Chappell & Shackleton 1986; Shackleton et al., 2003; Kopp et al., 2009) and higher temperature (CLIMAP 1984; Sejrup & Larsen 1991; Funder et al., 2002) than at present. Eemian marine deposits of the Baltic Sea are well known from western Norway, Denmark, northern Germany, Poland, Finland, and along the northern margin of European Russia and Siberia (Ehlers et al., 2013). There was a rapid rise in relative sea level during the first 3 ka of the interglacial (Head et al., 2005), and reached sea level highstand in the first 6 ka (Fig. 4).

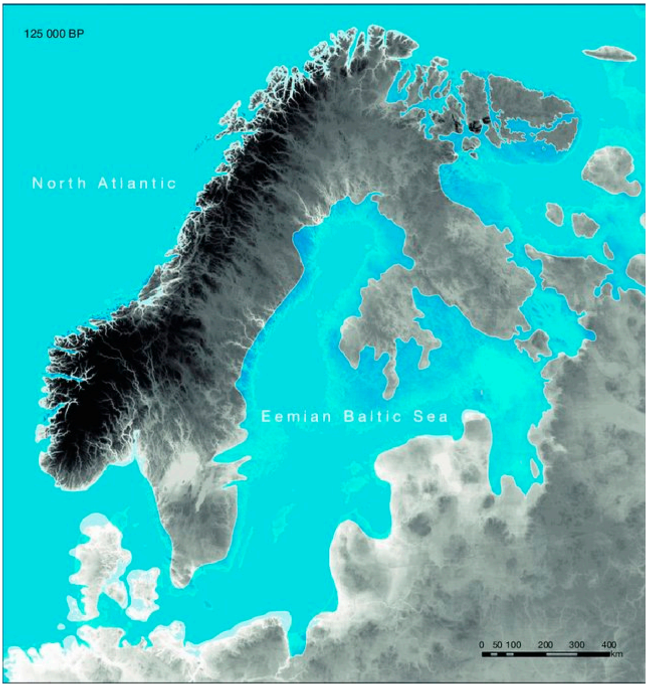

Figure 4. The extent of the Eemian Baltic Sea at 125 ka BP (Ehlers et al., 2013 and reference therein).

However, detailed Eemian marine records of northern Europe regarding bottom water conditions are very scarce, and the evolution of the Baltic Sea basin during the Eemian Stage remains unknown, particularly in relation to the higher global sea level and warming of that period. Prior work shows that hypoxia likely happened during the period of relatively high sea level, temperature and salinity conditions during the Eemian (Knudsen et al., 2011). This is shown by the Cyprina Clay, usually grey, often with whole but always broken mollusc shells, which has been found in southern Denmark, indicating that the southwestern Baltic region suffered from oxygen stress of varying degrees during the Eemian (Funder & Balic-Zunic 2006).

Travel back in time through foraminifera

The climate variation today can be recorded with the help of satellite sensors for surface ocean temperatures, CTD (i.e. Conductivity, Temperature, Depth) for water temperature, salinity and oxygen concentrations, etc. When studying past climates, we can't obtain data from the methods above, therefore, we need to look in the depths of the ocean. Marine organisms with skeletons such as foraminifera, ostracods, corals, and mollusc are buried in the sediment and can potentially record aspects of their living environment. Foraminifera are unicellular microorganisms that have a short life cycle, usually from a few weeks to a year. Benthic foraminifera are usually less than 1 mm in size, living on or in seafloor sediment. They first appeared in the Cambrian and over the Phanerozoic and invaded most marginal to fully marine environments (Goldstein 1999). Benthic foraminifera are abundant and diverse on the modern seafloor (Sen Gupta, 2007). A large proportion of the foraminiferal faunal has calcium carbonate ($CaCO_3$) shells (so-called tests) and during the test formation, besides calcium (Ca), other trace elements will also incorporate into the calcium carbonate test. Foraminifera preserved in the sediment are commonly used tools to reconstruct past oceanic conditions due to their good fossilization potential (Murray 2006). Both foraminiferal assemblage composition and/or $CaCO_3$ tests chemistry are applied in the studies of paleoenvironmental changes.

Foraminiferal species assemblages (i.e. the relative abundances of different species with different environmental preferences) are often used as indicators of salinity, oxygen level, pH and organic matter content according to foraminiferal species ecology (e.g. Sen Gupta & Machain-Castillo 1993, Filipsson & Nordberg 2004, Filipsson et al., 2011, McKay et al., 2016). Low-oxygen tolerant species may become dominant under oxygen depleted environments, because there will be less competition from species requiring high-oxygen. The assemblages accompanying sediment geochemistry and other microfossil records (e.g. diatoms, and ostracods) are usually used for improving the interpretation of past variability of temperature, salinity, ventilation and organic matter fluxes.

Trace element and stable isotopes analyses

The chemical compositions of calcifying organisms such as in the tests of foraminifera, coral skeletons and mollusc shells are widely used as tracers of environmental conditions (e.g. Hillaire-Marcel & de Vernal 2007). During calcification, dissolved trace elements in the seawater are incorporated into biogenic $CaCO_3$ (Fig. 5). The ratios of trace elements to Ca incorporated into foraminiferal calcite depend on the physical and chemical conditions (temperature, pH, salinity, oxygen concentration) in the calcification environment, and therefore can represent past marine environmental conditions. The incorporation of Mg^{2+} into $CaCO_3$ is mainly influenced by seawater temperature at the depth of foraminiferal calcification (e.g. Lea et al., 1999; Toyofuku et al., 2000; Reichart et al., 2003; Barker et al., 2005; Cleroux et al., 2008) and can be also related to other environmental parameters such as salinity, pH or saturation state ($[CO_3^{2-}]$) (e.g. McCorkle et al., 1995; Ries, 2011; Groeneveld et al., 2018). The Ba^{2+} concentration in seawater behaves similarly to nutrients in the ocean and its concentration in the seawater is highly variable depending on water depth and locality. Seawater Ba/Ca is inversely correlated to salinity in relatively enclosed coastal areas such as the Baltic Sea, as river water is high in Ba relative to the seawater (Groeneveld et al., 2018). Ba/Ca ratios in foraminiferal calcite in the coastal area have been proposed as a proxy of dissolved Ba/Ca ratios in seawater (e.g. Lea and Boyle, 1989, 1991; McCulloch et al., 2003; LaVigne et al., 2011; De Nooijer et al., 2017; Groeneveld et al., 2018) and therefore, may provide information on salinity, nutrients and alkalinity distributions in the ocean (Gillikin et al., 2006).

Mn cycling is largely internal to the sediment. Dissolved Mn^{2+} is released to the pore water at depth, resulting from solid oxide reduction in the sediment and diffused upward into the surface sediment and the bottom water (e.g. Lenz et al., 2015). Sediments under hypoxic conditions are often sources of Mn^{2+} to the water column. In deeper basins under hypoxic or anoxic conditions, diffusive Mn^{2+} fluxes from the sediment to the pore water and water column can be ascribed to either dissolution of Mn carbonates due to undersaturation or reduction of Mn oxides. Mn enrichment in geological deposits can be used as an indicator of oxic and anoxic depositional environments of bottom waters (Lenz et al., 2015). More Mn incorporation into benthic foraminiferal $CaCO_3$ is expected during calcification under hypoxic condition, which reflects the ambient environmental conditions, i.e. bottom water oxygenation and Mn redox chemistry (e.g. Munsel et al., 2010; Ní Fhlaithearta et al., 2010; Groeneveld & Filipsson, 2013; Koho et al., 2017).

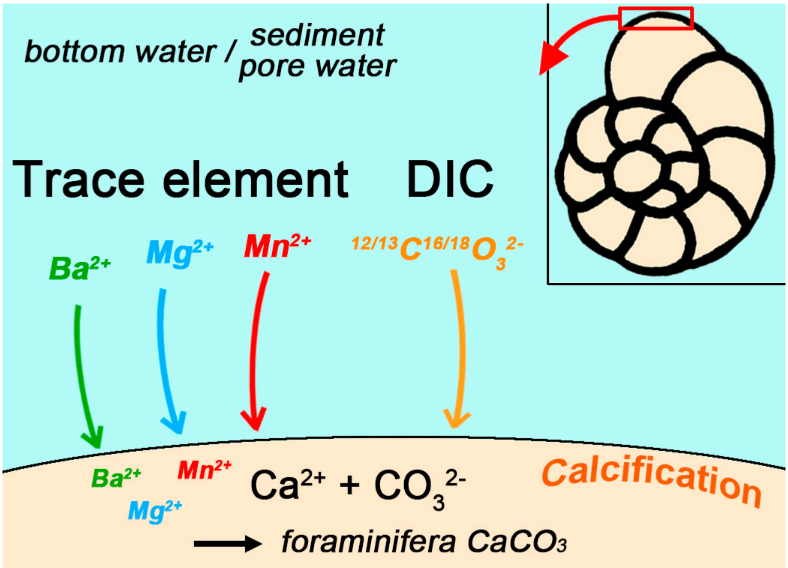

Figure 5. Trace elements and stable carbon and oxygen isotopes incorporation into the benthic foraminiferal calcite during calcification.

The oxygen isotopic composition of benthic foraminiferal calcite ($\delta^{18}O$) is a well-established and the most widely used paleoclimate proxy for seawater temperature and salinity reconstruction (see Pearson, 2012 for review). The $\delta^{18}O$ of foraminifera is affected by the $\delta^{18}O$ of the ambient seawater where the tests are precipitated from, the temperature during calcification, and to a minor extent, the carbonate ion concentration (Pearson, 2012). In the Baltic Sea, a relationship between seawater $\delta^{18}O$ and salinity can be constructed (e.g. Fröhlich et al., 1988; Harwood et al., 2008). This relationship can reveal salinity changes resulting from isotopic fractionation through evaporation and precipitation, freshwater runoff and sea ice processes (e.g. LeGrande & Schmidt, 2006; Rohling & Cooke, 1999). Stable carbon isotopes ($\delta^{13}C$) recorded in foraminifera can reflect the conditions of water mass exchanges and ventilation rates, productivity, and carbon cycling (e.g. Filipsson & Nordberg, 2010; Schmiedl & Mackensen, 2006). The foraminiferal $\delta^{13}C$ is controlled by the carbon isotopic composition of dissolved inorganic carbon (DIC) of seawater (CO_2, HCO_3^- and CO_3^{2-}), and vital effect during calcification (Filipsson et al., 2017). Together with Mn/Ca, $\delta^{13}C$ in benthic foraminifera can be used for evaluating past seawater circulation and ventilation conditions.

Study Site

The Baltic Sea

The study area in this thesis focuses on the transition zone between the North Sea and the Baltic Sea – the Skagerrak, Kattegat and the Danish Straits, the southern Baltic coastal area, and the deepest basin in the Baltic Sea – western Gotland Basin. High accumulation rate sediment cores were retrieved for the Holocene (0-8 ka BP) during IODP Exp. 347: Baltic Sea Paleoenvironment; these cores from two sites, including the Little Belt, Danish Straits (Site M0059) and the Landsort Deep, the deepest basin of the Baltic Sea (Site M0063), are the basis for the study of environmental conditions during Holocene Baltic warm periods (Fig. 6). For the study of the climate during the Last Interglacial period (130 – 115 ka BP), we have access to a unique sample set collected in the 1980s-1990s that covers the Eemian period along the Danish and Polish coastal area (Fig. 6).

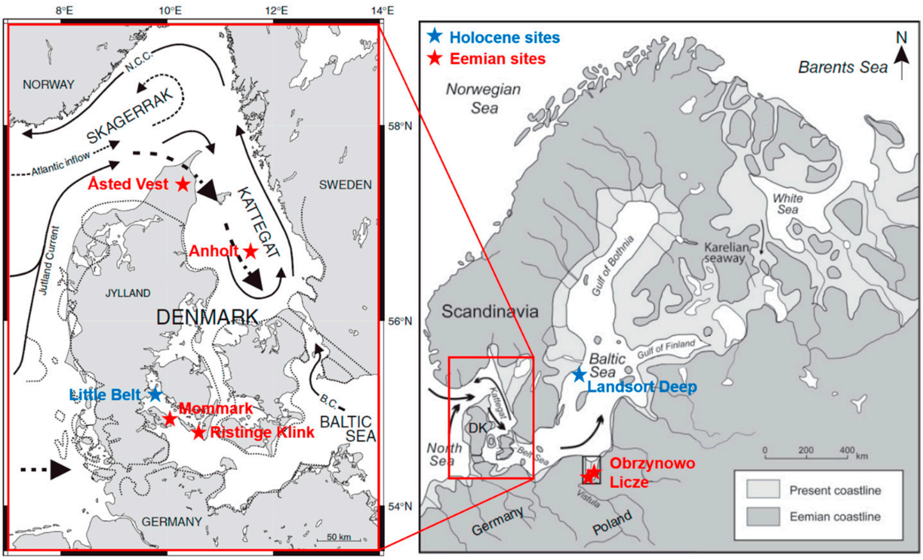

Figure 6. Location map with an indication of the maximum marine inundation in the Baltic Sea region during the early Eemian dashed line (left) and dark grey (right). Base maps were modified after Knudsen et al., 2011 and Funder et al. 2002. The left figure is the magnified map of the right figure (red box), showing the southwest part of the Baltic Sea. Blue stars show the study sites in the Little Belt and Landsort Deep and red stars show six Eemian study sites. The present-day marine circulation is shown by thin arrows in the left figure (black arrow: surface current; stippled arrow: deeper current). The suggested Eemian inflow directions of Atlantic and North Sea waters through the Kattegat–Belt seas and through northern Germany are indicated by thick stippled arrows. B.C.=Baltic Current; DK=Denmark; N.C.C.=Norwegian Coastal Current.

The Skagerrak-Kattegat front, and the Danish Straits area hydrographically represent the transitional area between the Baltic Proper and the North Sea, where the incoming saline water from the North Sea meets the low salinity outflow from the Baltic Sea (Lass & Matthäus, 2008; Erbs-Hansen et al., 2012). The transition zone plays an important role in the global ocean as it connects the largest brackish water system in Northern Europe to the Nordic Seas and the Atlantic Ocean. It shows a decreasing gradient of bottom water salinity from Skagerrak and Kattegat to the Straits and into the brackish Baltic Sea (Fig. 7). The salinity in the Straits shows larger seasonal variations compared to the other sites, which makes the area an ideal site for seasonal water exchange study. Seasonal hypoxia occurs in the bottom water during autumn in the Straits, while in the Landsort Deep the bottom water is permanently hypoxic and even under anoxic conditions ($[O_2] = 0$).

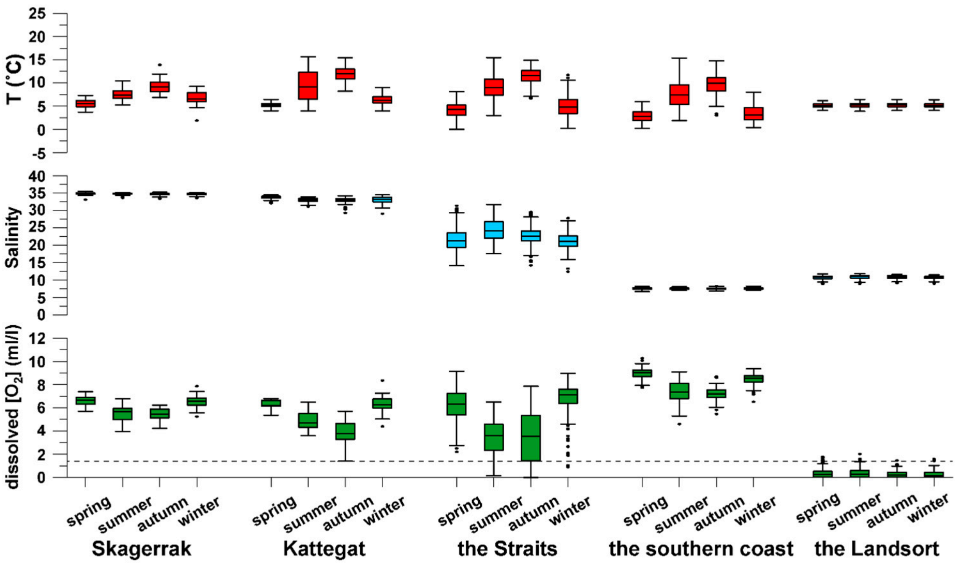

Figure 7. Seasonal bottom water variability of temperature, salinity and dissolved oxygen concentration in the Skagerrak (>50 m), Kattegat (>25 m), Straits (>25 m), southern coastal area (20 – 50 m) and the Landsort Deep (400 – 440 m). The hydrographic monitoring data were measured since 1951 for the Landsort Deep, and 1926 – 2020 for the rest locations by the Swedish Meteorological and Hydrological Institute (SMHI). The dashed line indicates the hypoxic level ($[O_2]$ <1.4 ml/L). The dots indicate outliers with 1.5 Interquartile Rule.

Santa Barbara Basin

Santa Barbara Basin (Fig. 8), a depression between the California mainland and the northern Channel Islands, is well known by its permanent low-oxygen conditions with restricted bottom water exchange, high surface primary productivity, and the water inflows from the eastern North Pacific oxygen minimum zone (e.g. Bernhard et al., 2000; Kienast et al., 2002; van Geen et al., 2003). The sill depth is about 475 m and the maximum depth is 627 m (Bernhard & Reimers, 1991). Oxygen conditions of the bottom water are severely depleted with a gradient ranging from ~0.02 to 0.5 ml/l (Bernhard et al., 1997). The bottom water (>560 m) shows a relatively constant temperature (6 – 7 ºC) and salinity (~34) (Komada et al., 2016).

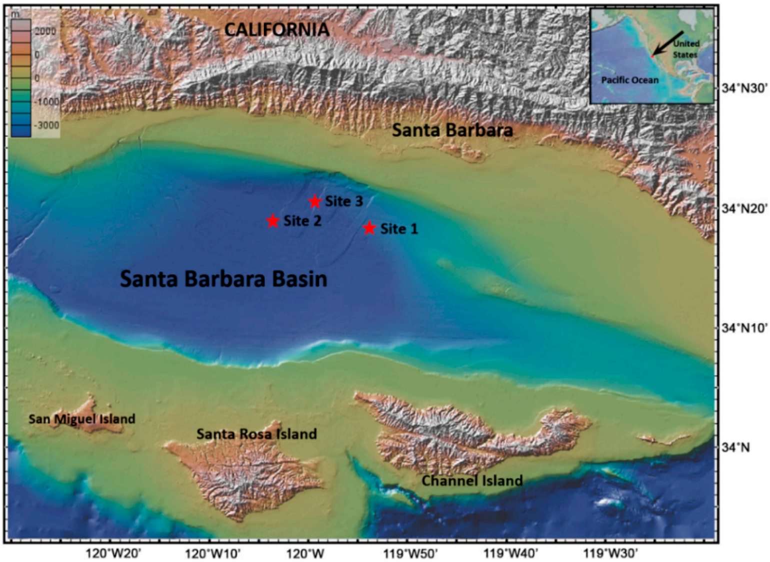

Figure 8. Map of the Santa Barbara Basin (base map from geomapapp). The position of study sites (Site 1 'Shallow Site'; Site 2 'Far North Site'; Site 3 '507 Site') are shown as red stars.

Dissolved oxygen concentrations of bottom water regulate foraminiferal species occurrence. On a relative scale, a vertical species progression indicative of the degree of low oxygen concentration can be established (Bernhard et al., 1997). We have sampled living benthic foraminifera from SBB and measure oxygen and pH profiles of pore water and the bottom water-sediment interface to evaluate how bottom water oxygen levels affect Mn incorporation and distribution in foraminiferal calcite.

Material and Methods

We performed geochemistry analyses on several specific species which were abundant in the sediment cores of the study sites (Fig. 6). We also used foraminiferal fauna analyses from previous studies in some of our study sites for helping track past environmental conditions as foraminiferal communities are specific for different types of environmental conditions (e.g. Seidenkrantz 1993; Kristensen & Knudsen 2006; Knudsen et al., 2009; 2011).

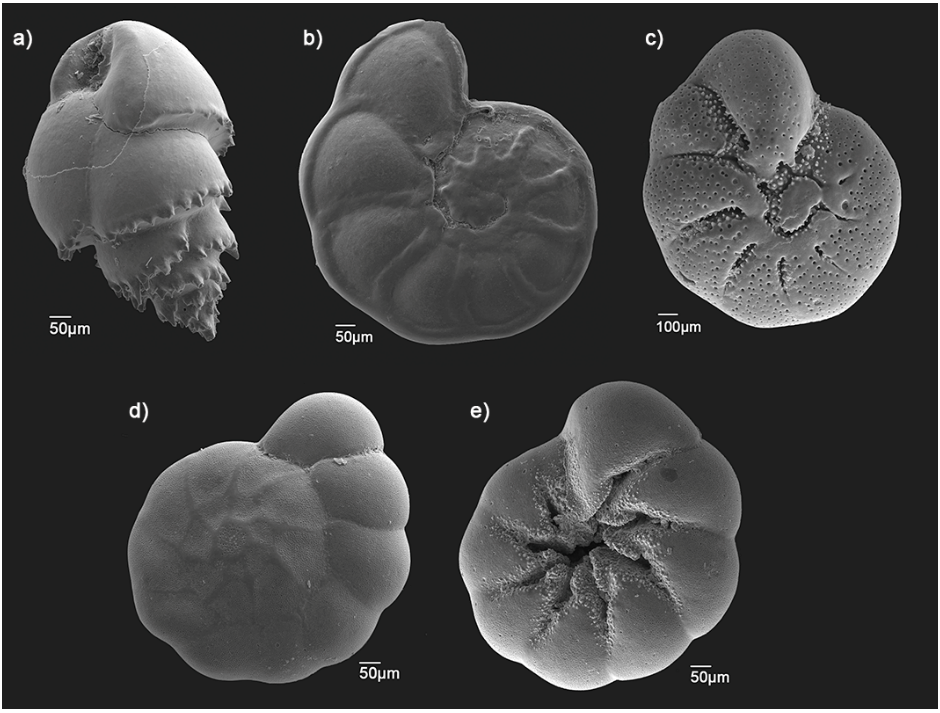

Figure 9. Benthic foraminifera from Baltic sites. a) *Bulimina marginata*, b) *Hyalinea balthica*, c) *Elphidium clavatum-selseyensis* complex d) & e) *Ammonia batava*

Elphidium and *Ammonia* are two of the most abundant benthic foraminiferal genera in world oceans. *Elphidium* species can be found from tropical to polar regions, living from the intertidal zones to the continental slope, while *Ammonia* species occur from the subtidal to the outer continental shelves (Murray 2006). They are important constituents of the benthic foraminiferal faunas from the European marginal seas (Schweizer et al., 2010). They are widely distributed in the North Sea and the Baltic Sea and preserved in sediments and commonly for coastal assemblage studies. *Elphidium clavatum* (Cushman, 1930) and *Elphidium selseyense* (Heron-

Allen and Earland, 1932) are common in marginal marine environments and have a wide salinity and oxygen tolerance, constituting a high proportion of the foraminiferal assemblages in the Baltic Sea under restricted oxygen concentration conditions (e.g. Feyling-Hanssen 1972; Kristensen & Knudsen 2006; Kotthoff et al., 2017). We assigned *E. clavatum* and *E. selseyensis* to an *E. clavatum-selseyensis* complex due to the difficulties of reliably distinguishing the gradational morphologies (Groeneveld et al., 2018). *E. clavatum-selseyensis* complex sampled from two Holocene sites (the Little Belt and Landsort deep, Fig. 6) covering the past ~ 7.5 ka and from four Eemian sites (Mommark, Ristinge, Licze and Obrzynowo, Fig. 6) covering the Last Interglacial period were used for geochemical analyses in the thesis. *Ammonia batava* (Hofker, 1951) from three Eemian sites (Ristinge, Licze and Obrzynowo) were used due to the relatively high abundance. *Bulimina marginata* (d'Orbigny, 1826) and *Hyalinea balthica* (Schroeter, 1783) (Fig. 9) were more abundant in the higher salinity region, the Skagerrak and Kattegat, that we used for trace element analyses for two Eemian sites.

We employed $\delta^{18}O_{foraminifera}$ - $\delta^{18}O_{water}$ -temperature calibration under the assumption that the isotopic composition of foraminifera is in equilibrium with that of the past seawater and species-specific Mg/Ca-temperature calibrations for bottom water temperature reconstructions. Different from fossil samples, to investigate the relationship between trace element incorporation into foraminiferal calcite and the environmental conditions (i.e. temperature, salinity, oxygen condition), we need calibrations for the geochemistry of living foraminifera against known/measurable environmental conditions, under which the foraminiferal calcite precipitated.

Living foraminifera sampled from the SBB were differentiated from dead ones by using CellTracker™ Green (CTG) staining method (Bernhard et al., 2006). The foraminifera displaying clear fluorescence under an epifluorescence-microscope were considered alive. These living foraminifera were picked out of core top sediment, identified and prepared for trace element analyses.

Trace element analyses

We measured trace element concentrations of foraminiferal calcite by using different state of the art, high resolution analytical techniques in this thesis, including Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), synchrotron-based micro-X-ray fluorescence (µXRF), and Energy Dispersive Spectroscopy (EDS).

The LA-ICP-MS elemental ratios analyses allow us to measure individual foraminiferal chambers and also distinguish between primary calcite and diagenetic coatings containing high trace metals on the surface of the foraminiferal tests. The LA-ICP-MS measurements are also preferred when the availability of foraminifera specimens is limited. We conducted LA-ICP-MS analyses at Lund University using a Bruker Aurora Elite (quadrupole) ICP-MS and a 193 nm Cetac Analyte G2 excimer laser installed with a two volume HelEx2 sample cell. We calculated the element/calcium ratios (Mg/Ca, Mn/Ca, and Ba/Ca) based on averaging measured concentrations during each ablation after selecting the non-contaminated part of the ablation profile (removing the outer and inner secondary layers) to obtain the element concentrations of the primary calcite.

We used solution-based ICP-OES for trace element analyses of a large number of specimens to reduce uncertainties due to inter-test variability, and it enables analyses of a large number of samples. Before the measurement, we gently crushed the foraminiferal tests and cleaned the fragments according to the standard cleaning protocol 'Cd cleaning' for foraminiferal Mg/Ca analyses to remove authigenic minerals on the surface of the tests (Barker et al., 2003, Groeneveld et al., 2018). The standard 'Cd cleaning' method (e.g. Barker et al., 2003) used for foraminiferal samples cleaning prior to analyses aims to remove clay particles, organic matter (by oxidative cleaning), Mn-Fe-oxide coatings and barite (by reductive cleaning) attached to the surface of the foraminifera tests. We performed ICP-OES analyses (Agilent Technologies, 700 Series with autosampler (ASX-520 Cetac) and micro-nebulizer) at the MARUM – Centre for Marine Environmental Sciences, University of Bremen, Germany.

We generated high resolution element concentration and distribution maps by using µXRF at the NANAOSCOPIUM scanning nanoprobe beamline of the 2.75-GeV high- brilliance third-generation synchrotron Soleil, Saint-Aubin, France. The beam size was 150 nm (Somogyi et al., 2015). We performed elemental mapping (Ca, Mn, Fe and Ba) at 11.2-keV incident X-ray energy with a spatial resolution down to 200 nm on epoxy resin (Epitek 301) mounted and polished foraminiferal specimens. The highly resolved, in-situ mapping capabilities of synchrotron based µ-XRF is an ideal tool to investigate differences in trace element partitioning that correspond to the fine-scale architecture of the test, to study the correlation between trace elements (e.g. Mn) and environmental conditions. Similarly, the EDS technique is mostly used for providing semi-quantitative chemical analyses as well. EDS can detect concentrations of major (>10 wt %) and minor (1 – 10 wt%) elements, and usually is equipped with Scanning Electron Microscope (SEM), producing secondary and backscattered electrons for imaging and morphological analyses. We used EDS to identify and quantify the secondary mineral composition of heavily coated foraminifera samples from the Landsort Deep.

Oxygen and Carbon stable isotopes analyses

We measured $\delta^{13}C$ and $\delta^{18}O$ on bulk samples (usually 10 – 20 pooled foraminiferal specimens from the Baltic sites) for information on paleoceanographic conditions, productivity, water temperature and salinity. We performed the measurements on a Thermo Fisher Scientific 253plus gas isotope ratio mass spectrometer (IRMS) with Kiel IV automated carbonate preparation device at MARUM, University of Bremen. The stable isotopic data are reported in per mil (‰) relative to the Vienna Peedee belemnite (V-PDB) using the NBS19 standard.

Summary of Papers

Paper I

Ni, S., Quintana Krupinski, N. B., Chonewicz, J., Lu, Z., Zhang, Q., Groeneveld, J., Knudsen, K. L., Seidenkrantz, M. S., Filipsson, H. L. Proxy-based reconstructions and model simulations of Eemian climate in the Baltic Sea. Manuscript.

In this study, we presented both proxy-based past environmental reconstruction during Eemian and model-based climate simulation at 127 ka BP. The proxy-based reconstructions, including bottom water temperature, salinity and oxygen condition, were based on benthic foraminiferal geochemistry data from six sites in the western and southern Baltic Sea. We applied a multiproxy (trace elements and stable isotopes) approach to allow more robust quantitative bottom water reconstructions in the Baltic during the Eemian. The reconstructed results show an initial bottom water salinity increase in the first 1 ka of Eemian in the Belt Sea and an increasing seasonality based on different benthic foraminiferal species. Reconstructed bottom water temperatures were ~2 - 3 °C higher in Skagerrak and Kattegat compared to the modern bottom water temperatures of late spring.

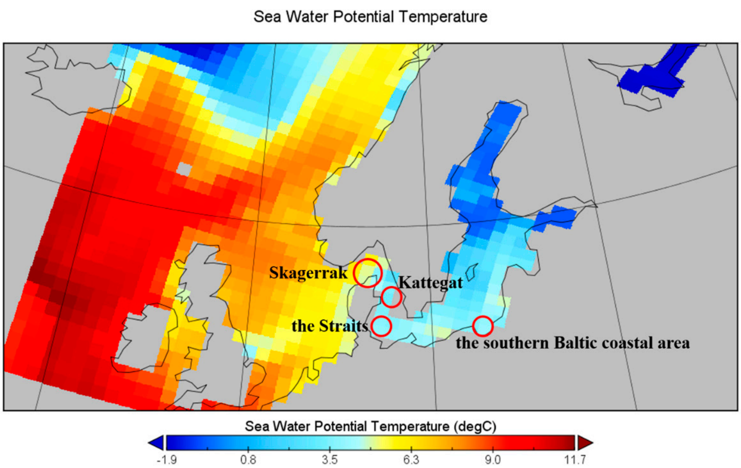

Figure 10. Example map of simulation of sea surface temperature (0 – 1 m) in the North Sea and Baltic Sea region. The red circles indicate the selected area.

The simulations focus on the four locations in the Baltic Sea (Skagerrak, Kattegat, the Straits, and the southern Baltic coastal area). We applied a high resolution general circulation model (Fig. 10) to examine the impact of radiative forcing on regional climate changes, and responses of oceanic parameters such as sea water temperature and salinity. We aimed to link the changes of regional climate (i.e. NAO, precipitation) to the seasonal variations of the Baltic water conditions. The reconstructed results were in general agreement with the simulated results of the bottom water salinities and temperatures.

Paper II

Ni, S., Quintana Krupinski, N.B., Groeneveld, J., Fanget, A.S., Böttcher, M.E., Liu, B., Lipka, M., Knudsen, K.L., Naeraa, T., Seidenkrantz, M.S. and Filipsson, H.L., 2020. Holocene hydrographic variations from the Baltic-North Sea transitional area (IODP site M0059). *Paleoceanography and Paleoclimatology*, 35(2), p.e2019PA003722.

Our goal of this study was to determine the extent and severity of hypoxia in the region over the Holocene from 7.5 ka BP to the present. To achieve this, we used high accumulation rate sediment cores retrieved during IODP Exp. 347, Site M0059, spanning the past 8 ka BP. We applied benthic foraminiferal geochemistry and faunal assemblage data to reconstruct past marine conditions (i.e. temperature, salinity, and oxygenation). We analyzed the trace elemental composition (Mg/Ca, Mn/Ca, and Ba/Ca) and oxygen and carbon isotopes of the low-oxygen tolerant foraminifera species *Elphidium selseyense* and *Elphidium clavatum* from the Little Belt, Danish Straits (Site M0059). For trace element analysis, we used laser ablation (LA-)ICP-MS to avoid the influence of surface diagenetic coatings on these foraminifera. Mg/Ca and Mn/Ca results showed a general decrease from 7.5 ka to present. These proxies suggest high temperature and low bottom oxygen conditions ~7 ka BP and between 4.5 and 3.5 ka BP. Ba/Ca and oxygen stable isotopes indicated an increasing bottom water salinity from 7.5 to 3 ka BP in the Little Belt. The changes in bottom water conditions in the Danish Straits over the Holocene were influenced by larger scale climate changes, including the North Atlantic Oscillation and eustatic sea level change.

Paper III

Ni, S., Quintana Krupinski, N.B., Groeneveld, J., Persson, P., Somogyi, A., Brinkmann, I., Knudsen, K.L., Seidenkrantz, M.S. and Filipsson, H.L., 2020. Early diagenesis of foraminiferal calcite under anoxic conditions: A case study from the Landsort Deep, Baltic Sea (IODP Site M0063). *Chemical Geology*, p.119871.

Authigenic minerals formed on and inside the foraminiferal shells can significantly interfere with the application of traditional foraminiferal elemental and isotopic proxies. It is important to characterize these authigenic minerals and understand their formation and the diagenetic processes to determine how post-depositional processes may alter foraminiferal geochemistry. This study details the element composition of authigenic minerals and formation sequence of diagenetic coatings on foraminiferal shells formed under extreme anoxic conditions in the deepest basin, the Landsort Deep in the Baltic Sea. It provides a case study of early diagenesis of foraminiferal calcite and serves as a valuable guide when interpreting foraminiferal trace element records from low oxygen environments. We have focused on determining the composition of the authigenic coatings and the environmental conditions under which they precipitated, and the links to the microbial organic matter degradation and dissolved metal sources. We applied various geochemical methods, including synchrotron-based μXRF, Raman, EDS, LA-ICP-MS and imaging methods (i.e. light microscopy, SEM, Fig. 11) to identify different degrees of diagenetic alteration, different types of authigenic minerals, and to ascertain their formation sequence, and also the sedimentary diagenesis processes. The results have the potential to be used for the interpretation of both primary and authigenic foraminiferal proxies in low oxygen settings both in this region and elsewhere in the world.

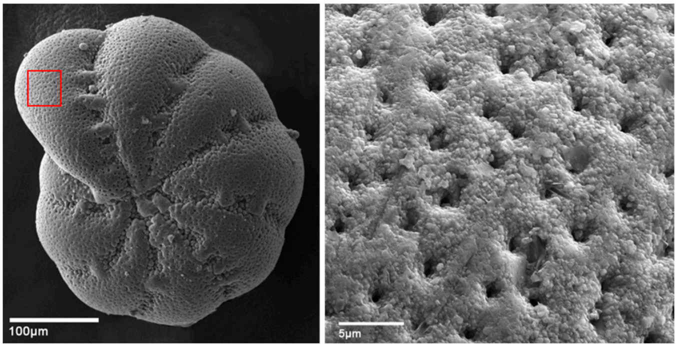

Figure 11. SEM image of an example of authigenic minerals coated foraminifera test. The right figure is the magnification of the left figure (red box), showing authigenic minerals (Mn carbonate) covering the outer surface.

Paper IV

Brinkmann I., Ni S., Schweizer M., Oldham V., Quintana Krupinski N.B., Medjoubi K., Somogyi A., Whitehouse M., Hansel C., Barras C., Bernhard J.M., Filipsson H. L. Foraminiferal Mn/Ca as bottom-water hypoxia-proxy: an assessment of Nonionella stella in the Santa Barbara Basin, USA. Manuscript.

This study aims to explore foraminiferal Mn incorporation under present-day hypoxic conditions in the Santa Barbara Basin (SBB), USA. We investigated the trace element concentrations and distribution in the foraminiferal calcite of low-oxygen tolerant species *Nonionella stella* which is abundant in the SBB region, to better understanding and improve the proxy application of redox condition in a low oxygen environment. We applied µXRF analyses and plasma-based Secondary Ion Mass Spectrometry (SIMS) to determine Mn distribution and concentration in *N. stella* calcite (Fig. 12). Stained living foraminifera were identified and tested for rDNA sequencing to distinguish the species (phylotype T6) among the cryptic species. The dissolved oxygen concentration in the surface sediment porewater was measured by the microsensor, which was 2.7 – 9.6 µmol/l. The pore water Mn was measured, varying from 2.12 to 21.59 µmol. The Mn incorporation of *N. stella* on population-level in relation to both ambient Mn availability and bottom-water oxygenation changes shows the potential of the foraminiferal Mn/Ca as a proxy for redox condition. The distribution coefficient (D_{Mn}) was very low (<0.05), indicating low Mn incorporation into foraminiferal calcite, which limited the proxy sensitivity of this species.

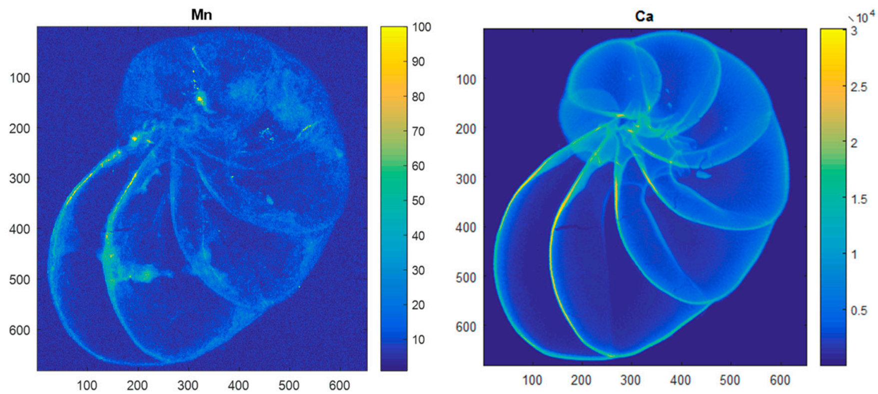

Figure 12. Intensities of Mn (left) and Ca (right) of *N. stella* test. The resolution is 0.3 µm (pixel-size) with 100 ms dwell time per pixel.

Discussion

Reconstruction of past environmental conditions

The bottom water temperature and salinity during two warm periods (i.e. Holocene and Eemian) were reconstructed based on foraminiferal trace element (Mg/Ca) and oxygen isotopes. The variations in salinity were caused by the combined effects of precipitation, evaporation, freshwater runoff, saline water inflow and the mixing processes in the Baltic Sea. Foraminiferal $\delta^{18}O$ can be affected by both temperature and seawater oxygen isotope composition, which is correlated with water salinity. Under complex hydrographic settings such as the entrance of the Baltic Sea, it is difficult to divide the respective influence of temperature and salinity, and the paleo-seawater oxygen isotopes are not normally easy to access. We used the present day relationship between water salinity and $\delta^{18}O$ in the Baltic Sea (the mixing line) for paleo-seawater $\delta^{18}O$ estimation. Therefore, the uncertainties of salinity reconstruction include the uncertainties of the mixing line, Mg/Ca-based temperature estimation, and the assumption of oxygen isotope fractionation was in equilibrium between foraminiferal $\delta^{18}O$ and seawater.

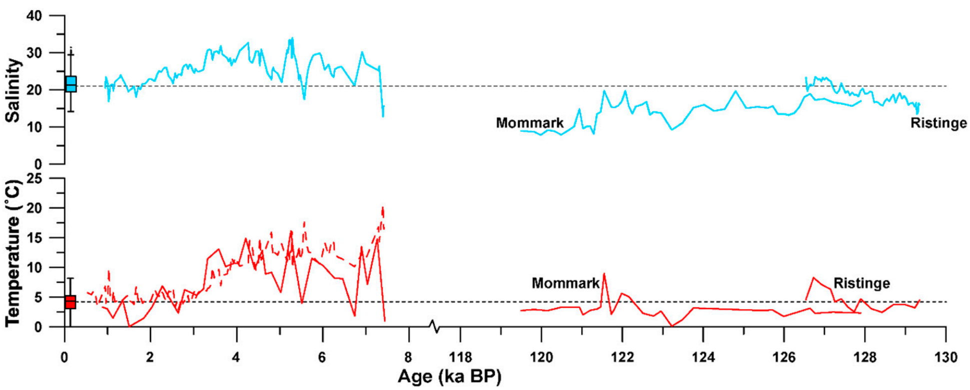

Figure 13. Spring temperature and salinity reconstruction using *E. selseyense-clavatum* complex from the Straits in the Baltic Sea during the Holocene (0 – 8 ka BP, site the Little Belt) and Eemian (118 – 130 ka BP, site Mommark and Ristinge) periods. The red dashed line indicates the temperature reconstructed with oxygen isotope, while solid lines indicate the Mg/Ca-based temperature reconstruction. The salinity was calculated based on $T_{Mg/Ca}$ and oxygen isotopes. The box plots show modern salinity and temperature during spring in the Straits.

We used *E. clavatum-selseyensis* from the Straits for the reconstruction. Due to their reproducing and the most abundant season is in connection with phytoplankton blooms during late winter/early spring (i.e. in cold seasons) (Gustafsson & Nordberg 1999; Gustafsson & Nordberg 2001; Schönfeld & Numberger 2007a; Schönfeld & Numberger 2007b), we considered the most part of the calcite formed during late winter/early spring. Therefore, the reconstructed bottom water conditions using *E. clavatum-selseyensis* indicated that of the cold season. The winter bottom water salinity and temperature in the Straits during the HTM were much higher than the modern conditions and those of the Eemian period (Fig. 13). The winter bottom water temperature during Eemian was generally similar to the modern values, but occasionally there were periods that warmer than the present (i.e. ~122 and ~127 ka BP, Paper I). The bottom water salinity during the mid-Holocene was much higher than that of the Late-Holocene and the Eemian periods, probably due to a relatively lower precipitation-evaporation rate, more saline water inflows from the North Sea and a greater water depth in the region of the Little Belt than the Mommark and Ristinge. In the southern coastal area, low salinity tolerant species *A. batava* and *E. clavatum-selseyensis* were abundant during the Eemian. The bottom water salinity indicated by foraminiferal Mg/Ca and $\delta^{18}O$ of *A. batava* and *E. clavatum-selseyensis* showed higher values and more seasonal variations than the present conditions. Skagerrak and Kattegat bottom water temperature and salinity were in general higher than those of the Straits and the Baltic sea during the cold season. In the late Eemian, the bottom water became more stagnant in the Skagerrak, coinciding with increasing temperature and salinity, due to a comparatively little water exchange and reduced current velocity, and possibly higher productivity with more organic matter deposition.

It is challenging to reconstruct past oxygenation conditions in the bottom water because of complicated redox reactions and biomineralization processes, and few quantitative bottom water oxygen proxies are robust. As mentioned in the former chapter, redox-sensitive element concentrations in $CaCO_3$ may be altered by the oxygen condition in seawater where organisms calcified. Mn is a redox-sensitive element. It has an increased concentration in bottom waters and sedimentary pore waters in hypoxic conditions, which may result in higher Mn/Ca in calcite foraminifera shells. Pore-water Mn-concentrations may reflect bottom-water oxygen and organic carbon flux to the seafloor (Froelich et al., 1979). Pore water oxygen in the sediment is diminished by ongoing organic matter remineralization, and in low oxygen conditions, Mn-(hydr)oxides (MnO_2 or MnOOH) as coatings on the sediment are reduced to aqueous Mn^{2+}. In low oxygen environments, free Mn^{2+} in the pore water is incorporated into benthic foraminifera tests at higher rates than in oxic environments, thus, Mn/Ca ratios in benthic foraminifera test record ambient seawater Mn concentrations and potentially oxygenation of bottom seawater. However, species-specific proxy calibrations are needed to reduce uncertainties in the interpretation of foraminiferal Mn/Ca trends under different oxygen conditions (Paper IV). We explored Mn incorporation of *Nonionella stella* in a modern low oxygen environment (i.e. Santa Barbara Basin) as potential proxy for redox conditions. Distribution mapping and in-situ analysis of elemental concentrations showed high inter- and intra-specimen geochemical heterogeneity due to both vital effects and environment-driven variability. The trace elements of *N. stella* are probably not ideal as oxygen proxy under suboxic conditions in the SBB due to low sensitivity and incorporation rate.

We have observed high Mn/Ca in the foraminifera calcite from the Holocene sediment (7.5 – 3.3 ka BP) in the Little Belt (Paper II), suggesting hypoxic conditions during this period, which coincide with the HTM in the Baltic Sea. This period of hypoxia overlap in time with hypoxic events in the Baltic Proper (Jilbert & Slomp, 2013; Zillén et al., 2008). During the late Eemian, in the Skagerrak, the stagnant bottom water with potential oxygen deficiency was indicated by higher Mn/Ca and more negative $\delta^{13}C$. The period coincides with the increasing water temperature and salinity, suggesting sea level regression and enhanced stratification (Paper I). The simulated monthly water temperature and salinity were in agreement with the reconstructed results. The higher water temperatures were also indicated by foraminifera and ostracods assemblages and stable isotopes in northern Denmark (Seidenkrantz & Knudsen 1997; Knudsen et al., 2014), and the eastern North Atlantic region (Sejrup & Larsen 1991), associated with an enhanced North Atlantic Current (Knudsen et al., 2014).

Some other parameters that can be also used to distinguish past low bottom water oxygen levels include using sedimentological and biological characteristics to determine bottom water O_2 concentration, indices of sedimentary fabric, biological structures and sediment colour. Characteristics of sediments under relatively lower O_2 concentrations are laminated and dark sediments, absence or smaller diameter of burrows, high concentrations of bacteria in a thin surficial mat with tufts. Bulk sediment geochemical records from deep basins of the Baltic Sea were used to investigate the frequency, intensity, and rate of change of hypoxia throughout the Holocene. The C_{org}/P_{tot} and sediment lamination and bioturbation intervals indicated hypoxia occurred during the same period in the Holocene as in the Little Belt (Jilbert & Slomp, 2013; Zillén et al., 2008).

Foraminifera samples from the low oxygen environment such as the Landsort Deep are often with authigenic minerals growing attached to the primary foraminifera calcite, and became another challenge for reconstructing the past environmental conditions. Authigenic minerals (i.e. Mn-, Mg-, and Fe-rich carbonates, and non-carbonate minerals) on/inside the foraminiferal tests found in the Landsort Deep during the Holocene significantly affected the application of the traditional elemental proxies (Paper III). The formation of authigenic carbonates in the Baltic Sea sediments is caused by high rates of organic matter degradation and high dissolved ion concentrations in the pore water. Mn-rich sediments containing massive Mn oxide were reduced by Mn-reducing bacteria thrive through Mn reduction or Mn-mediated anaerobic oxidation of methane (AOM) in methane bearing sediments, and provided free Mn ion in the pore water. During the oxidation of organic matter, the production of bicarbonate increased the alkalinity. Both high alkalinity and Mn^{2+} concentrations in the sediment and pore water where the foraminifera buried became the key factors for foraminifera-coatings formation.

Effect of hypoxia on the environment and our lives

Understanding of the condition, development and consequences of hypoxia is urgent within the field of environmental sciences. Hypoxia is emerging as a significant problem for marine ecosystems, coastal habitats and species, fisheries, and human societies (Breitburg, 2002; Conley et al., 2009b, 2011; Ning et al., 2018). The environment of the Baltic Sea is unique and fragile, and very sensitive to hypoxic conditions. Besides the effects of temperature and salinity on the development of hypoxia, the interaction between climate and nutrients may also enhance the conditions for hypoxia to occur (Conley et al., 2009a). The studies of hypoxia history will provide a better insight into the response and feedback of the ecosystem and the expected types to occur with current and future anthropogenic climate change.

The correlations between increased nutrient discharges, increased primary production in coastal areas, population growth and increased occurrence of hypoxia are well established (Diaz 2001). Hypoxia not only influences benthic communities but also causes severe ecosystem disturbances and alters biogeochemical cycles of nutrients such as phosphorus (P) and nitrogen (N) which are essential for biological communities. It affects nutrient removal processes directly (Carstensen et al., 2014a). During 2011 – 2016, more than 97% of the Baltic Sea area suffers from eutrophication due to past and present excessive inputs of P and N (Helcom, 2018). Phosphate is released from the sediments during the hypoxic condition (e.g. Van Amstel et al., 2007) and hypoxia often leads to large releases of ammonium (NH_4^+) (Conley et al., 2007). Ammonium (NH_4^+) released in organic matter mineralization is nitrified in oxic conditions, with the products nitrite (NO_2^-) and nitrate (NO_3^-) feeding the anoxic denitrification and anammox processes (Carstensen et al., 2014a). Enhanced fluxes of PO_4^{3-} and NH_4^+ from sediments to the water column occur with hypoxia, resulting in significantly increased concentrations in the water column when hypoxia becomes severe (Conley et al., 2007).

Effects on eutrophication from climate change and nutrient input reductions will both take substantial time, and a deepened understanding of the development is needed to support management. Regional policies and management are required, and international agreements and cooperation are necessary to assess future environmental changes and reduce the effects of hypoxia and eutrophication on ecosystems and human lives. The Baltic Marine Environment Protection

Commission (HELCOM) and the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) are international organizations to address the increasing environmental challenges and protect the Baltic Sea and the North-East Atlantic. Ecological objectives related to eutrophication were adopted in the HELCOM Baltic Sea Action Plan (BSAP, HELCOM, 2009), including concentrations of nutrients close to natural levels, clear water, natural level of algal blooms, natural distribution and occurrence of plants and animals, and natural oxygen levels. The nutrient inputs from land to the Baltic Sea sub-basins have decreased considerably comparing the year 2015 with the reference period 1997–2003 (Fig. 14, HELCOM, 2018), but the recovery of the environment needs continuous efforts in reducing nutrient loading, further pollution reductions, good monitoring and modeling are still evidently required to remain a healthy status, especially under a changing climate.

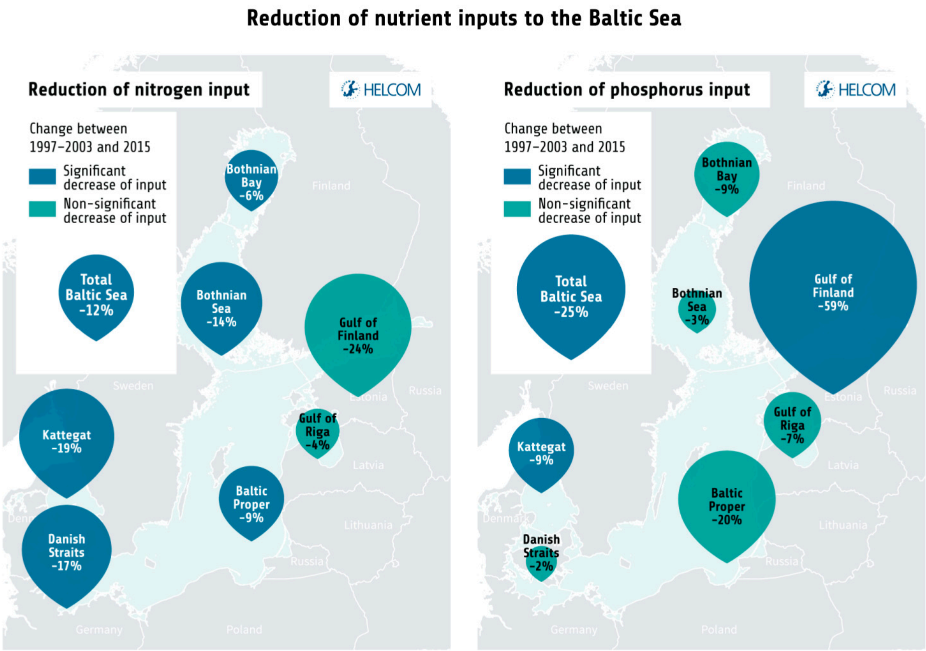

Figure 14. The comparison of nutrient inputs (N: left and P: right) into the Baltic Sea between 1997 – 2003 and 2015. The size of each drop shape is proportional to the amount of change. Significance is determined based on trend analyses (HELCOM, 2018).

Conclusions and Future Outlook

Within the framework of my dissertation, I have contributed new and more detailed knowledge about the environmental conditions of the oceans during the warm periods in the past and how exactly, and with what accuracy, we can reconstruct the oxygen levels. The key conclusions are:

- Foraminiferal elemental, isotopic and assemblage data together with pore water oxygen isotope records document temperature, salinity and oxygen concentration changes at the entrance of the Baltic Sea and the southern Baltic Sea during the warm periods in the past.
- Both proxy-based reconstructions and model-based simulations show more variable seasonality of water temperature and salinity in the Baltic Sea during the Eemian period. Seasonal salinity variations were directly influenced by precipitation-evaporation balance and the NAO pattern. During the early Eemian, the salinity and the seasonal temperature differences increased due to the eustatic sea level rise and the wider entrance of the Baltic Sea. During the late Eemian, the bottom water became more stagnant with lower oxygen content.
- The bottom water in the Little Belt was warmer and hypoxic between about 7.5 and 3.3 ka BP, generally coinciding in time with the Holocene Thermal Maximum (HTM) and became fresher, cooler and more ventilated since ~4.1 ka BP. Reconstructed bottom water conditions in the Little Belt are linked to large scale climate changes such as the NAO and sea level change and reflect the balance between saline water inflows and brackish water outflows.
- The reconstructions need to be based on species specific calibration and geochemistry analyses of 'pure' foraminiferal calcite. The authigenic carbonates formed on and in the foraminiferal tests in the anoxic basin, the Landsort Deep, were characterized by elevated Mn/Ca, Mg/Ca, Ba/Ca and Fe/Ca compared to typical primary foraminiferal calcite, which are of early diagenetic origin and formed within the sediments under hypoxic, anoxic or sometimes euxinic bottom water conditions.
- We used synchrotron- and plasma-based microanalytical techniques for exploring benthic foraminiferal Mn/Ca as low-oxygen proxy variable. Although with small oxygen gradient and species-specific control on Mn uptake, foraminiferal Mn/Ca show a significant correlation with bottom-water dissolved oxygen.

The benthic ecosystems in complex environments are impacted by multiple stressors, including ocean acidification, pH, temperature, and salinity. The concentration of carbon dioxide (CO_2) in the atmosphere is steadily increasing, from about 280 to 411 µatm, since the beginning of the industrial era (NOAA-ESRL) due to human activities such as fossil fuel burning and deforestation. During the Last Interglacial period (also referred to as the Eemian, 130-115 ka BP), the pCO_2 level was similar to the preindustrial level, ~ 275 ppm (Bereiter et al., 2015). The recent rapid CO_2 rise is a source of ocean acidification including pH reductions and alterations in fundamental chemical balances (Doney et al., 2009). The processes of calcification of marine organisms can be influenced by the seawater pH, pCO_2 and DIC speciation (Weiner & Dove, 2003; Melzner et al., 2009). Ocean acidification may be a challenge to marine calcifying species forming their shell of $CaCO_3$ and further affecting local ecosystems and their roles as carbon sinks. The calcareous tests of benthic foraminifera may reflect seawater chemistry (e.g. pH, alkalinity, and calcium carbonate saturation state) and can be potentially used for the reconstruction of ocean acidification events. In order to investigate the effect of different stressors on the foraminifera test formation, we performed high resolution X-ray micro-tomography analyses on the same species from the Eemian (Fig. 15) and the last decades, obtaining different parameters of shell structure, such as mass, size, surface/volume ratio and density. We are investigating the variations of these tomographic parameters during the Eemian related to rapid changes of bottom water conditions and comparing these responses to the modern foraminiferal samples. Benthic foraminiferal tests may show some differences regarding morphology and structure in the Last Interglacial with relatively low pCO_2 and the present with much higher pCO_2.

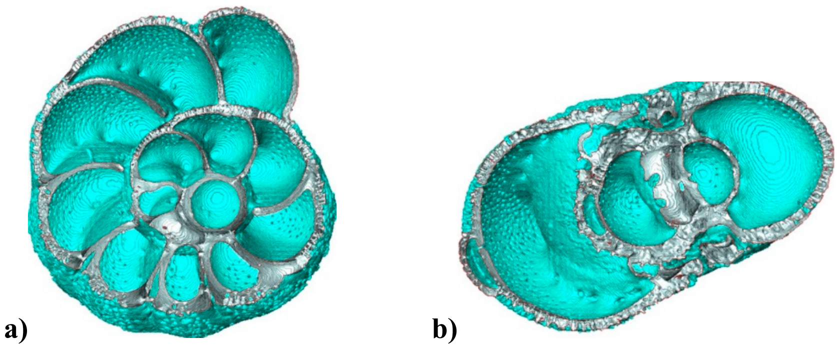

Figure 15. The ultra-high resolution synchrotron-based X-ray tomographic images of a) cross section b) longitudinal section of *Elphidium clavatum* from the southeastern Baltic Sea during Eemian period.

Our study of Eemian climate based on global climate models focusing on the Baltic Sea has limitations at a certain level in terms of the effects of regional/local features. The Baltic Sea ocean model studies of the past climate are still very scarce until today (Hansson & Gustafsson, 2011; Schimanke et al., 2012). Further investigation of variability and long-term climate change in the Baltic Sea region may be conducted by a finer resolution regional climate model that includes bathymetry, sea level and ice volume differences during different interglacial periods.

Newly developed proxy using the elemental composition of authigenic foraminiferal coatings (i.e. U/Mn, Mn- and Fe-mineral formations) provides an opportunity to understand sedimentary diagenesis and sedimentary redox environmental conditions (Burke & Kemp, 2002; Gottschalk et al., 2016; Chen et al., 2017; Detlef et al., 2020). An increase in uranium/calcium (U/Ca) and Mn/Ca ratios can be observed in foraminiferal tests when there is a higher degree of diagenetic alteration, implying changes in the sedimentary redox chemistry (Detlef et al., 2020). Whether the foraminifera-bound authigenic minerals in the Landsort Deep can be used as a proxy for the redox history of the bottom water can be as an extension study of Paper III.

Svensk populärvetenskaplig sammanfattning

En av vår tids största marina miljöutmaningar är minskad syrgashalt i världshaven. Minskningen i syrgaskoncentration påverkar marina organismer och hela ekosystem, samt gör att biogeokemiska cykler ändras. Områden med svår syrebrist, även kallat hypoxi, ökar i utbredning. Hypoxi råder när det finns < 2 mg O_2/l havsvatten men > 0 mg O_2/l. Orsakerna till den ökande syrebristen är bland annat den globala uppvärmningen och kustnära övergödning. Den globala uppvärmningen har två effekter på havsvatten: 1) ett varmare vatten kan hålla mindre mängd löst syre än ett kallt, 2) det orsakar större densitetsskillnader vilket ger ett ökad vertikal skiktning av vattenmassor. Övergödning har främst betydelse i kustnära system, där ökade utsläpp av näringsämnen ger en högre produktion av organiskt material och när det ska brytas ner förbrukas det syre.

Östersjön är ett utsatt havsområde med avsevärd mänsklig påverkan. Havet är mycket känsligt för hypoxi och perioder med syrebrist har förekommit under flera gånger under Östersjöns historia, främst när det har varit ett varmare klimat. Genom att studera forna tiders perioder med syrebrist kan vi bättre förstå dagens miljösituation, de ingående processerna och effekterna på marina ekosystem.

I den här avhandlingen återskapar jag de tidigare miljöförhållandena, dvs. vattentemperatur, salthalt och syrgaskoncentrationer från åtta platser i Östersjön med hjälp av flera olika metoder, inklusive synkrotronljus- och plasma-baserade. Några av mina viktigaste verktyg är encelliga mikroorganismer – foraminiferer. De finns i alla marina miljöer och har ofta ett kalkskal. I skalet byggs det in olika grundämnen och dess isotoper, hur mycket som byggs in beror bland annat på vattentemperatur och salthalt. När ett grundämne finns i mycket låga koncentrationer kallar vi det för ett spårämne och det behövs särskilt avancerad analysutrustning för att bestämma dessa låga halter. Jag använder spårämnes- och stabila isotopanalyser på bottenlevande foraminiferer från två varma perioder: eeminterglacialen, för ~130 till 115 000 år före nu, och holocen (från 11 500 år före nu fram till idag) för att studera omfattningen och hur svårighetsgraden av hypoxi och andra miljöfaktorer har varierat i Östersjön över tid. De kalkskalförsedda foraminifererna finns bevarade i sedimenten och genom att vi provtar dessa sediment kan vi återskapa forna tiders marina miljöer. Mg/Ca kan användas som en indikator för temperatur, Ba/Ca för salthalt och Mn/Ca för hypoxi, särskilt att använda Mn/Ca som en hypoxiindikator är ett nytt användningsområde och vi utforskar dess potential och möjligheter.

För min studie av havsmiljön under eem, använde jag mig av spårämnesanalyser från sex platser i södra och västra Östersjön tillsammans med modellsimuleringar. Under eem visar det sig att bottenvattnet i södra och västra Östersjön hade större säsongsvariationer än idag. Det skedde en snabb salthaltökning i tidig eem på grund av en bredare och djupare passage från Nordsjön till Östersjön. Temperaturskillnaderna mellan kalla och varma årstiden ökade under den första halvan av eem. Under mitten och sen eem blev bottenvattnet allt mer stagnant med ett lägre syrgasinnehåll. Trenderna som vi ser genom foraminiferanalyserna stämmer väl överens med resultat från vår genomförda klimatmodellering. Detta tyder på att vi ser en tydlig påverkan från den Nordatlantiska oscillationen (NAO) och variationer i balansen mellan nederbörd och avdunstning. Under holocen, den period vi lever i nu, ökade salthalt i Östersjöns bottenvatten dramatiskt för ~ 7700-7500 år sedan och minskade ~ 4100-2500 år sedan. Dessa variationer sammanfaller väl med variationer i bottenvattnets syrgashalt och temperatur. Miljörekonstruktionerna för eem och holocen baserades på artspecifika kalibreringar och geokemiska analyser av "ren" kalciumkarbonat från foraminifererna.

Det finns utmaningar med spårämnesanalyser av foraminiferer, det kan till exempel bildas sekundära beläggningar på foraminiferernas skal eller skalen kan påverkas i sediment efter deposition, dvs. de utsätts för diagenes. Detta kan påverka resultaten från spårämnesanalyserna och ha betydelse för våra miljörekonstruktioner. En annan viktig aspekt är att olika foraminiferarter kan ge olika resultat bland annat beroende på art, var de lever i sediment och deras ålder. Det är därför viktigt att använda artspecifika kalibreringar och vara säker på taxonomin. Dessa utmaningar arbetade jag med i två studier inom mitt avhandlingsarbete.

Jag genomförde en studie av sekundära beläggningar som har tillkommit post-mortem på och i foraminiferers skal under extrema låga syrgasförhållandena i den djupaste bassängen i Östersjön (Landsortsdjupet). Bottenmiljön, och sedimentens porvatten är kraftigt anrikade på olika spårämnen, dessa kan avsevärt påverka foraminiferers skalsammansättning. Den här studien kan användas som vägledning vid tolkning av spårämnesanalyser från extrema miljöförhållanden. Slutligen har vi även studerat foraminiferer får Santa Barbara bassängen, NÖ Stilla Havet med avseende på spårämnessammansättningen. Vi har även använt molekylära tekniker för artbestämning. Santa Barbara bassängen är ett område med mer eller mindre permanent syrebrist. Studien visar betydelsen av artspecifika kalibreringar och att foraminiferer har en viss kontroll över koncentrationerna av olika ämnen som de bygger in i sina skal. Vi belyste och undersökte möjligheter med att använda Mn/Ca som en indikator för syrebrist i Santa Barbar bassängen.

Jag har inom ramen för mitt avhandlingsarbete bidragit med ny och mer detaljerad kunskap om forna tiders hav och hur exakt, och med vilken noggrannhet, vi kan återskapa forna tiders syrgashalter.

中文摘要

脱氧，即海洋中的氧气损失，通常会极大地影响水生生物和整个生态系统，并改变生物地球化学循环。这所导致的底部低氧区域增加（<2 mg / l 溶解氧含量）主要归因于全球变暖和水体富营养化程度加剧。因此研究人类在当今沿海环境中引起的环境变化（例如低氧及其后果）至关重要。波罗的海对低氧高度敏感，曾发生在过去几个温暖的时期。研究过去温暖季节中可比较的低氧事件可以帮助我们更好地了解当今环境变化的原因，严重性和潜在后果。

在本论文中，我采用了包括同步加速器 X 射线光谱法和等离子体分析方法在内的多方法方法，重构了波罗的海八个地点过去的环境条件，即水温，盐度和溶解氧浓度。本文对过去两个温暖时期的底栖有孔虫进行了微量元素和稳定同位素分析，即 Eemian（距今 13 万年至 11.5 万年前）和全新世（距今 1.2 万年前至今），从而研究波罗的海在这些时期缺氧事件的严重程度和其他环境因素是如何变化的。

在 Eemian 时期，波罗的海的南部和西部的底层水表现出较大的季节性变化。由于从北海到波罗的海的连接相比更宽和更深，所以 Eemian 早期海水盐度迅速上升。在 Eemian 时期的前半段，冷季和暖季之间的温度差异逐步增加。在 Eemian 中后期，底部水变得更加停滞，溶解氧含量降低。标志物重建的结果与模型模拟的结果相吻合，表明了北大西洋涛动和降水蒸发平衡对盐度变化的影响。在全新世时期，底层水含盐量在距今 7.7－7.5 千年前急剧增大，而在距今 4.1－2.5 千年前开始降低，这个变化趋势与底层水的温度和溶解氧含量的变化同步。古气候重建必须基于特定有孔虫属种的替代性指标建立和 “干净” 的有孔虫碳酸钙壳体的地球化学，而避免受到自生矿物的污染。在波罗的海最深的盆地中，在极低氧气甚至无氧条件下形成的在有孔虫上附着的次生矿物层富含多种元素，这十分可能显着影响有孔虫的地球化学应用。对于有孔虫表面次生矿物的研究可以应用于解释极端氧化还原环境下有孔虫微量元素分析。来自低氧盆地圣塔芭芭拉盆地的校准研究表明，在受限的氧气环境下进行特定有孔虫属种替代性指标校准的重要性，并改进了使用微量元素（即锰元素在有孔虫碳酸钙中的结合）作为水体溶解氧替代指标的应用。

References

Andrén, T., Björck, S., Andrén, E., Conley, D., Zillén, L. & Anjar, J., 2011. The Development of the Baltic Sea Basin During the Last 130 ka. *The Baltic Sea Basin.*

Barker, S., Cacho, I., Benway, H. and Tachikawa, K., 2005. Planktonic foraminiferal Mg/Ca as a proxy for past oceanic temperatures: a methodological overview and data compilation for the Last Glacial Maximum. *Quaternary Science Reviews*, *24*(7), pp.821-834.

Bereiter, B., Eggleston, S., Schmitt, J., Nehrbass-Ahles, C., Stocker, T.F., Fischer, H., Kipfstuhl, S. and Chappellaz, J., 2015. Revision of the EPICA Dome C CO_2 record from 800 to 600 kyr before present. *Geophysical Research Letters*, 42(2), pp.542-549.

Bernhard, J. M., and Reimers, C. E., 1991. Benthic foraminiferal population fluctuations related to anoxia: Santa Barbara Basin. *Biogeochemistry*, 15(2), 127–149. https://doi.org/10.1007/BF00003221

Bernhard, J.M., Gupta, B.K.S. and Borne, P.F., 1997. Benthic foraminiferal proxy to estimate dysoxic bottom-water oxygen concentrations; Santa Barbara Basin, US Pacific continental margin. *Journal of Foraminiferal Research*, 27(4), pp.301-310.

Bernhard, J.M., Buck, K.R., Farmer, M.A. and Bowser, S.S., 2000. The Santa Barbara Basin is a symbiosis oasis. *Nature*, 403(6765), pp.77-80.

Bernhard, J. M., Ostermann, D. R., Williams, D. S., & Blanks, J. K., 2006. Comparison of two methods to identify live benthic foraminifera: A test between Rose Bengal and CellTracker Green with implications for stable isotope paleoreconstructions. *Paleoceanography*, 21(4), PA4210. https://doi.org/10.1029/2006PA001290

Björck, S., 2008. The late Quaternary development of the Baltic Sea basin. *Assessment of climate change for the Baltic Sea Basin*, pp.398-407.

Breitburg, D., 2002. Effects of hypoxia, and the balance between hypoxia and enrichment, on coastal fishes and fisheries. *Estuaries*, 25(4), 767–781. https://doi.org/10.1007/BF02804904

Burke, I.T., Kemp, A.E., 2002. Microfabric analysis of Mn-carbonate laminae deposition and Mn-sulfide formation in the Gotland Deep, Baltic Sea. *Geochim. Cosmochim. Acta,* 66 (9), 1589–1600.

Carstensen, J., Andersen, J. H., Gustafsson, B. G. & Conley, D. J. 2014a. Deoxygenation of the Baltic Sea during the last century. *Proc Natl Acad Sci U S A*, 111, 5628-33.

Carstensen, J., Conley, D.J., Bonsdorff, E., Gustafsson, B.G., Hietanen, S., Janas, U., Jilbert, T., Maximov, A., Norkko, A., Norkko, J. and Reed, D.C., 2014b. Hypoxia in the Baltic Sea: Biogeochemical cycles, benthic fauna, and management. *Ambio*, 43(1), pp.26-36.

Chen, P., Yu, J., Jin, Z., 2017. An evaluation of benthic foraminiferal U/Ca and U/Mn proxies for deep ocean carbonate chemistry and redox conditions. *Geochem. Geophys. Geosyst*. 18 (2), 617–630.

Cleroux, C., Cortijo, E., Anand, P., Labeyrie, L., Bassinot, F., Caillon, N. and Duplessy, J.C., 2008. Mg/Ca and Sr/Ca ratios in planktonic foraminifera: Proxies for upper water column temperature reconstruction. *Paleoceanography*, 23(3).

CLIMAP, 1984. The Last Interglacial Ocean. *Quat. Res*.. 21: 123 224.

Conley, D.J., Humborg, C., Rahm, L., Savchuk, O.P. and Wulff, F., 2002. Hypoxia in the Baltic Sea and basin-scale changes in phosphorus biogeochemistry. *Environmental science & technology*, 36(24), pp.5315-5320.

Conley, D.J., Carstensen, J., Ærtebjerg, G., Christensen, P.B., Dalsgaard, T., Hansen, J.L. and Josefson, A.B., 2007. Long-term changes and impacts of hypoxia in Danish coastal waters. *Ecological Applications*, 17(sp5).

Conley, D.J., Björck, S., Bonsdorff, E., Carstensen, J., Destouni, G., Gustafsson, B.G., Hietanen, S., Kortekaas, M., Kuosa, H., Markus Meier, H.E. and Müller-Karulis, B., 2009a. Hypoxia-related processes in the Baltic Sea. *Environmental Science & Technology*, 43(10), pp.3412-3420.

Conley, D. J., Carstensen, J., Vaquer-Sunyer, R. & Duarte, C. M. 2009b. Ecosystem thresholds with hypoxia. *Hydrobiologia*, 629, 21-29.

Conley, D. J., Carstensen, J., Aigars, J., Axe, P., Bonsdorff, E., Eremina, T., Haahti, B. M., Humborg, C., Jonsson, P., Kotta, J., Lannegren, C., Larsson, U., Maximov, A., Medina, M. R., Lysiak-Pastuszak, E., Remeikaite-Nikiene, N., Walve, J., Wilhelms, S. & Zillen, L. 2011. Hypoxia is increasing in the coastal zone of the Baltic Sea. *Environ Sci Technol*, 45, 6777-83.

Chappell, J. and Shackleton, N., 1986. Oxygen isotopes and sea level. *Nature*, 324(6093), pp.137-140.

De Nooijer, L.J., Brombacher, A., Mewes, A., Langer, G., Nehrke, G., Bijma, J. and Reichart, G.J., 2017. Ba incorporation in benthic foraminifera. *Biogeosciences*, 14(14), p.3387.

Detlef, H., Sosdian, S.M., Kender, S., Lear, C.H., Hall, I.R., 2020. Multi-elemental composition of authigenic carbonates in benthic foraminifera from the eastern Bering Sea continental margin (International Ocean Discovery Program Site U1343). *Geochim. Cosmochim. Acta,* 268, 1–21.

Diaz, R.J. and Rosenberg, R., 1995. Marine benthic hypoxia: a review of its ecological effects and the behavioural responses of benthic macrofauna. *Oceanography and marine biology*. An annual review, 33, pp.245-03.

Diaz, R.J., 2001. Overview of hypoxia around the world. *Journal of environmental quality*, 30(2), pp.275-281.

Diaz, R.J. and Rosenberg, R., 2008. Spreading dead zones and consequences for marine ecosystems. *Science*, 321(5891), pp.926-929.

Diaz, R. J. and Breitburg, D. L. 2009. Chapter 1 The Hypoxic Environment. *Hypoxia.*

Dijkstra, N., Slomp, C. P., Behrends, T., & Scientists, E., 2016. Vivianite is a key sink for phosphorus in sediments of the Landsort Deep, an intermittently anoxic deep basin in the Baltic Sea. *Chemical Geology*, 438, 58–72.

Dijkstra, N., Krupinski, N.B.Q., Yamane, M., Obrochta, S.P., Miyairi, Y., Yokoyama, Y. and Slomp, C.P., 2018. Holocene refreshening and reoxygenation of a Bothnian Sea estuary led to enhanced phosphorus burial. *Estuaries and Coasts*, 41(1), pp.139-157.

Doney, S.C., V.J. Fabry, R.A. Feely and J.A. Kleypas. 2009. Ocean Acidification: The Other CO_2 Problem. *Annual Review of Marine Science*. Doi: 10.1146 / annurev. marine.010908.163834.

Ehlers, J., Astakhov, V., Gibbard, P.L., Mangerud, J. and Svendsen, J.I., 2013. Glaciations. Late Pleistocene in Eurasia. In *Encyclopedia of Quaternary Science*, 2nd edition (pp. 224-235). Elsevier.

Erbs-Hansen, D.R., Knudsen, K.L., Gary, A.C., Gyllencreutz, R. and Jansen, E., 2012. Holocene climatic development in Skagerrak, eastern North Atlantic: Foraminiferal and stable isotopic evidence. *The Holocene*, 22(3), pp.301-312.

Feyling-Hanssen, R.W., 1972. The foraminifer Elphidium excavatum (Terquem) and its variant forms. *Micropaleontology*, pp.337-354.

Filipsson, H.L. and Nordberg, K., 2004. Climate variations, an overlooked factor influencing the recent marine environment. An example from Gullmar Fjord, Sweden, illustrated by benthic foraminifera and hydrographic data. *Estuaries*, 27(5), pp.867-881.

Filipsson, H. L., and Nordberg, K., 2010. Variations in organic carbon flux and stagnation periods during the last 2400 years in a Skagerrak fjord basin, inferred from benthic foraminiferal $\delta^{13}C$. *Geological Society, London, Special Publications*, 344(1), 261–270. https://doi.org/10.1144/SP344.18

Filipsson, H. L., Romero, O. E., Stuut, J.-B. W. & DONNER, B., 2011. Relationships between primary productivity and bottom-water oxygenation off northwest Africa during the last deglaciation. *Journal of Quaternary Science*, 26, 448-456.

Filipsson, H. L., McCorkle, D. C., Mackensen, A., Bernhard, J. M., Andersson, L. S., Naustvoll, L.-J., et al., 2017. Seasonal variability of stable carbon isotopes ($\delta^{13}C_{DIC}$) in the Skagerrak and the Baltic Sea: Distinguishing between mixing and biological productivity. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 483, 15–30. https://doi.org/10.1016/j.palaeo.2016.11.031

Froelich, P., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B. and Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochim. Cosmochim. Acta*, 43(7), pp.1075-1090.

Fröhlich, K., Grabczak, J., & Rozanski, K., 1988. Deuterium and oxygen-18 in the Baltic Sea. *Chemical Geology: Isotope Geoscience*, 72(1),77–83. https://doi.org/10.1016/0168-9622(88)90038-3

Funder, S., Demidov, I. and Yelovicheva, Y., 2002. Hydrography and mollusc faunas of the Baltic and the White Sea–North Sea seaway in the Eemian. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 184(3-4), pp.275-304.

Funder, S. and Balic-Zunic, T., 2006. Hypoxia in the Eemian: mollusc faunas and sediment mineralogy from Cyprina Clay in the southern Baltic region. *Boreas*, 35, 367-377.

Gillikin D. P., Dehairs F., Lorrain A., Steenmans D., Baeyens W., et al., 2006. Barium uptake into the shells of the common mussel (Mytilus edulis) and the potential for estuarine paleo-chemistry reconstruction. *Geochim. Cosmochim. Acta*, Elsevier, 70 (2), pp.395-407.

Goldstein, S.T., 1999. Foraminifera: a biological overview. *Modern foraminifera*, pp.37-55.

Gottschalk, J., Skinner, L.C., Lippold, J., Vogel, H., Frank, N., Jaccard, S.L., Waelbroeck, C., 2016. Biological and physical controls in the Southern Ocean on past millennial- scale atmospheric CO2 changes. *Nat. Commun*. 7 (1), 1–11.

Groeneveld, J. and Filipsson, H. L. 2013. Mg/Ca and Mn/Ca ratios in benthic foraminifera: the potential to reconstruct past variations in temperature and hypoxia in shelf regions. *Biogeosciences*, 10, 5125-5138.

Groeneveld, J., Filipsson, H. L., Austin, W. E., Darling, K., McCarthy, D., Krupinski, N. B. Q., et al., 2018. Assessing proxy signatures of temperature, salinity, and hypoxia in the Baltic Sea through foraminifera-based geochemistry and faunal assemblages. *Journal of Micropalaeontology*, 37(2), 403–429. https://doi.org/10.5194/jm-37-403-20

Gustafsson, M. and Nordberg, K., 1999. Benthic foraminifera and their response to hydrography, periodic hypoxic conditions and primary production in the Koljö fjord on the Swedish west coast. *Journal of Sea Research*, 41(3), pp.163-178.

Gustafsson, M. and Nordberg, K., 2001. Living (stained) benthic foraminiferal response to primary production and hydrography in the deepest part of the Gullmar Fjord, Swedish West Coast, with comparisons to Hoglund’s 1927 material. *The Journal of Foraminiferal Research*, 31(1), pp.2-11.

Gustafsson, BG and Westman, P., 2002. On the causes for salinity variations in the Baltic Sea during the last 8500 years. *Paleoceanography*, 17 (3).

Hansson, D. and Gustafsson, E., 2011. Salinity and hypoxia in the Baltic Sea since AD 1500, *J. Geophys. Res*., 116, C03027, doi:10.1029/2010JC006676.

Harwood, A. J., Dennis, P. F., Marca, A. D., Pilling, G. M., & Millner, R. S., 2008. The oxygen isotope composition of water masses within the North Sea. Estuarine, *Coastal and Shelf Science*, 78(2), 353–359. https://doi.org/10.1016/j.ecss.2007.12.010

Head, M. J., Seidenkrantz, M.-S., Janczyk-kopikowa, Z., Marks, L. & Gibbard, P. L., 2005. Last Interglacial (Eemian) hydrographic conditions in the southeastern Baltic Sea, NE Europe, based on dinoflagellate cysts. *Quaternary International*, 130, 3-30.

HELCOM, 2009 Eutrophication in the Baltic Sea – An integrated thematic assessment of the effects of nutrient enrichment and eutrophication in the Baltic Sea region. *Balt. Sea Environ. Proc*. No. 115B.

HELCOM, H., 2013. Technical Report on the HELCOM Underwater Biotope and habitat classification. In *Balt. Sea Environ. Proc* (Vol. 139).

HELCOM, 2018. State of the Baltic Sea - Second HELCOM Holistic Assessment 2011-2016. Available at: http://www.helcom.fi/baltic-sea-trends/holistic-assessments/state-of-the-baltic-sea-2018/reports-and-materials/

Hillaire-Marcel, C. and de Vernal, A., 2007. Proxies in Late Cenozoic Paleoceanography: Introduction. *Proxies in Late Cenozoic Paleoceanography*. Elsevier, pp.1-15.

Jakobsson, M., Stranne, C., O'Regan, M., Greenwood, S.L., Gustafsson, B., Humborg, C. and Weidner, E., 2019. Bathymetric properties of the Baltic Sea. *Ocean Science*, 15(4).

Jilbert, T. and Slomp, C. P., 2013. Rapid high-amplitude variability in Baltic Sea hypoxia during the Holocene. *Geology*, 41, 1183-1186.

Kabel, K., Moros, M., Porsche, C., Neumann, T., Adolphi, F., Andersen, T. J., et al., 2012. Impact of climate change on the Baltic Sea ecosystem over the past 1,000 years. *Nature Climate Change*, 2(12), 871. https://doi.org/10.1038/nclimate1595

Kamykowski, D. and Zentara, S.J., 1990. Hypoxia in the world ocean as recorded in the historical data set. Deep Sea Research Part A. *Oceanographic Research Papers*, 37(12), pp.1861-1874.

Karlson, K., Rosenberg, R. and Bonsdorff, E., 2002. Temporal and spatial large-scale effects of eutrophication and oxygen deficiency on benthic fauna in Scandinavian and Baltic waters: a review. *Oceanography and Marine Biology*, 40, pp.427-489.

Kotthoff, U., Groeneveld, J., Ash, J., Fanget, A.-S., Krupinski, N. Q., Peyron, O., et al., 2017. Reconstructing Holocene temperature and salinity variations in the western Baltic Sea region: A multi-proxy comparison from the Little Belt (IODP Expedition 347, Site M0059). *Biogeosciences*, 14(23), 5607–5632. https://doi.org/10.5194/bg-14-5607-2017

Kienast, S.S., Calvert, S.E. and Pedersen, T.F., 2002. Nitrogen isotope and productivity variations along the northeast Pacific margin over the last 120 kyr: Surface and subsurface paleoceanography. *Paleoceanography*, 17(4), pp.7-1.

Knudsen, K.L., Kristensen, P. and Larsen, N.K., 2009. Marine glacial and interglacial stratigraphy in Vendsyssel, northern Denmark: foraminifera and stable isotopes. *Boreas*, 38(4), pp.787-810.

Knudsen, K.L., Jiang, H., Kristensen, P., Gibbard, P.L. and Haila, H., 2011. Early Last Interglacial palaeoenvironments in the western Baltic Sea: benthic foraminiferal stable isotopes and diatom-based sea-surface salinity. *Boreas*, 40(4), pp.681-696.

Knudsen, K. L., Ditlefsen, C., Penney, D. N., Kristensen, P., Kronborg, C., & Eiríksson, J., 2014. E lsterian-H olsteinian deposits at Kås Hoved, northern Denmark: sediments, foraminifera, ostracods, and stable isotopes. *Boreas*, 43(1), 251-271.

Koho, K. A., De Nooijer, L. J., Fontanier, C., Toyofuku, T., Kazumasa, O., Kitazato, H. & Reichart, G. J. 2017. Benthic foraminiferal Mn/Ca ratios reflect microhabitat preferences. *Biogeosciences*, 14(12), p.3067.

Komada, T., Burdige, D. J., Li, H.-L., Magen, C., Chanton, J. P., & Cada, A. K., 2016. Organic matter cycling across the sulfate-methane transition zone of the Santa Barbara Basin, California Borderland. *Geochimica et Cosmochimica Acta*, 176, 259–278.

Kopp, R.E., Simons, F.J., Mitrovica, J.X., Maloof, A.C. and Oppenheimer, M., 2009. Probabilistic assessment of sea level during the Last Interglacial stage. *Nature*, 462(7275), pp.863-867.

Kristensen, P.H. and Knudsen, K.L., 2006. Palaeoenvironments of a complete Eemian sequence at Mommark, South Denmark: foraminifera, ostracods and stable isotopes. *Boreas*, 35(2), pp.349-366.

Laine, A.O., 2003. Distribution of soft-bottom macrofauna in the deep open Baltic Sea in relation to environmental variability. *Estuarine, Coastal and Shelf Science*, 57(1), pp.87-97.

Lass, H. U., and Matthäus, W., 2008. General oceanography of the Baltic Sea. State and Evolution of the Baltic Sea, 1952–2005. In R. Feistel, G. Nausch, & N. Wasmund (Eds.), A Detailed 50-Year Survey of Meteorology and Climate, Physics, Chemistry, Biology, and Marine Environment (pp. 5–43). Hoboken, NJ: John Wiley & Sons, Inc. https://doi.org/10.1002/9780470283134.ch2

LaVigne M., Hill T. M., Spero H. J., and Guilderson T. P., 2011. Bamboo coral Ba/Ca: calibration of a new deep ocean refractory nutrient proxy, *Earth Planet. Sc. Lett*., 312, 506–515.

Lea D. W., and Boyle E., 1989. Barium content of benthic foraminifera controlled by bottom- water composition. *Nature* 338, 751-753.

Lea D. W., and Boyle E., 1991. Barium in planktonic foraminifera. *Geochim. Cosmochim. Acta,* 55, 3321-3331.

Lea D. W., Mashiotta T. A., and Spero H. J., 1999. Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing, *Geochim. Cosmochim. Acta*, 63, 2369–2379.

LeGrande, A. N., and Schmidt, G. A., 2006. Global gridded data set of the oxygen isotopic composition in seawater. *Geophysical Research Letters*, 33, L12604. https://doi.org/10.1029/2006GL026011

Lenz, C., Jilbert, T., Conley, D. J., Wolthers, M. & Slomp, C. P. 2015. Are recent changes in sediment manganese sequestration in the euxinic basins of the Baltic Sea linked to the expansion of hypoxia? *Biogeosciences*, 12, 4875-4894.

Leppäranta, M. and Myrberg, K., 2009. Physical oceanography of the Baltic Sea. *Springer Science & Business Media*.

Lindahl, O., Belgrano, A., Davidsson, L. and Hernroth, B., 1998. Primary production, climatic oscillations, and physico-chemical processes: the Gullmar Fjord time-series data set (1985–1996). *ICES Journal of Marine Science*, 55(4), pp.723-729.

McCorkle D. C., Martin P. A., Lea D. W. and Klinkhammer G. P., 1995. Evidence of a dissolution effect on benthic foraminiferal shell chemistry: $\delta^{13}C$, Cd/Ca, Ba/Ca, and Sr/Ca results from the Ontong Java Plateau. *Paleoceanography*, vol. 10, No. 4, pages 699-714.

Meier, H.E., Edman, M.K., Eilola, K.J., Placke, M., Neumann, T., Andersson, H.C., Brunnabend, S.E., Dieterich, C., Frauen, C., Friedland, R. and Gröger, M., 2018. Assessment of eutrophication abatement scenarios for the Baltic Sea by multi-model ensemble simulations. *Frontiers in Marine Science*, 5, p.440.

Melzner, F., Gutowska, M. a., Langenbuch, M., Dupont, S., Lucassen, M., Thorndyke, M. C., Bleich, M. and Pörtner, H.-O., 2009: Physiological basis for high CO_2 tolerance in marine ectothermic animals: pre-adaptation through lifestyle and ontogeny? *Biogeosciences*, 6, 2313–2331.

McCulloch M., Fallon S., Wyndham T., Hendy E., Lough J., and Barnes D., 2003. Coral record of increased sediment flux to the inner Great Barrier Reef since European settlement, *Nature*, 421, 727–730.

McKay, C. L., Filipsson, H. L., Romero, O. E., Stuut, J. B. W. & Björck, S. 2016. The interplay between the surface and bottom water environment within the Benguela Upwelling System over the last 70 ka. *Paleoceanography*, 31, 266-285.

Möllmann, C., Kornilovs, G., Fetter, M. and Köster, F.W., 2005. Climate, zooplankton, and pelagic fish growth in the central Baltic Sea. *ICES Journal of Marine Science*, 62(7), pp.1270-1280.

Munsel, D., Kramar, U., Dissard, D., Nehrke, G., Berner, Z., Bijma, J., Reichart, G. J. & Neumann, T. 2010. Heavy metal incorporation in foraminiferal calcite: results from multi-element enrichment culture experiments with Ammonia tepida. *Biogeosciences*, 7, 2339-2350.

Murray, J.W., 2006. Ecology and applications of benthic foraminifera. *Cambridge University Press*.

Ning, W., Nielsen, A. B., Ivarsson, L. N., Jilbert, T., Åkesson, C. M., Slomp, C. P., et al., 2018. Anthropogenic and climatic impacts on a coastal environment in the Baltic Sea over the last 1000 years. *Anthropocene*, 21, 66–79. https://doi.org/10.1016/j.ancene.2018.02.003

Ní Fhlaithearta, S., Reichart, G. J., Jorissen, F. J., Fontanier, C., Rohling, E. J., Thomson, J. & De Lange, G. J. 2010. Reconstructing the seafloor environment during sapropel formation using benthic foraminiferal trace metals, stable isotopes, and sediment composition. *Paleoceanography*, 25(4).

Nixon, S.W., 1995. Coastal marine eutrophication: a definition, social causes, and future concerns. *Ophelia*, 41(1), pp.199-219.

NOAA-ESRL. www.esrl.noaa.gov/gmd/ccgg/trends

Pearson, P. N., 2012. Oxygen isotopes in foraminifera: Overview and historical review. *The Paleontological Society Papers*, 18, 1–38. https://doi.org/10.1017/S1089332600002539

Pyhälä, M., Fleming-Lehtinen, V. and Laamanen, M., 2014. Eutrophication status of the Baltic Sea 2007-2011. A concise thematic assessment. In *Baltic Sea Environment Proceedings* (No. 143).

Rabalais, N.N., Turner, R.E., Díaz, R.J. and Justić, D., 2009. Global change and eutrophication of coastal waters. *ICES Journal of Marine Science*, 66(7), pp.1528-1537.

Reichart, G.J., Jorissen, F., Anschutz, P. and Mason, P.R., 2003. Single foraminiferal test chemistry records the marine environment. *Geology*, 31(4), pp.355-358.

Ries J.B. 2011. Skeletal mineralogy in a high-CO_2 world. *Journal of Experimental Marine Biology and Ecology*, 403 54–64.

Rohling, E. J., and Cooke, S., 1999. Stable oxygen and carbon isotopes in foraminiferal carbonate shells. In B. K. Sen Gupta (Ed.), *Modern foraminifera* (pp. 239–258). Dordrecht: Springer. https://doi.org/10.1007/0-306-48104-9_14

Rosenberg, R., Hellman, B. and Johansson, B., 1991. Hypoxic tolerance of marine benthic fauna. *Marine ecology progress series*. Oldendorf, 79(1), pp.127-131.

Schimanke, S., Meier, H.E.M., Kjellström, E., Strandberg, G. and Hordoir, R., 2012. The climate in the Baltic Sea region during the last millennium simulated with a regional climate model. *Climate of the Past*, 8(5), pp.1419-1433.

Schmiedl, G., and Mackensen, A., 2006. Multispecies stable isotopes of benthic foraminifers reveal past changes of organic matter decomposition and deepwater oxygenation in the Arabian Sea. *Paleoceanography*, 21, PA4213. https://doi.org/10.1029/2006PA001284

Schönfeld, J. and Numberger, L., 2007a. Seasonal dynamics and decadal changes of benthic foraminiferal assemblages in the western Baltic Sea (NW Europe). *Journal of Micropalaeontology*, 26(1), pp.47-60.

Schönfeld, J. and Numberger, L., 2007b. The benthic foraminiferal response to the 2004 spring bloom inthe western Baltic Sea. *Marine Micropaleontology*, 65(1-2), pp.78-95.

Schweizer, M., Polovodova, I., Nikulina, A. & Schönfeld, J. 2010. Molecular identification of Ammonia and Elphidium species (Foraminifera, Rotaliida) from the Kiel Fjord (SW Baltic Sea) with rDNA sequences. *Helgoland Marine Research*, 65, 1-10.

Seidenkrantz, M.S., 1993. Foraminifera from the Quaternary sequence in the Anholt boring, Denmark. *Boreas*, 22(4), pp.283-290.

Seidenkrantz, M.S., and Knudsen, K. L., 1997. Eemian climatic and hydrographical instability on a marine shelf in Northern Denmark. *Quaternary Research*, 47(2), 218-234.

Sen Gupta, B. K. and Machain-Castillo, M. L. 1993. Benthic foraminifera in oxygen-poor habitats. *Marine Micropaleontology*, 20, 183-201.

Sen Gupta, B. K., 2007. Modern Foraminifera. Springer Science & Business Media.

Sejrup, H.P. and Larsen, E., 1991. Eemian-early weichselian NS temperature gradients; North Atlantic-NW Europe. *Quaternary International*, 10, pp.161-166.

Shackleton, N.J., Sánchez-Goñi, M.F., Pailler, D. and Lancelot, Y., 2003. Marine isotope substage 5e and the Eemian interglacial. *Global and Planetary change*, 36(3), pp.151-155.

Somogyi, A., Medjoubi, K., Baranton, G., Le Roux, V., Ribbens, M., Polack, F., Philippot, P., Samama, J.P., 2015. Optical design and multi-length-scale scanning spectro-microscopy possibilities at the Nanoscopium beamline of Synchrotron Soleil. *J. Synchrotron Radiat*. 22 (4), 1118–1129.

Sternbeck, J., Sohlenius, G. and Hallberg, R.O., 2000. Sedimentary trace elements as proxies to depositional changes induced by a Holocene fresh-brackish water transition. *Aquatic Geochemistry*, 6(3), pp.325-345.

Toyofuku, T., Kitazato, H., Kawahata, H., Tsuchiya, M., and Nohara, M, 2000. Evaluation of Mg/Ca thermometry in foraminifera: Comparison of experimental results and measurements in nature, *Paleoceanography*, 15, 456–464.

Tyson, R.V. and Pearson, T.H., 1991. Modern and ancient continental shelf anoxia: an overview. *Geological Society, London, Special Publications*, 58(1), pp.1-24.

Van Amstel, M., De Neve, W., De Kraker, J. & Glasbergen, P. 2007. Assessment of the potential of ecolabels to promote agrobiodiversity. *Ambio*, 36, 551-8.

van Geen, A., Zheng, Y., Bernhard, J.M., Cannariato, K.G., Carriquiry, J., Dean, W.E., Eakins, B.W., Ortiz, J.D. and Pike, J., 2003. On the preservation of laminated sediments along the western margin of North America. *Paleoceanography*, 18(4).

van Helmond, N. A., Krupinski, N. B. Q., Lougheed, B. C., Obrochta, S. P., Andrén, T., & Slomp, C. P., 2017. Seasonal hypoxia was a natural feature of the coastal zone in the Little Belt, Denmark, during the past 8 ka. *Marine Geology*, 387, 45–57. https://doi.org/10.1016/j.margeo.2017.03.008

van Wirdum, F., Andrén, E., Wienholz, D., Kotthoff, U., Moros, M., Fanget, A.-S., et al., 2019. Middle to late Holocene variations in salinity and primary productivity in the central Baltic Sea: A multiproxy study from the Landsort Deep. *Frontiers in Marine Science*, 6, 51. https://doi.org/10.3389/fmars.2019.00051

Villnäs, A. and Norkko, A., 2011. Benthic diversity gradients and shifting baselines: implications for assessing environmental status. *Ecological Applications*, 21(6), pp.2172-2186.

Wakelin, S.L., Woodworth, P.L., Flather, R.A. and Williams, J.A., 2003. Sea-level dependence on the NAO over the NW European Continental Shelf. *Geophysical Research Letters*, 30(7).

Weiner S, Dove PM. 2003. An overview of biomineralization processes and the problem of the vital effect. In Biomineralization, *Reviews in Mineralogy and Geochemistry*. Volume 54. eds. PM Dove, JJ De Yoreo, S Weiner, pp. 1–29. Mineralog. Soc. Am., Geochem. Soc

Wulff, F., Savchuk, O.P., Sokolov, A., Humborg, C. and Mörth, C.M., 2007. Management options and effects on a marine ecosystem: assessing the future of the Baltic. *AMBIO: A Journal of the Human Environment*, 36(2), pp.243-249.

Zillén, L., Conley, D. J., Andrén, T., Andrén, E. & Björck, S. 2008. Past occurrences of hypoxia in the Baltic Sea and the role of climate variability, environmental change and human impact. *Earth-Science Reviews*, 91, 77-92.

Zhang, J., Gilbert, D., Gooday, A. J., Levin, L., Naqvi, S. W. A., Middelburg, J. J., Scranton, M., Ekau, W., Peña, A., Dewitte, B., Oguz, T., Monteiro, P. M. S., Urban, E., Rabalais, N. N., Ittekkot, V., Kemp, W. M., Ulloa, O., Elmgren, R., Escobar-Briones, E. & Van Der Plas, A. K. 2010. Natural and human-induced hypoxia and consequences for coastal areas: synthesis and future development. *Biogeosciences*, 7, 1443-1467.