Faculty of Science and Technology
Department of Geosciences

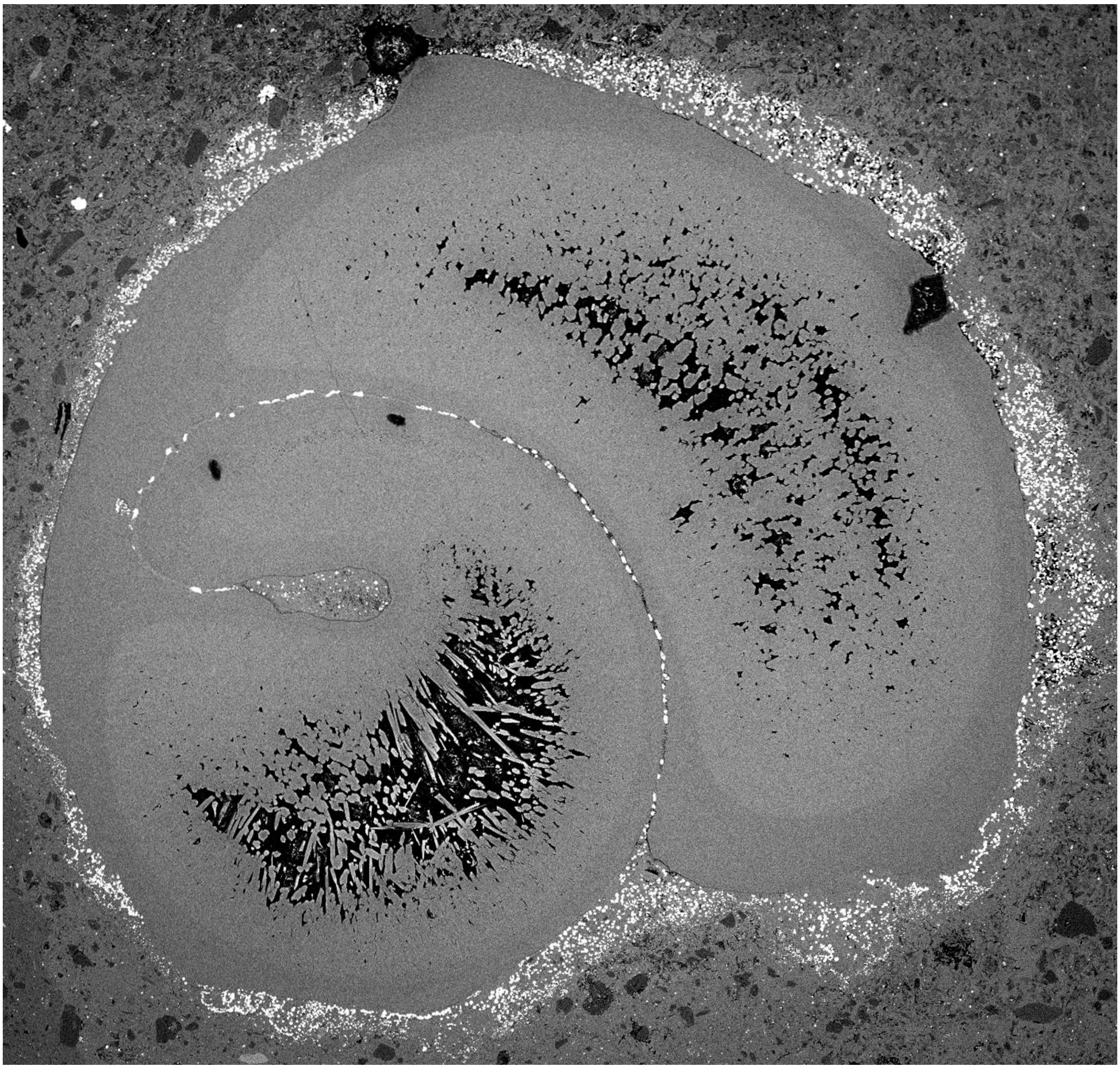
Diagenetically altered benthic foraminifera reveal paleo-methane seepage

Reconstructing the Late Pleistocene and Holocene seafloor methane release history from Vestnesa Ridge

—

Andrea Schneider

A dissertation for the degree of Philosophiae Doctor, March 2018



Diagenetically altered benthic foraminifera reveal paleo-methane seepage

Reconstructing the Late Pleistocene and Holocene seafloor methane release history from Vestnesa Ridge

Andrea Schneider

Thesis for the degree of philosophiae doctor (PhD)

Department of Geosciences, UiT The Arctic University of Norway

Centre for Arctic Gas Hydrate, Environment and Climate (CAGE)

March 2018

Date of public defence: May 2nd 2018

Year: 2018
Title: Diagenetically altered benthic foraminifera reveal paleo-methane seepage Reconstructing the Late Pleistocene and Holocene seafloor methane release history from Vestnesa Ridge
Author: Andrea Schneider
Print: Skipnes Kommunikasjon AS. Trondheim, Norway.

Cover image:

A microfossil in the beauty salon: methane jacuzzi, permanent aragonite-pyrite makeup, and now ready for a catwalk. (Aivo Lepland)

A shell of *Limacina* (cf. *helicana*), an Arctic pteropod, got preserved in a nodule of methane-derived authigenic carbonate from NW Svalbard, 79°N, 477 cm below the seafloor in 16-17 cal ka old sediments. The aragonitic shells are rarely found in marine sediments since they are prone to dissolution already in the water column. This shell is filled with acicular aragonite and surrounded by pyrite framboids.

Antoine Crémière prepared the thin section from a carbonate nodule.
Andrea Schneider and Antoine Crémière photographed the specimen at NGU Trondheim in November 2015.
Steven De Decker performed the image processing.

A mind that is stretched by new experiences can never go back to its old dimensions.

Oliver Wendell Holmes, Jr.

Abstract

The amplification of global warming raises concern about the role of methane, a powerful greenhouse gas. A large amount of methane is present in continental margin sediments worldwide and may be released into the water column and atmosphere during future climate warming. Therefore, it is important to evaluate the character, timing, and drivers of past seafloor methane seepage.

Vestnesa Ridge, located at 79°N in 1200 m water depth offshore north-western Svalbard, is one of the northernmost known active methane seep sites. It is characterised by a subseafloor fluid flow system, numerous seafloor pockmarks, and gas flares in the water column.

The PhD project presented here aims to establish more detailed insights in characteristics, timing, duration, and drivers of seafloor methane seepage at Vestnesa Ridge throughout the Late Pleistocene and Holocene by combining multiple proxies. Among them, the most useful tools are $\delta^{13}C$ records from diagenetically altered foraminifera, fossil chemosynthetic macrofauna, mineralogical and $\delta^{13}C$ composition of methane-derived authigenic carbonates, sediment geochemical data, and a $\delta^{13}C$ mass balance.

Calcareous foraminiferal tests are ubiquitous in marine sediments and offer suitable templates for the precipitation of methane-derived authigenic carbonate. Diagenetically altered foraminifera were found to offer a unique set of information on shallow subseafloor diagenesis and seepage and therefore are remarkably sensitive proxies. Taking advantage of diagenetically altered benthic foraminifera, it can be estimated that the duration required for the precipitation of methane-derived authigenic carbonate is in the range of centuries to millennia. This approach expands the traditional set of methodological tools applied for studying past methane seepage.

Several seepage episodes at Vestnesa Ridge coincide with the Last Glacial Maximum extent of the former Svalbard Barents Sea Ice Sheet, with the Heinrich Event 1, and multiple events occur in the early Holocene. Geological evidences for enhanced methane flux and seafloor methane seepage imply that glacio-isostatic adjustments during ice sheet advance and retreat are likely important controls on fluid migration and methane seepage at Vestnesa Ridge.

This research helps understanding whether methane release is a recent phenomenon or a natural process that persists over long time scales, contributes to our understanding of climate change, and can inform models used for predictions of future climate change.

Acknowledgements

Having a background in glacier and permafrost studies on land, I would have never dreamed of getting the exceptional opportunity to work in the Ocean as well. Four years later, here I am, preparing to complete my PhD project about deep-sea methane release in the Arctic. Since life at seafloor methane seeps is sometimes compared to the origin of life on Earth and other planets … who knows what comes next?!

Therefore, I thank Giuliana Panieri for choosing me to work on this interesting PhD project, and for sending me on many cruises, field trips, and courses. I would like to acknowledge her help in finding fantastic collaboration partners and insightful discussions throughout the course of my PhD. Appreciated advice and patient guidance from Jochen Knies helped greatly improving my research work and keeping work progress on schedule. I would like to extend my thanks to Aivo Lepland whose enthusiastic habit of looking behind the numbers offered constructive criticism and valuable suggestions.

During altogether five visits to the Geological Survey of Norway in Trondheim, Antoine Crémière and Wei-Li Hong acquainted me with studying authigenic carbonates and introduced me to the art of translating my work into mathematical formulas. I thank both of you for your willingness to give your time so generously, your patience in answering all my questions, and your help in improving my scientific writing.

I wish to express my gratitude to my office mates, fellow micropaleontologists, methane researchers, and colleagues at the Department of Geosciences for a pleasant working environment, not necessarily scientific lunch break discussions, numerous the positive words and understanding in the moments when I was not such a social person. I am particularly grateful to my office mates who helped to keep the “office jungle” alive when I was away.

Teaching experience quickly became an important part of my PhD that I enjoyed very much. It was a pleasure working with Tine Rasmussen, Erland Lebesbye, Kamila, Siri, Kasia, Haoyi and all our students who - despite occasional cases of seasickness - were so dedicated to learning about the tiny critters from the seafloor. Ulli it was great meeting you in Tromsø again and watching you make everyone falling in love with diatoms. Successful cruises and laboratory work would be almost impossible without the dedicated technical support and advice from everyone in the GeoLab, on board *R/V Helmer Hanssen*, and the department administration.

I would like to thank Bernhard Nitz, who was one of my first teachers at Humboldt University. He inspired me to attempt understanding the secrets of geology and taught me not to be shy of doing this in different languages. I am grateful to my former advisors Lutz Schirrmeister and Sebastian Wetterich, and everyone at AWI who kept in touch with me, shared expedition experiences, and let me join the Christmas dinners in Potsdam. A similar gratitude goes to my friends and teachers in Stockholm who always had an open door and ear for me.

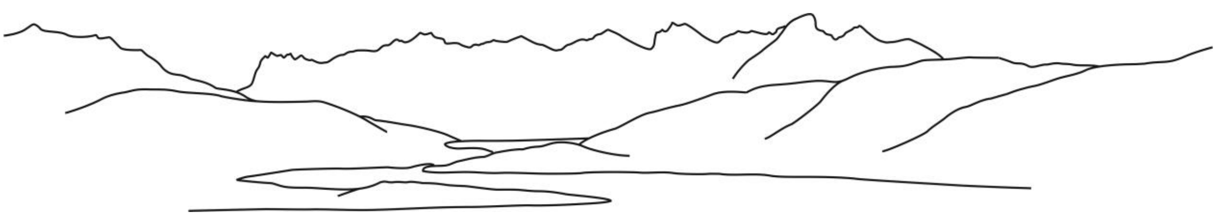
Living above the Arctic Circle and experiencing the everyday amazingness and the challenges was a precious gift. The great nature of Tromsø and Svalbard would not have been the same without the people I shared those moments with.

Anne, Dani, Nina, Pete, Samuel, and Oscar thanks for the ski trips we did together next to the North Pole, those improvised dinners, and for inventing our own Svalbard Mojito.

Steven you kept me on toast when I was close to giving up. Thank you for listening, your advice and encouragement that helped turning things from shallow up and down wiggles into that hockey stick curve. Your passion for the frozen vertical world also took me to finally getting on with something that was holding me back for long; what started as fear of heights therapy sparked yet another outside addiction.

Disa, Edda, Philipp, Jana, Filippo, Sina, Hanne, Johanna, Tim, Kamila, Laura, Aniek, Rebekka, Ieva, Tara, Tord, Jenny, Katrin, Karin, Fiona, Ilona, Petr, Serina, Sophie, Dan, Annamari, Jacob, all our days skiing, climbing, hiking, running, biking, kayaking, swimming, and camping in this amazing backyard of ours – sometimes several sports in one day – made my mind relax and enjoy life at its best. You all deserve a gigantonormous thanks for the memories.

Finally yet importantly, I want to thank my mother, sister, and niece for years of patient encouragement, support, and pleasant diversion during visits at home. Whatever I was aiming to do and no matter where I went, I could always fully count on you. Vielen Dank für alles!



Preface

This thesis is the outcome of a four-year PhD project carried out between 2014 and 2018 at the Centre for Arctic Gas Hydrate, Environment and Climate (CAGE) that is located at the Department of Geosciences at The Arctic University of Norway in Tromsø (UiT). The PhD project is part of CAGE work package 5 on “Paleo-methane history – Neogene to Pleistocene.” whose overall goal is to evaluate the character and timing of past seafloor methane emissions on the Norwegian Shelf, the Barents Sea, and offshore western Svalbard. Advisors during the PhD have been Giuliana Panieri (CAGE, UiT), Jochen Knies (NGU), and Aivo Lepland (NGU). Gravity cores for the PhD project were collected in October 2013 before the start of the PhD project, and in 2014. Laboratory work and data acquisition was performed at UiT, at the Geological Survey of Norway (Norges Geologiske Undersøkelse, NGU) in Trondheim, and at the University of Barcelona, Spain. This research was supported by the Research Council of Norway through its Centre of Excellence funding scheme for CAGE (project number 223259), the NORCRUST project (grant number 255150), the Faculty of Science and Technology at UiT, and the PNRA Project FORMAT.

During my PhD, I enjoyed the opportunity to participate in seven research cruises offshore western Svalbard including Prins Karls Forland and Vestnesa Ridge, to the Barents Sea, to the fjords around Tromsø, and to the edge of the Norwegian Shelf on board *R/V Helmer Hanssen*. In April 2014, I participated in the course “The Marine Cryosphere and its Cenozoic History” (AG-342) at the University Centre on Svalbard (UNIS) gaining an advanced understanding of the Arctic Ocean`s sea ice history, particularly related to concepts and dynamics of marine based ice sheets, ice rises, and submarine permafrost. The “Arctic Marine Geology and Geophysics” (AMGG, GEO-3144/-3145) workshop and cruise in summer 2014 provided a solid background in contemporary and innovative research methodology that is applied at methane seeps. During a summer school on “Subseafloor Biosphere” organized by the European Consortium for Ocean Research Drilling (ECORD) in September 2014 at the Centre for Marine Environmental Sciences (MARUM) in Bremen, Germany, I learned about life in deep seafloor sediments as well as core handling and sample processing within the International Ocean Discovery Program (IODP) network. I took part in the “8th International Course on Foraminifera” at the University of Urbino in Italy in June 2015. The course was focusing on the taxonomic evolution of foraminifera, as well as their environmental and industrial applications. I joined the “Bert Bolin Summer School on Isotopes in the Climate System” that was held in Port Charlotte, Islay, Scotland, in August 2015.

I was associated with the AMGG trainee network at the department of Geosciences at UiT, the Norwegian national Graduate School for Climate Research (ResClim), and the Research School on Changing Climates in the Coupled Earth System (Chess). During field trips to the Northern Apennines and Sicily, Italy, in September 2015 and October 2016, I learned how to compare fossil fluid flow features exposed on land to those at the inaccessible seafloor, and explored different types of terrestrial mud volcanoes. The “Bubbles” summer school, held in June 2017 at UiT, was providing an interdisciplinary overview on the role of methane in marine and terrestrial environments, summarizing the generation of methane, its migration, consumption and impact on the seafloor, the fate of methane in the water column, and its potential to reach the atmosphere.

One year of my PhD has been assigned to duty work where I engaged as a teaching assistant in three different courses at the Department of Geosciences. During the autumn term in 2014, I have been leading exercises of the Bachelor level course „Introduction to Geology“ (GEO-1001). During the autumn term in 2015, 2016, and 2017, I have been supporting the Master level courses in “Micropaleontology” (GEO-3122) and “Reconstructing Quaternary Marine Climate and Environments” (GEO-3111) that follow a research-based educational approach. My tasks included preparing and conducting multiple-day teaching cruises, introducing the students to working onboard a research vessel and different types of sampling, supervising laboratory work, data analyses and interpretation, and providing feedback on student reports.

Beyond the thesis work, I have contributed to three publications as a co-author. The first study was featuring a chemosynthetic shell bed that was established at two different pockmarks at Vestnesa Ridge at 17-16 cal ka ago (Ambrose et al. 2015). The second study was focusing on interpreting porewater profiles to constrain methane consumption and carbon sequestration (Hong et al. 2016). The third project was a high-resolution study of authigenic carbonate coating on two different benthic foraminifera species (Panieri et al. 2017a).

In addition, I have designed logos for the Eleventh International Conference on Permafrost (ICOP) that was held in June 2016 in Potsdam, Germany, and the Chess research school that commenced its activities in March 2017.

Table of contents

1 Introduction

Methane (CH_4) receives a large amount of international attention since it has moved into focus as a powerful greenhouse gas. Methane is the most abundant greenhouse gas after carbon dioxide (CO_2). However, the global warming potential of methane, which is nearly 25 times stronger than that of CO_2 (IPCC 2013), is highlighting its role in the global climate system. Methane originates from a variety of anthropogenic and natural sources. Currently, the Earth is experiencing a nearly unprecedented rise in atmospheric methane concentrations that is predominantly sourced from biogenic emissions, such as the expansion of tropical wetlands and agriculture, but also fossil fuel burning (IPCC 2013, Nisbet et al. 2016, Saunois et al. 2016).

In addition, large amounts of methane are stored in gas hydrate, a naturally occurring ice-like crystalline substance, as free gas and dissolved gas in marine sediments along continental margins worldwide. Throughout the past decades, significant progress has been made in understanding methane in marine geosystems by visualising subseafloor fluid flow systems, characterising chemosynthetic ecosystems, and investigating geochemical processes related to gaseous hydrocarbons in the sediment, porewater, and in the water column. Past methane release has been studied using authigenic carbonates, fossil chemosynthetic macrofauna, molecular fossils, and negative carbon isotope ($\delta^{13}C$) excursions in foraminiferal records.

Negative $\delta^{13}C$ excursions recorded in both planktic and benthic foraminifera have long been recognized as indicators for past methane release, possibly due to gas hydrate dissociation during the Paleogene and the Quaternary (Kennett et al. 2000, Dickens et al. 2011, Thomas et al. 2002). To explain the origin of anomalous foraminiferal $\delta^{13}C$ signatures in the sedimentary record, a wide array of studies has investigated the $\delta^{13}C$ composition of the test calcite and cytoplasm of living and dead foraminifera from methane seeps worldwide (Martin et al. 2010 and references therein). In particular, diagenetic alteration was found to have a major impact on the $\delta^{13}C$ values (Torres et al. 2003, Panieri et al. 2017a). Consequently, the diagenetic alteration of foraminifera can be related to episodes when methane was present in seafloor sediments. However, time constrains of such episodes are difficult because diagenesis occurs out of stratigraphic order and complicates age determination through conventional methods (Torres et al. 2003, Uchida et al. 2008). Hence, the quantitative interpretation of foraminiferal $\delta^{13}C$ records is challenging and present literature struggles with constraining the timing and duration of diagenetic episodes, which would provide fundamental information for reconstructing seepage timing and identifying its drivers.

The PhD project presented here aims to establish a better insight in characteristics, timing, duration, and drivers of seafloor methane seepage by combining multiple proxies. Among them, the most useful tools are $\delta^{13}C$ records from benthic and planktic foraminifera, fossil chemosynthetic macrofauna, mineralogical and $\delta^{13}C$ composition of methane-derived authigenic carbonates, sediment geochemical data, and a $\delta^{13}C$ mass balance.

The doctoral thesis consists of an introduction and three first-authored scientific articles. In the following section, I provide an overview about methane at the seafloor and the most important geochemical processes. Chapter three presents an overview of the most common indicators of past seafloor methane seepage and focuses of foraminiferal $\delta^{13}C$ records. Chapter four states the contextual framework of my PhD project and the specific research objectives. The section comprises background information on the study area, the chosen methods, and a summary of each paper. The final chapters are dedicated to a synthesis of diagenetically altered benthic foraminifera as proxies for methane seepage, the timing and drivers of methane release from Vestnesa Ridge, the main conclusions, and an outlook to future research directions. The three scientific articles are:

Paper I

Schneider A, Crémière A, Panieri G, Lepland A, Knies J. 2017. Diagenetic alteration of benthic foraminifera from a methane seep site on Vestnesa Ridge (NW Svalbard). Deep Sea Research Part I: Oceanographic Research Papers 123, 22-34.

Paper II

Schneider A, Panieri G, Lepland A, Consolaro C, Crémière A, Forwick M, Johnson JE, Plaza-Faverola A, Sauer S, Knies J. Seafloor methane seepage at Vestnesa Ridge (NW Svalbard) since the Last Glacial Maximum. Submitted to Quaternary Science Reviews on December 18, 2017. Minor revisions of the manuscript were requested on March 1, 2018.

Paper III

Schneider A, Hong W-L, Panieri G. Diagenetic alteration of foraminifera reveals minimum methane seepage duration. Manuscript in preparation for submission to Geology.

2 Methane at the seafloor

Seeps are locations at the seafloor where fluids enriched in hydrocarbons, primarily methane, reach the seafloor (e.g. Torres and Bohrmann 2006, Etiope 2015). They occur on both active and passive continental margins worldwide (Beaudoin et al. 2014). Active methane seeps are commonly identified from gas flares in the water column, elevated methane concentrations in the sediment, pore and bottom water, seep-specific seafloor morphology such as pockmarks or craters, authigenic carbonate features, living chemosynthetic micro- and macrofauna, and fluid flow features in the subsurface.

In oxygenated seawater, sulfate anions (SO_4^{2-}) are present with an average concentration of 28 mmol kg^{-1} (Morris and Riley 1966). The ions can penetrate the surface sediments while being dissolved in porewater. Where methane from deeper reservoirs interacts with porewater sulphate in anoxic surface sediments, the sulphate-methane transition zone (SMTZ) establishes and anaerobic oxidation of methane (AOM) counterbalances the upward migration of methane and the downward flux of sulphate (Barnes and Goldberg 1976, Reeburgh 1976, Valentine 2002, Figure 1). The process of AOM establishes the SMTZ as invisible boundary between methane-rich sediments below and sulfate-rich sediments above. It is mediated by consortia of methane-oxidising bacteria and sulfate-reducing archaea that produce hydrogen sulphide and bicarbonate (Boetius et al. 2000, Knittel and Boetius 2009). The activity of those microbes is estimated to consume the majority of the methane and therefore limits the amount of methane that may enter the water column (Niemann et al. 2006, Sommer et al. 2006, Reeburgh 2007, Knittel and Boetius 2009).

Furthermore, the process of AOM leads to an increase of porewater alkalinity at the SMTZ (Ritger et al. 1986, Paull et al. 1992) and thus promotes the precipitation of calcium, magnesium, and/or strontium-carbonate ($Ca(Mg/Sr)CO_3$) as methane-derived authigenic carbonate (MDAC) (Aloisi et al. 2000, Bohrmann et al. 2001, Greinert et al. 2001, Naehr et al. 2007) (Figure 1).

Seepage monitoring studies are challenging and therefore quantitative information on AOM rates and carbon sequestration in authigenic carbonate are rare (Hong et al. 2016 and references therein). At the study site of this thesis, the estimated methane efflux rate is 1600 µmol CH_4 $year^{-1}$ (SMTZ at 2 cm bsf), microbial methane consumption ranges from 1.1 to 4.9 tons $year^{-1}$, and authigenic carbonate precipitation ranges from 0.3 to 1.2 tons $year^{-1}$

(Hong et al. 2016, Panieri et al. 2017b). Similar to other studies, spatial heterogeneity is large (Torres et al. 2002, Sahling et al. 2002). Since microbial activity and authigenic carbonate precipitation sequesters much of the methane, shallow subseafloor diagenesis may be documented in the sedimentary record, but should be distinguished from seepage where the methane bypasses the SMTZ and enters the water column.

A variety of factors controls the depth and thickness of the SMTZ such as methane flux intensity (Borowski et al. 1996), sedimentation rate (Riedinger et al. 2005), organic carbon burial (Meister et al. 2013), sulphate penetration, and methane production (Jørgensen and Kasten 2006, Boetius and Wenzhoefer 2013). In response to changes of these factors, the SMTZ can migrate vertically through the sediment column, leading to the precipitation of diagenetic products out of stratigraphic order.

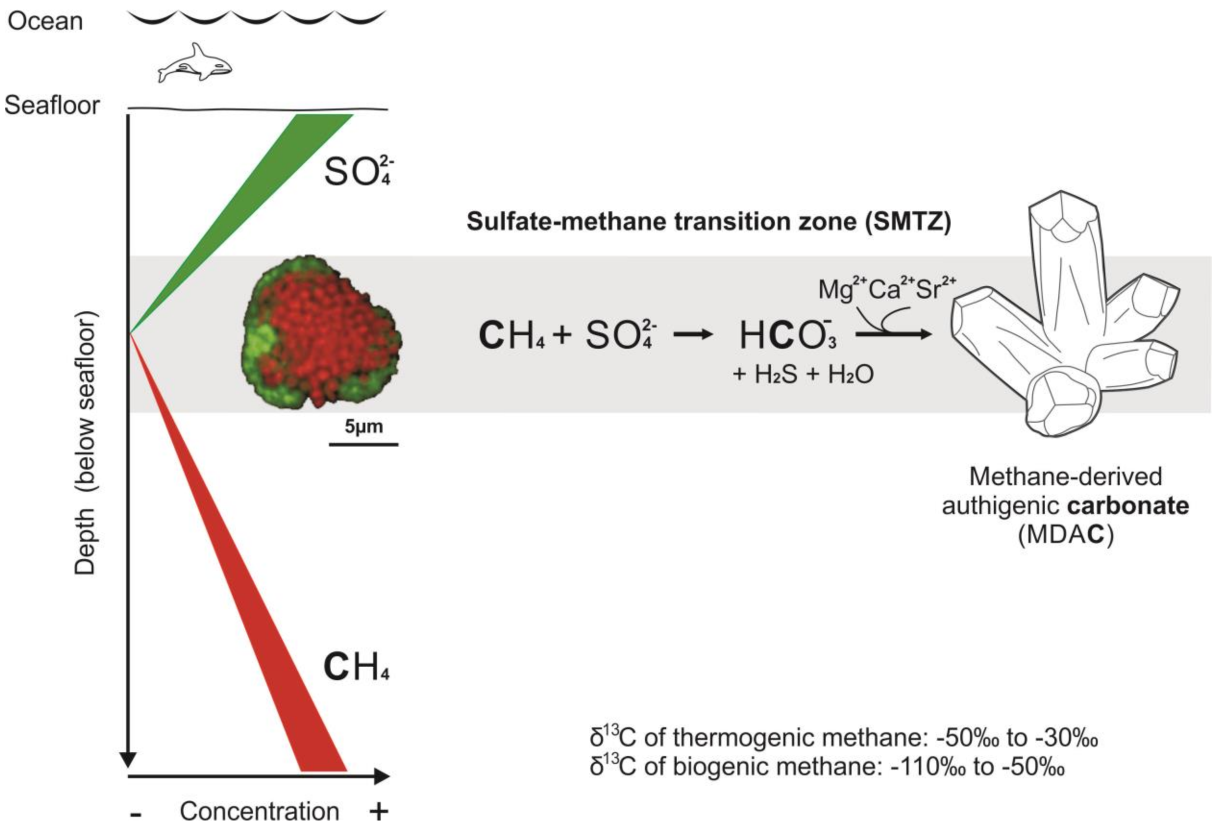


Figure 1. Schematic illustration of the key biogeochemical processes at the sulphate-methane transition zone (SMTZ, grey zone): the anaerobic oxidation of methane (AOM) performed by consortia of sulfate-reducing archaea (in green) and methane-oxidising bacteria (in red, image from Boetius et al. 2000), and the precipitation of methane-derived authigenic carbonate (MDAC). $\delta^{13}C$ values of methane from Claypool and Kaplan (1974) and Whiticar (1999).

3 Proxies of paleo-methane seepage

In the sediment interval where the SMTZ is located, the process of AOM and its products may heavily overprint initial sedimentary attributes and preserved microfossils may experience diagenesis. Proxies of shallow subseafloor diagenesis and methane seepage include the diagenetic alteration of the sediment composition, the precipitation of authigenic carbonates, the occurrence of fossil chemosynthetic macrofauna, microfossils and molecular fossils.

3.1 Changes in sediment properties

The alteration of the initial sediment composition and magnetic properties is common in methane seeps due to reducing conditions and AOM that leads to elevated hydrogen-sulphide concentrations. When iron-oxides such as ferromagnetic magnetite (Fe_3O_4) are exposed to hydrogen-sulphide, they experience reduction to paramagnetic pyrite (FeS_2) that is leading to significant reduction or loss of the magnetic susceptibility signal (Canfield and Berner 1987, Riedinger et al. 2005, Novosel et al. 2005, März et al. 2008, Dewangan et al. 2013).

3.2 Methane-derived authigenic carbonate (MDAC)

During early diagenesis, the precipitation of aragonite and high-Mg calcite cement lithifies unconsolidated fine-grained sediment particles. Such MDAC can be distinguished from biogenic or detrital carbonates based on their morphology, mineralogy, and stable isotope composition. For example, MDAC precipitation in methane seeps produces a variety of fragile features such as cemented bioturbation trails and fractures, microcrystalline carbonate nodules, mudstones, breccia, thick and solid layered crusts, pavements, slabs, and large structures such as domes, chimneys, and chemoherms (Bohrmann et al. 1998, 2002, Aloisi et al. 2000, Teichert et al. 2005, Naehr et al. 2007).

Aragonite, high-Mg Calcite, and dolomite are considered the main carbonate phases associated with methane seeps; their mineralogy corresponds to the predominant porewater ion composition at the depth of formation (Burton 1993, Ferrell and Aharon 1994, Greinert et al. 2001, Bohrmann et al. 1998, 2002). Aragonite forms acicular needles that are filling bioclasts or cavities (Aloisi et al. 2000, Teichert et al. 2005, Naehr et al. 2007, Sauer et al. 2017, cover image of the thesis), while calcite grows as irregular 1-5 µm sized crystals preferentially on calcitic surfaces (Aloisi et al. 2000, Panieri et al. 2017a, Schneider et al. 2017). In solid, thick and large carbonate crusts, aragonite is often the dominant phase. Unlike microcrystalline carbonates that are rich in detrital or organic impurities, aragonitic carbonates contain little impurities and are therefore suitable for U/Th age determination (Peckmann et al. 2001). Hydrocarbon-derived seep-carbonates are known from the middle Devonian to Recent times (Peckmann et al. 1999, Teichert et al. 2003, Bayon et al. 2009, Crémière et al. 2013, Sauer et al. 2017).

Since the AOM microbes preferentially utilize the lighter carbon isotope (Orphan et al. 2001), carbonates precipitating from methane-derived carbon sources preserve the strongly depleted $\delta^{13}C$ signatures (Claypool and Kaplan 1974, Whiticar 1999, Figure 1). Consequently, carbonates with $\delta^{13}C$ values more negative than approximately -30‰ are consistent with carbon sourced from AOM (Whiticar 1999, Greinert et al. 2001). In addition, carbonates derived from methane hydrate dissociation often have elevated $\delta^{18}O$ signatures (Davidson et al. 1983, Bohrmann et al. 1998, 2001, Aloisi et al. 2000, Teichert et al. 2005, Naehr et al. 2007). Along with AOM, MDAC is an important carbon sink. It has been estimated between 10-20 % (Luff and Wallmann 2003) or 25-29 % (Hong et al. 2016) of the methane oxidized by AOM is sequestered in authigenic carbonate.

3.3 Chemosynthetic macrofauna

Astonishing findings of unusual and dense benthic macrofaunal communities, which were later identified as chemosynthetic invertebrates, were among the first descriptions of active methane seeps in the Gulf of Mexico (Paull et al. 1984) and the North Eastern Pacific Ocean (Suess et al. 1985). Once taxonomic information and ecological characterisation of seep-associated chemosynthetic macrofauna was established, ancient methane seeps have been identified based on their fossil macrofauna assemblages between the Devonian and the Pliocene (Van Dover et al. 2002, Campbell 2006, Conti et al. 2010, Kiel 2010). Fossil chemosynthetic macrofauna is among the most reliable direct evidence for ancient methane seepage. For example, findings of a discrete shell bed at Vestnesa Ridge, which was dominated by Vesicomydae (*Phreagena*, *Isorropodon*), greatly improved our understanding of the seepage history at this particular Arctic seep (Ambrose et al. 2015, Schneider et al. 2017, Schneider et al. in prep.).

Bivalves, gastropods, clams, brachiopods, and tubeworms dominate methane-seep habitats (Sibuet and Olu 1998, Sahling et al. 2002, Campbell 2006, Levin 2005). The majority of such chemosynthetic invertebrates are endemic, although similar communities were found at hydrothermal vents and large organic falls (Van Dover et al. 2002, Dubilier et al. 2008, Bernardino et al. 2012). Chemosynthetic invertebrates often host bacterial symbionts in specialised cells and tissue instead of having an own digestive system (Dubilier et al. 2008). The bacterial symbionts use the oxidation of methane and the reduction of sulfate as principal energy source (Sibuet and Olu 1998, Van Dover et al. 2002). Thus, seeps support "islands" of elevated biomass in the deep sea, and also support benthic food webs in the vicinity of the seep (Levin 2005, Dubilier et al. 2008, Nieman et al. 2013, Levin et al. 2016, Åstrom et al. 2017). Depending on spatial and temporal variations in the availability of sulphide and oxygen, spatial heterogeneity of seep-associated macrofauna is high and temporal successions have been suggested throughout a seep`s activity phase (Levin 2005, Bowden et al. 2013, Levin et al. 2016).

3.4 Molecular fossils

Molecular fossils such as fatty acids and membrane lipids, referred to as lipid biomarkers, with negative $\delta^{13}C$ signature are biogeochemical evidence for microbially mediated methane consumption and sulfate reduction (Hinrichs et al. 1999, Birgel and Peckmann 2008, Niemann and Elvert 2008). Similar to authigenic carbonates, the negative $\delta^{13}C$ signatures in microbial biomass are inherited from methane as the main carbon source (Hinrichs et al. 1999, Thiel et al. 1999).

Molecular evidence of chemosynthesis at methane seeps is well preserved in sediments and authigenic carbonate rock (Birgel et al. 2006, Birgel and Peckmann 2008). The $\delta^{13}C$-depleted lipid biomarkers in ancient seep carbonates allow identifying AOM in Cretaceous and Jurassic limestone (Peckmann et al. 1999, Thiel et al. 1999, Birgel et al. 2006). In sediments, isotopically depleted biomarkers coinciding with other seepage proxies such as foraminiferal $\delta^{13}C$ records provide strong evidence for methanotrophic activity in the Late Quaternary (Hinrichs 2001, Hinrichs et al. 2003). High concentrations of biomarkers in either sediment or carbonate rock have been interpreted to indicate strong and/or relatively long lasting methane flux that was fuelling methanotrophic activity (Cook et al. 2001, Hinrichs et al. 2003, Zhang et al. 2003).

3.5 Foraminifera as indicators of paleo-methane seepage

Foraminifera are single-celled amoeboid protozoans with reticulating pseudopods, fine strands of cytoplasm, which primarily live in the marine realm (Sen Gupta 2002). They either float freely in the water column (planktic) or live at the seafloor (benthic). Benthic foraminifera can be attached to sediment particles, rocks, vegetation, or sessil fauna (epibenthic), or live in the sediment pore space (infaunal). Most foraminifera construct an external shell, called a test, which can have one or multiple chambers and is mostly < 1 mm in size (Sen Gupta 2002). The test can be composed of calcium carbonate ($CaCO_3$) that is sourced from dissolved inorganic carbon (DIC) from the ambient water (Erez 2003, Bentov and Erez 2006, de Nooijer et al. 2009a, b, Nehrke et al. 2013). Because foraminiferal tests are ubiquitous in marine sediments, they are among the most important biological proxies in paleoceanographic research (Armstrong and Brasier 2005; Bradley 2015).

3.5.1 Foraminiferal species assemblages

Studies of epi- and infaunal species composition offshore Japan (Akimoto et al. 1994), in the Gulf of Mexico (Sen Gupta and Aharon 1994, Sen Gupta et al. 1997, Robinson et al. 2004), the North Eastern Pacific Ocean (Bernhard et al. 2010, Rathburn et al. 2000, 2003, Stott et al. 2002, Torres et al. 2003, Hill et al. 2003, 2004), the North Atlantic Ocean (Panieri and Sen Gupta 2008, Mackensen et al. 2000, 2006), the Mediterranean (Panieri 2003, 2005, 2006), and offshore New Zealand (Martin et al. 2010) suggest that benthic foraminifera may be capable of inhabiting methane seeps. Certain taxa including *Bolivina, Bulimina, Brizalina, Epistominella*, *Nonionella,* and *Uvigerina* may tolerate the low oxygen and high sulfide concentrations in methane seeps. It has been proposed that abundant food sources attract foraminifera (Sen Gupta and Aharon 1994, Sen Gupta et al. 1997, Hill et al. 2003, Panieri 2006, Panieri and Sen Gupta 2008, Rathburn et al. 2003, Martin et al. 2010), and endosymbionts or physiological adaptations aid to colonize methane seeps (Bernhard et al. 2001, 2010, Bernhard and Bowser 2008). To date, there are no known endemic seep foraminifera and trends in foraminiferal species assemblages between seep and non-seep sites are inconclusive. Similar results were reported from Miocene seeps in Italy (Barbieri and Panieri 2004, Panieri et al. 2009) and Pliocene seeps at the eastern Pacific coast (Martin et al. 2007). The only difference observed so far is a higher diversity and abundance of agglutinated species in non-seep sites compared to seep sites (Heinz et al. 2005, Panieri and Sen Gupta 2008, Herguera et al. 2014).

3.5.2 Stable carbon isotope composition

The $\delta^{13}C$ values of planktic foraminifera, for example *N. pachyderma*, in marine conditions in the absence of methane range between -0.5 and 0.5‰ (Knies and Stein 1998). The $\delta^{13}C$ values in benthic foraminifera, for example *C. neoteretis*, range between 0 and -1.15‰ are considered representative of normal marine conditions (Wollenburg et al. 2001, Mackensen et al. 2006). Foraminifera in seeps exhibit a clear distinction in $\delta^{13}C$ composition in cytoplasm and test calcite, which is characterized by a shift towards negative $\delta^{13}C$ values. Traditionally, species-specific vital effects, diet, and biomineralisation of test calcite from methane-derived ^{13}C-depleted DIC have been evoked to explain this shift (Figure 2).

Vital effects are species-specific variations in isotopic fractionation during metabolic activity in a range of 1-2‰ (Urey et al. 1951, McCorkle et al. 1990, Mackensen et al. 2006). In addition, rich microbial food sources in seeps may attract foraminifera and contribute to the $\delta^{13}C$ shift in their cytoplasm (Rathburn et al. 2003, Hill et al. 2003, 2004, Mackensen et al. 2006, Panieri 2006). Although some foraminifera are known to feed preferentially on seep-associated microbes (Sen Gupta and Aharon 1994, Panieri et al. 2009, Martin et al. 2010), diet was found to account for no more than 10 % of the measured $\delta^{13}C$ signal (Hill et al. 2003, Figure 2).

Controversy exists if foraminifera utilize methane-derived ^{13}C-depleted DIC from ambient water for biomineralisation. It was shown that foraminifera are in pronounced disequilibrium with the porewater DIC, suggesting biomineralisation does not occur during seepage (Rathburn et al. 2003, Torres et al. 2003, Herguera et al. 2014). In contrast, Wollenburg et al. (2015) conducted a culturing experiment with living *Cibicides wuellerstorffi* where the methane-derived DIC is reflected in the foraminiferal test calcite through its isotope composition, indicating test biomineralisation in presence of methane-derived DIC influences its $\delta^{13}C$ signal.

However, those reasons fail to explain large negative $\delta^{13}C$ amplitudes that can reach down to -15‰ in planktic and -29.5‰ in benthic fossil tests (Schneider et al. in review).

3.5.3 Diagenetic alteration

Diagenetic alteration has emerged as primary explanation for strongly negative and heterogeneous $\delta^{13}C$ signatures and elevated Mg-content in benthic and planktic foraminifera (Rathburn et al. 2000, 2003, Hill et al. 2003, Torres et al. 2003, Millo et al. 2005, Panieri et al. 2006, 2009, 2014, 2017a, Martin et al. 2007, 2010, Consolaro et al. 2015, Sztybor and Rasmussen 2017, Schneider et al. 2017, Schneider et al. in review, Schneider et al. in prep.). The diagenetic alteration of fossil foraminiferal test is characterised by the precipitation of MDAC with anomalously low $\delta^{13}C$ and elevated Mg-content that is overprinting the original geochemical composition of the tests (Torres et al. 2003, 2010, Panieri et al. 2017a, Figure 2). Polished sections from the benthic foraminiferal species *Nonionella labradorica* and *Melonis baarleanus* reveal MDAC coatings that surround foraminiferal tests as an additional carbonate layer exhibit the isotopically lightest carbonate as low as -34.1‰ (Panieri et al. 2017a). The authigenic overgrowth can be up to 10 µm thick, notably increases the shell weight, and accounts for 20 to 60 % of the $\delta^{13}C$ signal (Torres et al. 2003, Millo et al. 2005, Panieri et al. 2017a, Schneider et al. 2017, Schneider et al. in prep.). Furthermore, foraminifera discriminate against Mg during primary biomineralisation and the Ca/Mg ratio in biogenic carbonate is about 1.5 mmol mol^{-1} (Greinert 1999). Since authigenic overgrowth typically consists of high Mg-calcite, diagenetically altered fossil foraminiferal tests yield an elevated Ca/Mg ratio of > 20 mmol mol^{-1} (Torres et al. 2003, 2010, Panieri et al. 2017a, Figure 2).

It is important to highlight that diagenetic alteration of microfossils occurs out of stratigraphic order, thus seepage timing cannot be reconstructed straight forward from the stratigraphic record (Torres et al. 2003, Schneider et al. in review).

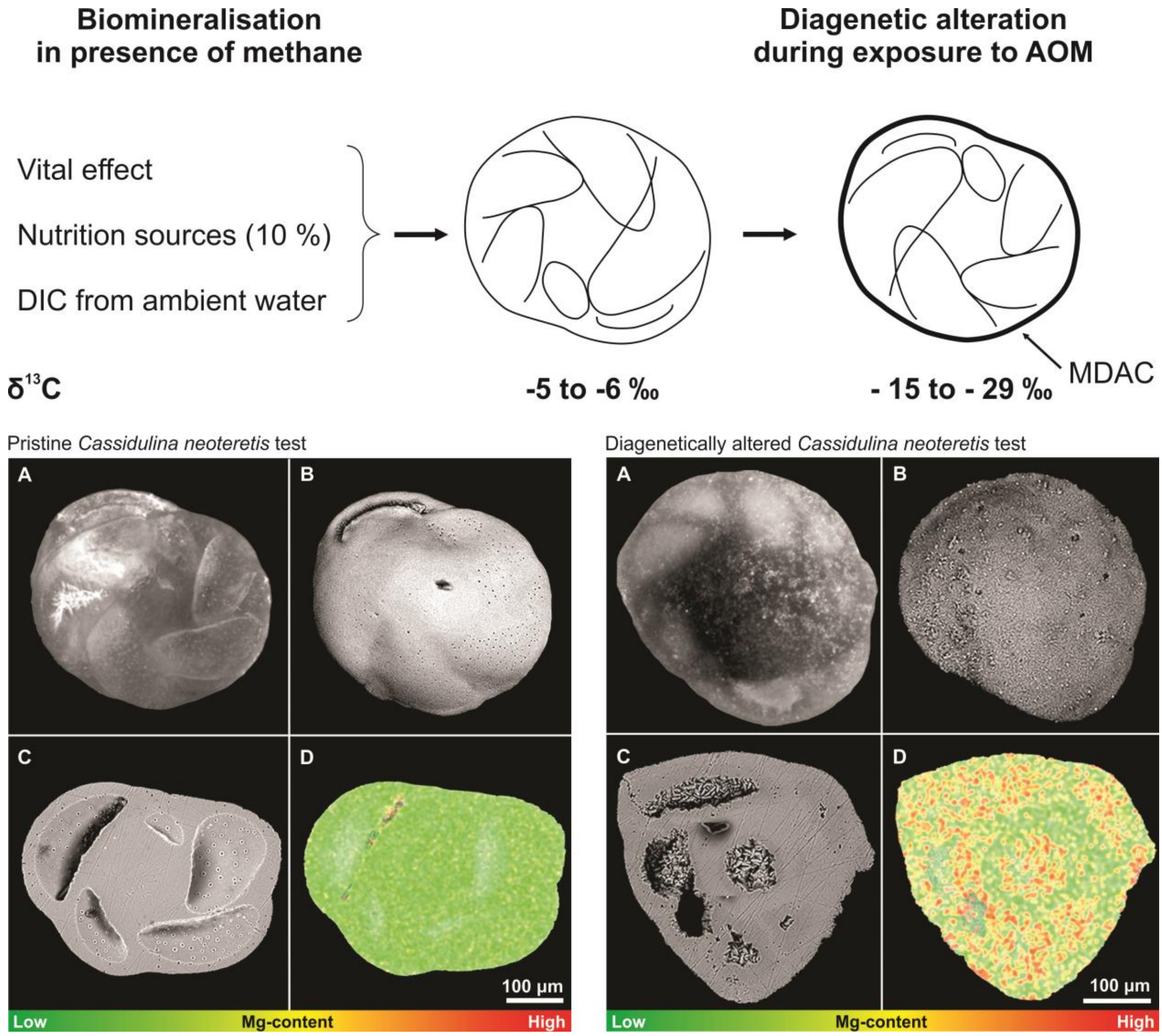


Figure 2. Compilation of traditional explanations for the observed $\delta^{13}C$ values, and the influence of diagenesis. For example, the benthic foraminiferal species *C. neoteretis* normally has hyaline calcareous finely perforated test wall. During diagenetic alteration, methane-derived authigenic carbonate precipitates on the exterior and interior test walls.

A) Test viewed in a light microscope. Foraminiferal tests having experienced major diagenetic alteration appear "frosty", with low reflectance and transparency. **B)** Scanning Electron Microscopy (SEM) image of the exterior test wall. MDAC causes the “frosty” appearance of the tests. **C)** SEM image of a polished wall cross section. MDAC crusts on the interior wall are up to 10 µm thick and appear slightly darker on SEM images due to lower backscatter response of high-Mg calcite compared to foraminiferal calcite. **D)** Correspondent Energy Dispersive X-ray Spectrometry image. The colour-change from green dominating on pristine foraminiferal calcite towards a yellow-orange hue reflects elevated Mg-content in the MDAC.

4 Framework of the PhD project

4.1 Motivation

The motivation behind this thesis is threefold. Diagenesis may affect the state of preservation of calcareous microfossils such as foraminifera due to exposure to AOM in seafloor sediments. By observing changes in the test microstructure and geochemical composition, and investigating changes in shell weight, the thesis presented here intends to establish a better understanding which information from diagenetically altered foraminiferal tests can contribute to paleo-seepage reconstructions from an Arctic deep-water methane seep site.

Furthermore, the thesis aims to collect new $\delta^{13}C$ records from benthic and planktic foraminifera from an Arctic deep-water methane seep site in order to investigate the timing and drivers for methane seepage. Vestnesa Ridge, located at 79°N in the Eastern Fram Strait, is one of the northernmost known active methane seeps. It connected to an approximately 6 million years (Ma) old hydrocarbon system, whose leakage commenced ca. 2.7 Ma ago (Plaza-Faverola et al. 2015, Knies et al. 2018). Recent publications by Panieri et al. (2014), Consolaro et al. (2015), and Sztybor and Rasmussen (2017a, b) have assessed past methane seepage from Vestnesa Ridge and found evidence for distinct seepage events occurring since the last deglaciation. The dataset presented in the thesis will increase the spatial coverage of this type of records along Vestnesa Ridge in unprecedented detail and spatiotemporal resolution. In a multiproxy approach, foraminiferal $\delta^{13}C$ data are combined with other proxies for seafloor methane seepage such as sediment geochemical records, MDAC nodules, and fossil chemosynthetic macrofauna. The timing of seepage episodes is of fundamental interest for gaining a comprehensive insight in phases of seepage activity or quiescence along Vestnesa Ridge, their correlation to major global and/or regional environmental changes, and seepage drivers.

In addition, an isotope mass balance disentangles the contribution of pristine foraminiferal calcite and authigenic carbonate in the $\delta^{13}C$ signal. Using the weight increase from MDAC precipitation precisely reveals the authigenic fraction of the $\delta^{13}C$ signal and thus permits estimating the duration required for the carbonate precipitation. This approach aims to expand the traditional set of methodological tools applied for studying past methane seepage and attempts to shed light into an unexplored type of data.

4.2 Aims and objectives

The thesis presented here aims to investigate characteristics of seafloor methane seepage at Vestnesa Ridge using micropaleontology, geochemistry, and an isotope mass balance approach to determine seepage characteristics, timing, duration, and drivers in relation to regional paleo-environmental changes since the Last Glacial Maximum.

The thesis addresses the following research questions:

- How do benthic foraminifera reveal methane seepage?
- How does diagenesis affect foraminiferal tests in methane seeps?
- Which information do diagenetically altered foraminiferal tests yield that contributes to methane seepage reconstructions?
- How can paleo-methane seepage be distinguished from shallow subseafloor diagenesis?
- Was the seepage at Vestnesa Ridge constant or episodic?
- When did methane release occur at Vestnesa Ridge during the past 24 000 years?
- How can the duration of seepage episodes be determined?
- Which (paleo-) environmental changes or Earth system processes drive methane seepage at Vestnesa Ridge?

4.3 Study area

Vestnesa Ridge is an approximately 100 km long sediment drift that located in the eastern Fram Strait and on the western continental margin of the Svalbard Archipelago in 1200-1300 m water depth (79°N, 5-7°E, Figure 3a). The Fram Strait is the only deep-water connection to the Arctic Ocean. Its opening commenced during late Oligocene to Miocene, ventilated circulation in the shallow strait started approximately 18 Ma ago, and allows circulation exceeding 2000 m water depth since 13.7 Ma (Engen et al. 2008).

4.3.1 Oceanographic setting

Two water masses dominate the present-day oceanographic setting of the Fram Strait: the West Spitsbergen Current (WSC) and the East Greenland Current (EGC) (Figure 3b). The WSC is the northernmost branch of the warm and saline Norwegian Atlantic Current and transports Atlantic-derived water northwards along the western Svalbard continental slope and into the Arctic Ocean (Aagaard et al. 1987, Figure 3b). It sustains ice-free conditions in the eastern Fram Strait throughout most of the year (Cokelet et al. 2008, Jessen et al. 2010, Beszczynska-Möller et al. 2012, Rebesco et al. 2013). The deposition of thick contourites along the continental slope document an ancestral WSC has been prevailing at least since the Early Pleistocene, and almost certainly since the Mid Weichselian (Howe et al. 2008, Rebesco et al. 2013). Mooring studies across the eastern Fram Strait (Figure 3b) reveal the present-day WSC has two branches with a narrow and strong core shallower than 1000 m and maximum northwards velocities of 20 cm s^{-1}, and an offshore branch below 1400 m with northwards velocities of only 5-10 cm s^{-1} (Beszczynska-Möller et al. 2012, Rebesco et al. 2013). The present-day bottom water temperature (BWT) at Vestnesa Ridge is between 1 and 3.3°C (Smith et al. 2014, Sztybor and Rasmussen 2017).

In the western Fram Strait, the EGC runs southwards and transports cold and less saline Polar Surface Water into the North Atlantic Ocean (Aagaard et al. 1987, Woodgate et al. 1995, Beszczynska-Möller et al. 2012, Figure 3b).

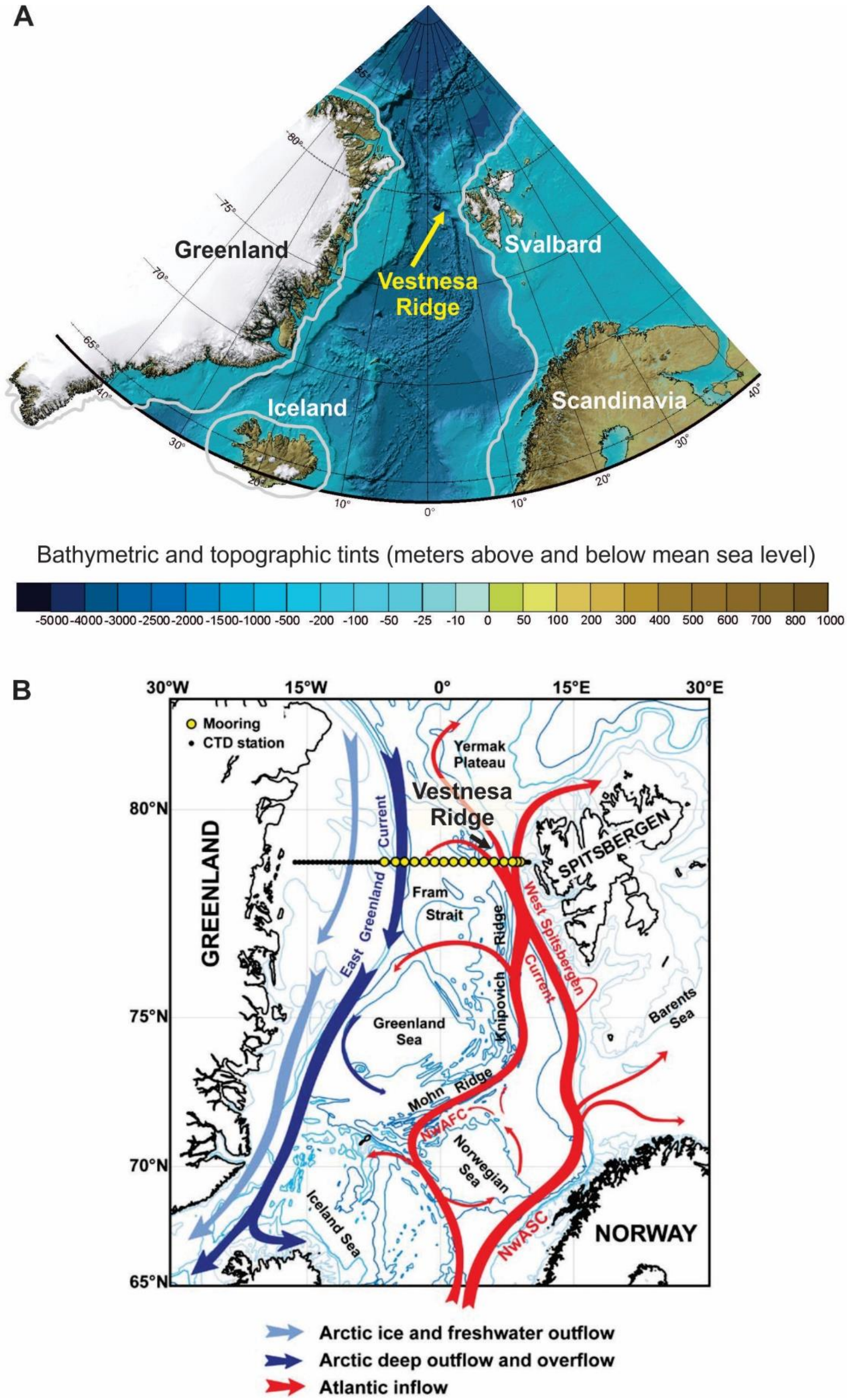


Figure 3. A) Overview map of the North Atlantic Ocean with the location of Vestnesa Ridge. Image section from IBCAO 3.0 (Jakobsson et al. 2012). Grey lines delineate the LGM extent of the SBIS, Iceland and Greenland Ice Sheets (Patton et al. 2015). **B)** Circulation patterns of the major water masses in the Nordic Seas and Fram Strait (Beszczynska-Möller et al. 2012).

4.3.2 Geological background

Vestnesa Ridge is located in close proximity to the Mid Atlantic Ridge and to the ultra-slow spreading ridge systems in the Fram Strait (Talwani and Eldholm 1977, Engen et al. 2008, Johnson et al. 2015, Figure 4). The ridge itself is characterised by compressional and extensional stresses and non-outcropping transform faults (Plaza-Faverola et al. 2015). Due to its setting between this complex tectonic regime and the western Svalbard continental margin, which hosted the former Svalbard Barents Sea Ice Sheet (SBIS), Vestnesa Ridge is a unique location to study seafloor methane seepage and its driving mechanisms.

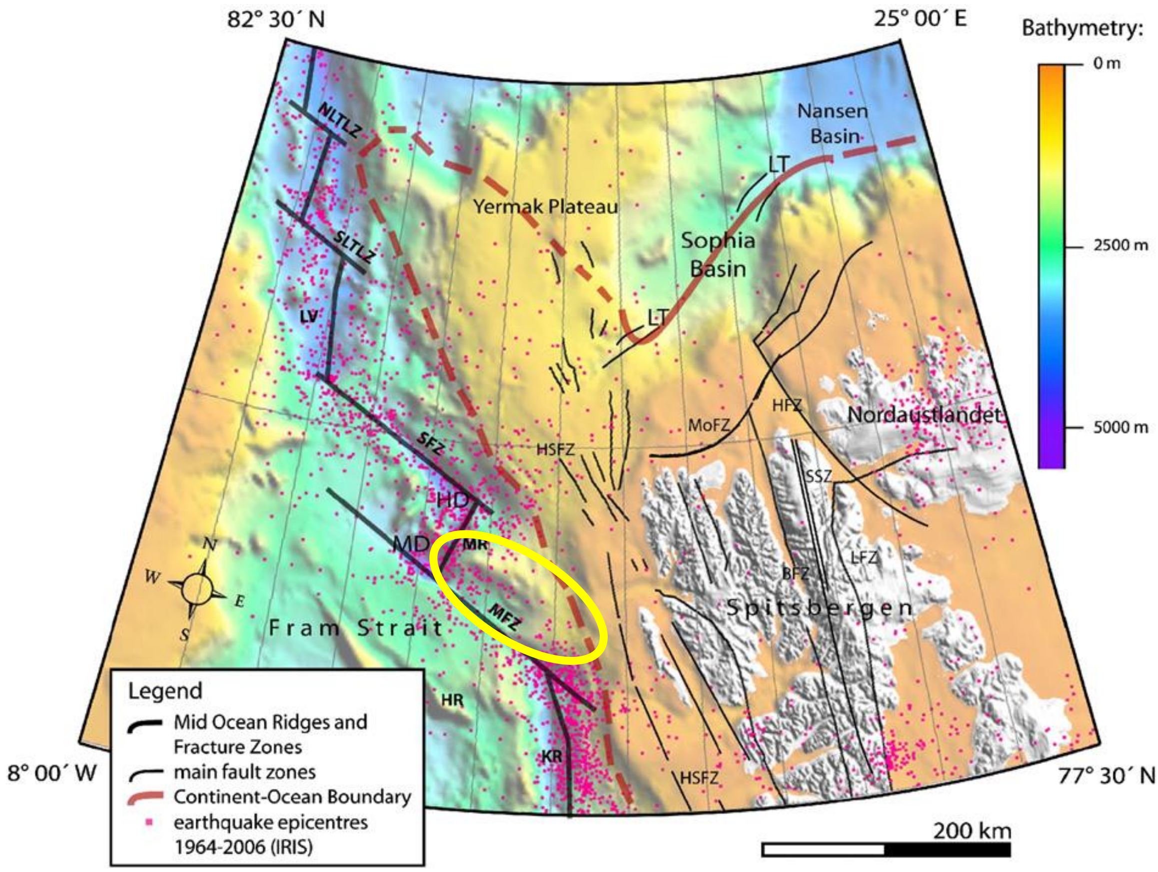


Figure 4. Location of Vestnesa Ridge (yellow circle) and the western Svalbard continental margin in the regional tectonic context. BFZ - Billefjorden Fault Zone; HD - Hayes Deep; HFZ - Hinlopen Fault Zone; HR – Hovgård Ridge; HSFZ - Hornsund Fault Zone; KR - Knipovich Ridge; LFZ - Lifdefjorden Fault Zone; LT - Littke Trough; LV- Lena Valley; MD - Molly Deep; MFZ – Molly Fracture Zone; MoFZ - Moffen Fault Zone; MR - Molly Ridge; NLTFZ - North Lena Trough Fracture Zone; SFZ - Spitsbergen Fracture Zone; SLTFZ - South Lena Trough Fracture Zone. From Winkelmann et al. (2008).

Vestnesa Ridge is composed of > 2 km thick Pliocene and Pleistocene sediments overlying < 20 Ma old oceanic crust (Eiken and Hinz 1993, Engen et al. 2008, Hustoft et al. 2009). Contourite deposition dominated the sedimentary environment along the western Svalbard continental margin since approximately 11 Ma (Eiken and Hinz 1993, Howe et al. 2008, Hustoft et al. 2009, Rebesco et al. 2013). Lithological investigations reveal that sedimentation during the Pleistocene and Holocene was characterized by muddy-silty contourites, and glaciomarine sedimentation of silty turbidites, suspension settling, and ice rafting associated with the development of the nearby SBIS throughout the Late Pleistocene (Howe et al. 2008, Jessen et al. 2010, Rebesco et al. 2013).

4.3.3 Seepage at Vestnesa Ridge: Fluid flow features and known episodes of past seepage

Vestnesa Ridge hosts a complex fluid flow system and shallow gas hydrate accumulations (Petersen et al. 2010, Bünz et al. 2012, Goswami et al. 2015, Plaza-Faverola et al. 2015, Panieri et al. 2017b, Figures 5a, b). Morphological evidence for seepage was initially mapped by Vogt et al. (1994, 1999) who recognized circular seafloor depressions of up to 700 m in diameter, known as pockmarks, that align along the crest of Vestnesa Ridge (Figure 5a). Pockmark formation is ascribed to vigorous release of upward-migrating fluids in unconsolidated sediments (Judd and Hovland 2007). One of the most prominent fluid flow features are up to 900 m high gas flares that originate above these pockmarks and probably emit a mixture of microbial and thermogenic gas to the water column (Smith et al. 2014, Panieri et al. 2017, Figure 5a). The emanating gas, measured from porewater samples, is composed of 99 % methane with $\delta^{13}C$ values between -44.8‰ and -62.9‰, and gas hydrate from Vestnesa Ridge has a methane $\delta^{13}C$ average value of -51.4‰ (Smith et al. 2014, Panieri et al. 2017b). Active methane seepage at the south-eastern Vestnesa Ridge segment is under regular observation since October 2008 (Hustoft et al. 2009, Bünz et al. 2012, Panieri et al. 2017b) and seems to be persistent for at least a decade.

High-resolution seafloor imagery reveals heterogeneous topography inside the Vestnesa Ridge pockmarks and allows insights in the local benthic faunal community composition (Panieri et al. 2017b). Internal depressions (pits) of ca. 50 m in diameter host patches of unconsolidated fine-grained sediment that are often colonized by white bacterial mats, and ridge-like structures appear to be associated with carbonate crusts or massive carbonate blocks that provide habitats for a diverse invertebrate fauna (Figures 5c, d).

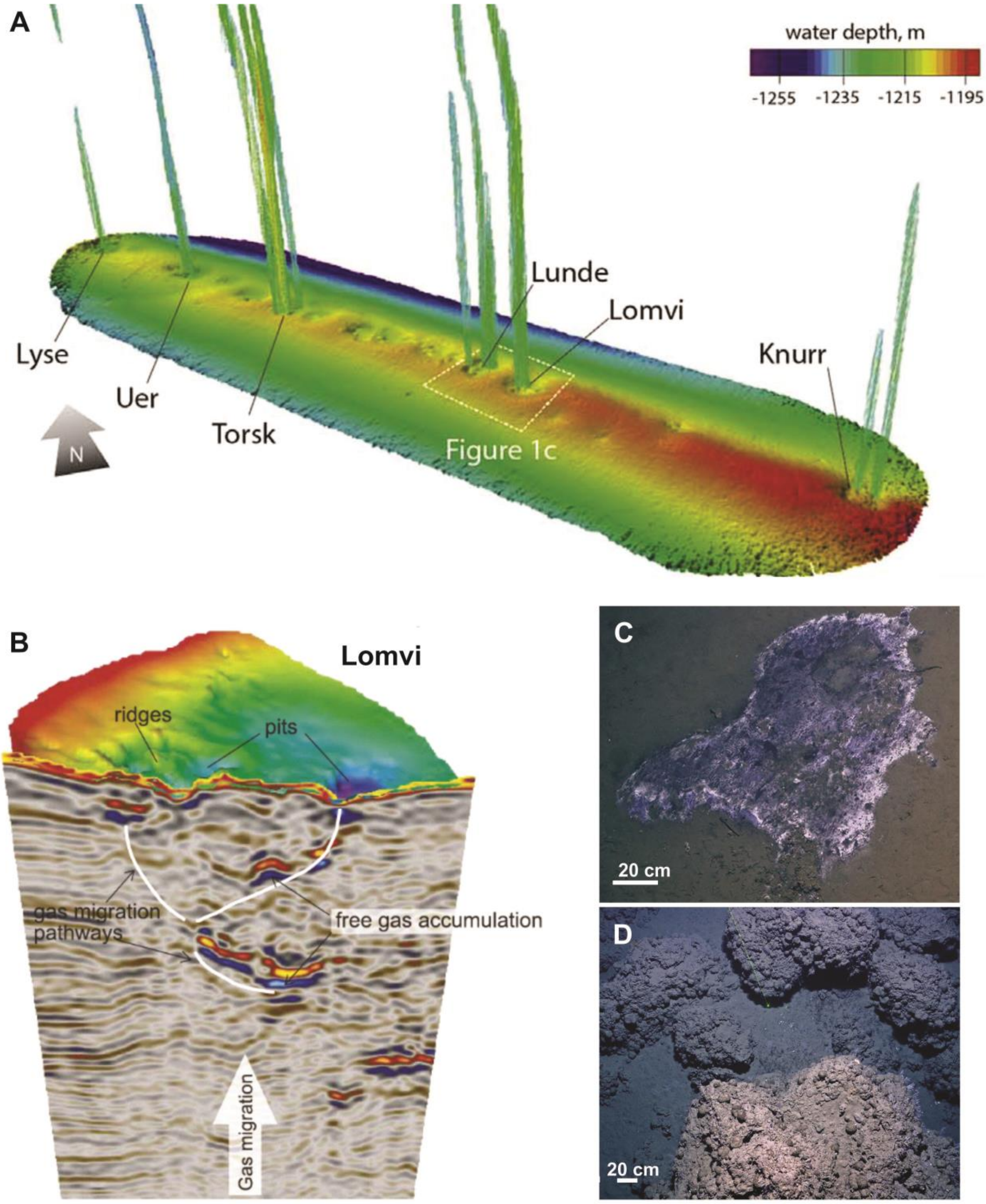


Figure 5. A) Seafloor reflection map showing the active pockmarks along the south-eastern Vestnesa Ridge segment. **B)** Seismic profile outlining vertically aligned and stacked acoustic anomalies beneath the Lomvi pockmark that are crosscutting disrupted strata and terminating into the pits inside the pockmark. **C)** Large patch of white bacterial mats on fine-grained black (iron-sulphide bearing) sediment. **D)** Massive, ca. 2m high carbonate blocks providing habitat for epifaunal invertebrates. Figures and photographs from Panieri et al. (2017b).

It has been suggested that an active petroleum system was established offshore north-western Svalbard approximately 6 Ma ago when hydrocarbon generation from deeply buried Miocene source rocks commenced due to elevated geothermal gradients (Knies et al. 2018). The onset of Northern Hemispheric glaciations ca. 2.7 Ma ago and associated increased sedimentation rates along high latitudinal continental slopes supported further hydrocarbon maturation and their vertical migration (Knies et al. 2018). Several seepage episodes since approximately 2.7 Ma ago have been inferred from seismic interpretation of buried surfaces revealing pockmarks and mounds within chimney structures were related to periods of regional glacial intensification (Plaza-Faverola et al. 2015). At the north-western Vestnesa Ridge segment where seepage is inactive today, observations of buried pockmarks intercalated with periods of undisturbed sedimentation suggest regular seepage cycles between 1.5 Ma and 0.2 Ma. The formation of those pockmarks was initiated approximately 1.5 Ma ago when the SBIS started to thicken and repeatedly advanced towards the shelf edge (Knies et al. 2009). At the currently active south-eastern ridge segment, observations of syn-depositional pockmark formation range from 2.7 Ma ago until present day (Plaza-Faverola et al. 2015).

Foraminiferal $\delta^{13}C$ records within sediments that were deposited during the past 24 cal ka shallow subseafloor diagenesis and seepage occurred during the late Pleistocene and Holocene (Panieri et al. 2014, Ambrose et al. 2015, Consolaro et al. 2015, Sztybor and Rasmussen 2017, Schneider et al. 2017, Schneider et al. in review). Data from fossil chemosynthetic macrofauna and foraminiferal records indicate some of those episodes on the south-eastern Ridge segment may have persisted for about 1000 years (Ambrose et al. 2015, Consolaro et al. 2015), and modelling of porewater profiles suggest seepage may have been active during the past 200 to 400 years (Hong et al. 2016).

4.4 Methodological approach

4.4.1 Core collection, description, and stratigraphic correlation

Ten sediment gravity cores were recovered from Vestnesa Ridge between 2008 and 2014 (Figure 6, Table 1). Sediment core JM10-330GC was collected from an inactive pockmark at the north-western ridge segment, while the remaining nine cores were retrieved from active and inactive pockmarks located at the Vestnesa Ridge south-eastern segment. Reference core HH-13-212 was collected from a non-seep site. The coring transect covers 35.8 km with distances between the cores varying from 0.1 to 27.7 km (Table 1).

After recovery, the cores were cut into 100 cm sections, split longitudinally, and kept cool at 5°C. Magnetic susceptibility and bulk density were measured using a GeoTek Multi-Sensor Core Logger. The cores were described visually, photographed (Jai L-107CC 3 CCD RGB Line Scan Camera), and X-ray-scanned (Geotek MSCL-XR 3.0).

Element-geochemical data from selected cores (HH-13-200; -203; -211; -213) were acquired with an Avaatech XRF core scanner at 1 cm steps using the following settings: down-core slit size 10 mm; cross-core slit size 12 mm; 10 kV; 1000 µA; no filter; and 10 seconds measuring time per step; same settings but 50 kV and 20 seconds measuring time per step for barium. The raw data were subsequently processed with the software WinAxil.

Stratigraphic correlation of the sediment cores is obtained through radiocarbon-dated magnetic susceptibility records and associated tie points known from established stratigraphic marker horizons that have been described along the western Svalbard continental margin between 76 and 79°N (Jessen et al. 2010). Defined stratigraphic marker horizons are clast-rich laminated sediments (within the LGM; 24-23.5 ka), fine-grained laminated sediments (Bølling interstadial; 14.7-14.3 ka), and a structureless layer rich in *Coscinodiscus* spp. diatoms (Early Holocene; 10.1-9.8 ka, Jessen et al. 2010). All calibrated ages presented in the following text are in calendar years before present (cal BP) A.D. 1950 with a standard deviation of 2σ.

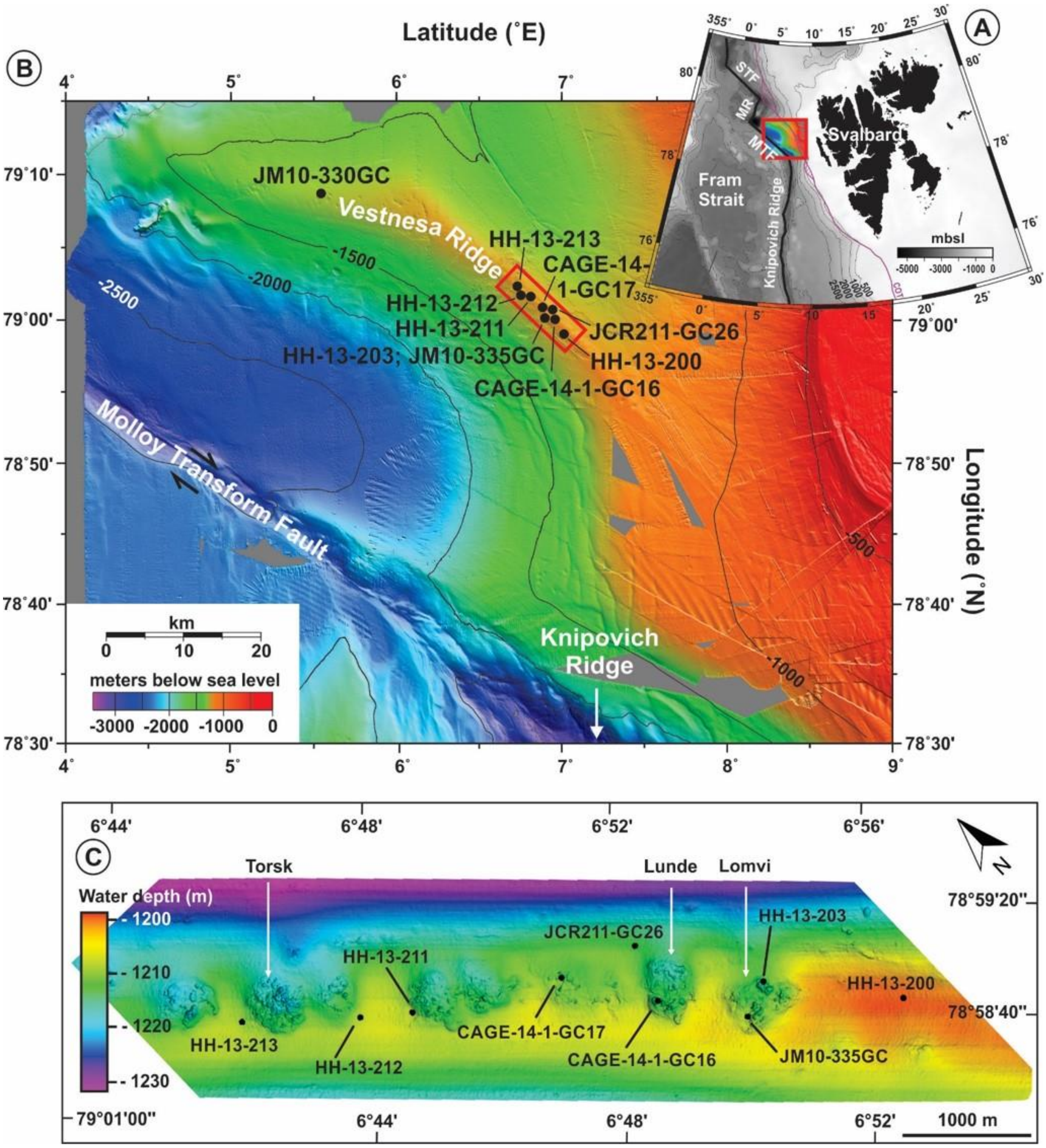


Figure 6. Map of the study area from Schneider et al. (in review). **A)** Bathymetric map of the western Svalbard margin and eastern Fram Strait. The red square indicates the location of Vestnesa Ridge. The continent-ocean transition (COT) is delineated in purple. MFZ – Molloy Fracture Zone. MR – Molloy Ridge. SFZ – Spitsbergen Fracture Zone. **B)** Bathymetric map of Vestnesa Ridge with the location of the studied cores (black dots). The red square indicates the location of (C). For areas shaded in grey, high-resolution bathymetric data are unavailable. Figure modified from Hustoft et al. (2009). **C)** Detailed bathymetric map of the pockmark field on the south-eastern Vestnesa Ridge segment with location of the studied cores.

Table 1. Coring locations, recovery, water depth and sea floor setting of the sediment gravity cores used in this study. Cores are listed from SE to NW. Table from Schneider et al. (in review).

Core ID (Year)	Coordinates	Recovery (cm)	Depth (m bsf)	Distance to next core (km)	Seafloor setting	Reference and cruise
HH-13-200 (2013)	78.981 °N 7.061 °E	270	1205	3.70	Undisturbed seafloor	This thesis, Cruise CAGE-HH-2013
HH-13-203 (2013)	79.002 °N 6.928 °E	300	1210	0.1	Pockmark with flare (Lomvi)	Ambrose et al., 2015, Schneider et al. 2017, Cruise CAGE-HH-2013
JM10-335GC (2010)	79.002 °N 6.922 °E	485	1197	0.7	Pockmark with flare (Lomvi)	Sztybor and Rasmussen 2017, Cruise JM10
CAGE-14-1-GC16 (2014)	79.008 °N 6.900 °E	475	1217	0.46	Pockmark with flare (Lunde)	This thesis, Cruise CAGE 14-1
JCR211-GC26 (2008)	79.011 °N 6.907 °E	386	1210	0.60	Pockmark with flare	Panieri et al. 2014, Cruise JR211
CAGE-14-1-GC17 (2014)	79.013 °N 6.880 °E	440	1207	1.18	Pockmark	This thesis, Cruise CAGE 14-1
HH-13-211 (2013)	79.018 °N 6.831 °E	498	1202	0.40	Pockmark	Ambrose et al. 2015, Cruise CAGE-HH-2013
HH-13-212 (2013)	79.020 °N 6.816 °E	516	1202	0.91	Undisturbed seafloor	Reference core This thesis, Cruise CAGE-HH-2013
HH-13-213 (2013)	79.025 °N 6.782 °E	520	1203	27.76	Pockmark with flare (Torsk)	This thesis, Cruise CAGE-HH-2013
JM10-330GC (2010)	79.130 °N 5.600 °E	420	1300		Pockmark	Consolaro et al. 2015, Cruise JM10

4.4.2 Stable isotope analyses of foraminifera and carbonate nodules

Samples for stable oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) isotope analysis of foraminiferal calcite tests were collected typically at 10 cm intervals and from the reference core HH-13-212 at 5 cm intervals. Selected samples from cores HH-13-203 and HH-13-211 were obtained at higher spatial resolution (Schneider et al. in review). The samples were freeze dried, weighed and wet-sieved (mesh sizes 63 µm, 100 µm, 1 mm). The sieve residues were dried at 40°C and were subsequently investigated using light microscopes. Benthic (*Cassidulina neoteretis* [Seidenkrantz 1995], *Melonis barleeanus* [Williamson 1858]) and planktic foraminifera (*Neogloboquadrina pachyderm*a sinistral (sin.) [Ehrenberg 1861]) were picked for isotope measurements from the dry residue of the > 100 µm size fraction. We selected those species since they are abundant throughout the cores, common in the Arctic Ocean, and were used in previous similar studies from Vestnesa Ridge.

The $\delta^{18}O$ and $\delta^{13}C$ composition of foraminiferal tests were analysed using a ThermoFinnigan MAT252 mass spectrometer coupled to a CarboKiel-II carbonate preparation device at the Serveis Cientifico-Técnics of the University in Barcelona in Spain, and at the Stable Isotope Laboratory at the department of Geosciences at UiT in Tromsø. $\delta^{18}O$ and $\delta^{13}C$ isotope analyses of carbonate nodules were performed using a ThermoScientific MAT253 mass spectrometer coupled to a Finnigan Gasbench II at the Stable Isotope Laboratory at UiT. Analytical precision was estimated to be better than ±0.08‰ for oxygen and ±0.03‰ for carbon.

4.4.3 Mineralogical composition of carbonate nodules

The mineralogical composition of carbonate nodules was investigated using a Bruker D8 Advance diffractometer (Cu K_α radiation in 3-75° 2θ range) at the Geological Survey of Norway in Trondheim (Schneider et al. in review, Schneider et al. in prep.). The quantitative mineralogical composition of the carbonate phases was interpreted and modelled by using the Rietveld algorithm-based code Topas-4 by Bruker. Following a displacement correction of the spectrum made on the main quartz peak, the displacement of calcite d_{104} was used to estimate the amount of $MgCO_3$ mol % (Goldsmith and Graf, 1958).

4.4.4 Visual investigations of foraminiferal tests

Light microscopy

Visible modifications in the foraminiferal test microstructure and wall surface texture due to diagenetic alteration have been described on complete tests and polished wall sections for planktic foraminifera (Sexton et al. 2006, Regenberg et al. 2007, Sexton and Wilson 2009, Edgar et al. 2013). In order to evaluate diagenetic alteration of *C. neoteretis* tests, unbroken tests were photographed using a Leica DFC 450 digital camera mounted on a Leica Z16 Apo light microscope.

Scanning Electron Microscopy (SEM)

In addition, complete tests and polished sections of selected foraminifera were examined with a Hitachi TM-3030 Scanning Electron Microscope (SEM) and a Carl Zeiss LEO 1450VP SEM. This allowed investigating the microstructure of the exterior test wall, wall cross sections, the interior of the chambers, and the pores.

Energy Dispersive X-ray Spectrometry (EDS)

Subsequently, the imaged foraminiferal specimens were analysed with a Hitachi TM-3030 SEM equipped with a Bruker Quantax 70 Energy Dispersive X-ray Spectrometer (EDS) to assess the elemental composition of both the test and secondary overgrowth. The uncalibrated EDS measurements do not provide an absolute quantification of the elemental composition of the studied material, but allow for a semiquantitative assessment. Element mapping was performed for a time interval of 360 seconds.

4.4.5 Size-normalised shell weight (SNSW) of foraminiferal tests

Between 5 and 12 *C. neoteretis* and *N. pachyderma* tests from core HH-13-200 (depth interval 50.5-240.5 cm) were weighed using a Mettler Toledo XP2U microbalance with a precision of 0.01 µg. We selected complete tests that were free of sediment and/or pyrite. For weighing, each individual test was placed in its own tin capsule and was stored for at least 12 hours to equilibrate with the ambient humidity. Each test was weighed three times.

To correct for test size variability, size-normalised shell weight (SNSW) was calculated by determining the weight/size ratio. Each test weight was normalised to the individual test size by measuring the minimum diameter from SEM images (Beer et al. 2010, Marshall et al. 2013).

4.4.6 Stable carbon isotope mass balance

In order to disentangle the bulk $\delta^{13}C$ signal measured in foraminifera and to assess the proportions of the original test calcite and the authigenic overgrowth, a mass-balance calculation was applied (Schneider et al. 2017, Schneider et al. in prep.). Schneider et al. (in prep) combine MDAC precipitation rates, which were estimated from porewater profiles, with the MDAC fraction of the $\delta^{13}C$ signal to constrain the duration required for the carbonate precipitation.

5 Summary of papers

Paper I

Diagenetic alteration of benthic foraminifera from a methane seep site on Vestnesa Ridge (NW Svalbard)

Anomalously low $\delta^{13}C$ values in foraminiferal calcite tests are due to diagenetic alteration in methane seep sites. Our study applies diagenetically altered fossil benthic foraminiferal tests as geochemical tracers in reconstructing past methane seepage episodes at Vestnesa Ridge, located at 79°N in 120 m water depth offshore NW Svalbard. We combine examinations of the test wall microstructure, mineralogical and stable carbon isotope composition of foraminifera, and co-occurring authigenic carbonate nodules.

We present a classification of visual and mineralogical characteristics of the exterior and interior test wall microstructure of the benthic foraminiferal species *Cassidulina neoteretis* having experienced different degrees of diagenetic alteration during methane seepage. Carbonate nodules comprising high-Mg calcite cement with 13-15 mol% $MgCO_3$ have $\delta^{13}C$ values as low as -32.3‰, which is consistent with a methane-derived origin. The visual, mineralogical and stable isotope investigations of *C. neoteretis* indicate a variable degree of diagenetic alteration and show $\delta^{13}C$ values between -0.63 and -16.86‰.

The negative $\delta^{13}C$ values in benthic foraminifera are largely caused by precipitation of isotopically light methane-derived authigenic carbonate as high-Mg-calcite coatings, whose relative contribution to the bulk foraminiferal carbonate is estimated to be up to 58 wt%. Another key finding is the identification of the first seepage episode concurrent with Heinrich Event 1 (HE 1), and a second seepage episode at the onset of the Bølling-Allerød Interstadial.

Paper II

Seafloor methane seepage at Vestnesa Ridge (NW Svalbard) since the Last Glacial Maximum

Multiple proxies in the geological record offshore NW Svalbard track shallow subseafloor diagenesis and seafloor methane seepage during the Last Glacial Maximum (LGM) extent and the disintegration of the Svalbard Barents Sea Ice Sheet (SBIS). Vestnesa Ridge, located at 79°N in 1200 m water depth, is one of the northernmost known active methane seep sites and is characterised by a subseafloor fluid flow system, numerous seafloor pockmarks, and gas flares in the water column. In this study, we develop a Late Pleistocene and Holocene stratigraphic framework, use stable oxygen and carbon isotope signatures ($\delta^{18}O$, $\delta^{13}C$) of benthic and planktic foraminifera, the mineralogical and carbon isotope composition of methane-derived authigenic carbonate (MDAC), and sediment geochemical data of ten sediment cores to assess methane seepage variability on Vestnesa Ridge.

The studied cores cover the age range between 31.9 and 10 cal ka BP and record 32 negative $\delta^{13}C$ excursions in benthic and planktic foraminifera with amplitudes down to -29‰ VPDB. These $\delta^{13}C$ excursions are often associated with elevated Ca/Ti and Sr/Ti elemental ratios in sediments, and methane-derived authigenic carbonate nodules. The precipitation of MDAC overgrowth on foraminiferal tests explains most of the negative $\delta^{13}C$ excursions. In this dataset, the oldest recorded methane emission episodes on Vestnesa Ridge occurred between the LGM (24-23.5 cal ka BP), and during Heinrich Event 1 (HE 1; 17.7-16.8 cal ka BP).

Geological indicators for past subseafloor methane cycling and seafloor methane seepage, such as negative foraminiferal $\delta^{13}C$ excursions, MDAC nodules, and elevated Sr/Ti elemental ratios recorded in post-LGM sediments, possibly represent vertical migration of the sulphate-methane transition zone (SMTZ) and post-date sedimentation by up to 13.4 ka. However, it is important to note that indications of post-LGM seafloor methane seepage at Vestnesa Ridge also correspond to the established methane efflux chronology for the adjacent Barents Sea shelf, implying that glacio-isostatic adjustments and associated re-activation of pre-existing deep-seated faults after disintegration of the SBIS are likely important controls on fluid migration towards the seafloor at Vestnesa Ridge.

Paper III

Diagenetic alteration of foraminifera reveals minimum methane seepage duration

Negative $\delta^{13}C$ excursions in foraminifera throughout the geological history have long been recognised as indicators for past methane cycling and explanations for the isotope shift have been intensely investigated. Despite many studies of negative $\delta^{13}C$ excursions, the quantitative interpretation of these records remains challenging.

Our study confirms that the precipitation of methane-derived authigenic carbonate around foraminiferal tests accounts for up to 60 % of the measured $\delta^{13}C$ signal, and test preservation deteriorates due to diagenetic alteration. For the first time, size-normalised shell weight data from foraminifera found at seep sites have been measured. In conjunction with the shift in carbon isotope values and preservation, the precipitation of methane-derived authigenic carbonate was found to increase foraminiferal size-normalised shell weight. The amount of authigenic carbonate coating the planktic foraminiferal species *Neogloboquadrina pachyderma* and the benthic species *Cassidulina neoteretis* is similar, although benthic foraminiferal tests tend to accumulate slightly more authigenic overgrowth.

The size-normalised shell weight data precisely reveal the authigenic fraction of the $\delta^{13}C$ signal and thus allow estimating the minimum duration required to precipitate the authigenic carbonate. Our calculations suggest that centuries to millennia (600 - 1100 years) are required to precipitate sufficient authigenic carbonate to explain the measured negative $\delta^{13}C$ excursions. With this approach, we expand the traditional set of methodological tools applied for studying past methane seepage and attempt to estimate the duration required for the precipitation of methane-derived authigenic carbonate.

6 Synthesis

6.1 Diagenetically altered foraminifera are sensitive proxies of methane seepage

This thesis gives a detailed rendition on how foraminifera can be used for reconstructing past methane seepage. This work underlines that benthic foraminifera are very sensitive to methane-derived diagenesis, and diagenetically altered foraminiferal tests are reliable seepage proxies.

Foraminiferal tests are small and abundant in the sediment, and since biogenic calcite and authigenic Mg-calcite were found to be structurally identical, they are excellent crystallisation templates for MDAC (Schneider et al. 2017, Panieri et al. 2017a). Through a unique set of multiple interdependent characteristics such as changes in test microstructure and geochemical composition, foraminiferal tests can document the occurrence of methane in sediments. For example, systematic observations reveal that *C. neoteretis* tests, which experienced methane exposure, exhibit a high degree of diagenetic alteration, and display considerable increases in shell weight and Mg-enrichment due to MDAC overgrowth (Schneider et al. 2017, Schneider et al. in prep.). These changes concur with the shift to the most negative $\delta^{13}C$ values.

In comparison with other common proxies for methane release such as MDAC nodules and fossil chemosynthetic macrofauna, benthic foraminifera appear more sensitive to methane-derived diagenesis. This is possible because their tests already occur in the sediment and provide precipitation templates when seepage begins. This advantage allows diagenetically altered benthic foraminiferal tests to capture the onset of seepage or weak seepage before solid MDAC crusts formed and before chemosynthetic macrofauna colonized the seep. As it was suggested for seepage during Heinrich Event 1 (Ambrose et al. 2015, Schneider et al. 2017), diagenetically altered foraminifera are able to refine seepage reconstructions.

The $\delta^{13}C$ values observed in diagenetically altered foraminifera can be explained by a fraction of pristine foraminiferal test calcite and a fraction of authigenic overgrowth. Isotope mass balance approaches disentangle the $\delta^{13}C$ signal and reveal that the diagenetic contribution is large (Torres et al. 2003, Millo et al. 2005, Schneider et al. 2017, Schneider et al. in prep.). In addition, the amount of the authigenic overgrowth can be determined by using changes in shell weight (Schneider et al. in prep.). Combining the authigenic amount and its fraction of the $\delta^{13}C$ signal with authigenic carbonate precipitation rates allowed constraining the duration of seepage for the first time (Schneider et al. in prep.). To date, this type of information is unexplored. Therefore, this is a promising approach to expand the traditional set of methodological tools applied for studying past methane seepage, and unlocks crucial information that will significantly improve our understanding of seafloor methane seepage.

6.2 The methane seepage history from Vestnesa Ridge aligns with SBIS deglaciation

A review of new and existing foraminiferal $\delta^{13}C$ records and the integration of these records with additional information from MDAC nodules, and fossil chemosynthetic bivalves offers a multidimensional perspective on past methane seepage from Vestnesa Ridge.

Modelling results propose a petroleum system established offshore north-western Svalbard around 6 Ma ago when hydrocarbon generation from buried Miocene source rocks commenced (Knies et al. 2018) and seismic data suggest seepage at Vestnesa Ridge initiated simultaneously with the onset of Northern Hemispheric glaciations ca. 2.7 Ma ago (Plaza-Faverola et al. 2015). Foraminiferal $\delta^{13}C$ records, MDAC nodules, and fossil chemosynthetic bivalves suggest seepage occurred between 24-23.5 cal ka BP when the former SBIS reached its Last Glacial Maximum extent, and between 17-16 cal ka BP when seepage coincided with an interval of elevated bottom water temperatures during deglaciation (Ambrose et al. 2015, Sztybor and Rasmussen 2017, Schneider et al. in review).

The timing of seafloor methane seepage from Vestnesa Ridge aligns with similar observations from carbonate crusts that formed shortly after the deglaciation of the shelf offshore western Svalbard, the Norwegian Shelf, and the Barents Sea (Berndt et al. 2014, Crémière et al. 2016, Sauer et al. 2017, Crémière et al. submitted manuscript). All those carbonates have formed during the retreat and thinning of adjacent major ice sheets. Ice sheets exert large horizontal and vertical stresses on the underlying Earth crust and mantle during growth and particularly during deglaciation, and can cause crustal subsidence or rebound, and horizontal flexure (Lambeck and Chappell 2001, Peltier 2001, Whitehouse 2009, Lund 2015). These stresses are known as glacio-isostatic adjustments (GIA) and may cause tectonic lineaments to fail. Tectonic lineaments are common on the western Svalbard continental margin and fluid migration driven by ice sheet dynamics and associated tectonic stresses has been suggested for north-western Svalbard (Winkelmann et al. 2008. Plaza-Faverola et al. 2015, Ambrose et al. 2016). Fluid discharge along faults has been inferred from the chemical characteristics of migrating gaseous hydrocarbons (Knies et al. 2004), from pockmark distribution in one of the major fjord systems on Svalbard's west coast (Roy et al. 2015), or was observed from the mapping of gas flares in the water column (Mau et al. 2017). Hence, GIA and associated tectonic stresses may have initiated structurally controlled fluid flow at Vestnesa Ridge. Fluid migration along tectonic lineaments may also explain the three negative $\delta^{13}C$ excursions and MDAC nodules that were found in core HH-13-200, which was recovered 3.5 km away from an active pockmark, but near non-outcropping faults (Schneider et al. in prep.).

Since GIA continue long after an ice sheet has vanished, this may help sustaining fluid flow and methane seepage after the deglaciation until present-day. Remaining stresses from GIA have been suggested to continue triggering earthquake activity, facilitating fluid flow, and driving methane seepage (Crémière et al. 2016, Sauer et al. 2017, Schneider et al. in review). Furthermore, evidence for shallow subseafloor diagenesis is recorded in host sediments that are younger than 14 cal ka BP, although recent diagenetic alteration near the present-day SMTZ cannot be excluded (Schneider et al. in review).

In addition, this work reveals that $\delta^{13}C$ records along Vestnesa Ridge differ in amplitude and number of excursions between the north-western ridge segment, where pockmarks are inactive today, and the currently active south-eastern ridge segment (Schneider et al. in review). Our understanding of methane emission episodes across Vestnesa Ridge may be biased by having only one record from the north-western segment available. However, this segment is characterized by two emission events with foraminiferal $\delta^{13}C$ excursions of down to -4.4‰ recorded in Bølling-Allerød and mid-Holocene-aged host sediments (Consolaro et al. 2015). In contrast, foraminiferal $\delta^{13}C$ records from the south-eastern segment exhibit 30 negative excursions with considerably larger amplitude down to -29.5‰ (Schneider et al. in review). In addition, MDAC nodules occur frequently and seepage supported chemosynthetic macrofauna (Panieri et al. 2014, Ambrose et al. 2015, Sztybor and Rasmussen 2017, Schneider et al. in review). Despite Vestnesa Ridge is located on average 1200 m below sea level, its complex tectonic setting appears susceptible to perturbations from glacio-isostatic adjustments. A major fault separating the north-western and south-eastern ridge segment (pers. comm. A. Plaza-Faverola) may have dampened ice sheet-induced tectonic activity in the north-west, while the south-eastern ridge segment experienced stronger tectonic stresses leading to intensified seepage, which is documented in multiple seepage proxies. This offers a scenario for explaining the regional differences of seepage at Vestnesa Ridge.

7 Conclusions

The overall objective of this PhD thesis was to investigate the characteristics, timing, duration, and drivers of methane seepage from Vestnesa Ridge, one of the northernmost known active methane seep sites, using diagenetically altered benthic foraminifera combined with additional proxies and mass balance calculations. The main conclusions that result from the research performed throughout the course of the PhD project are:

Foraminiferal tests provide suitable templates for authigenic carbonate precipitation. Therefore, diagenetically altered foraminifera offer a unique set of information comprising negative $\delta^{13}C$ values, increased shell weight, and variations in the degree of diagenesis. They are remarkably sensitive seepage proxies and hence may represent one end member of proxies indicating shallow subseafloor diagenesis and/or seafloor methane seepage.

Studying diagenetically altered foraminiferal $\delta^{13}C$ records offers the possibility to develop a conceptual idea for estimating the duration of authigenic carbonate precipitation episodes. This approach expands the traditional set of methodological tools applied for studying past methane seepage and unlocks crucial information that will significantly improve our understanding of seafloor methane seepage.

A systematic and comprehensive approach integrates new and published records of past seepage episodes at Vestnesa Ridge and results from other formerly glaciated continental margins in the Nordic Seas. The results show that seepage chronologies appear to align with the deglaciation of the adjacent major ice sheets. Glacio-isostatic adjustments accompany the disintegration of these ice sheets, which may have triggered tectonic instabilities, and initiated fluid migration. Therefore, Earth system processes such as glacio-isostatic adjustments are considered as important control of fluid migration and seafloor methane release at seeps that are located near former large ice sheets.

8 Future perspectives

Although this thesis provides new insights in the interpretation of foraminiferal negative $\delta^{13}C$ excursions, the post-depositional diagenesis of calcareous microfossils remains poorly understood. Suggestions for future studies emerged from the seepage duration estimation, which was leading to the question if the amount of available templates or the surface area of these templates controls MDAC precipitation. Thus, quantifying the internal and external surface area of foraminifera might allow to determine more precisely how much authigenic carbonate can precipitate in a given time. X-ray microcomputed tomography is a tool that provides high precision morphometric 3D data including volume and surface area (Iwasaki et al. 2015), a type of information that can be helpful to constrain the surface area that is available for precipitation. In addition, precipitation experiments under laboratory conditions combined with regular weighing of the precipitation templates may reveal insights in the process of mass accumulation through MDAC precipitation. Laboratory experiments may also shed light into the question if diagenesis commences on living or entirely on dead foraminifera after burial, and if authigenic carbonate precipitation varies between different foraminiferal species.

Another curiosity that was raised during this study is if the MDAC coating on foraminiferal tests is precipitated in a single diagenetic episode and as one layer. Similar to large carbonate crusts (Bayon et al. 2009, Crémière et al. 2016, Sauer et al. 2017), the authigenic carbonate precipitation around microfossils could contain multiple layers from different diagenetic episodes. Studies of polished foraminiferal mounds using SEM, EDS, electron microprobe analyses (Panieri et al. 2017a) or carbonate density measurements using X-ray microcomputed tomography (Iwasaki et al. 2015) to compare the geochemical composition of such layers may help answering this question.

Furthermore, AOM at the present-day SMTZ can cause recent diagenesis. Particularly at the south-eastern Vestnesa Ridge segment where the surface sediment dates to around 10 cal ka BP and the present-day SMTZ is located in this old host sediment, negative foraminiferal $\delta^{13}C$ excursions cannot be interpreted straight forward. When porewater profiles are absent, Schneider et al. (in review) suggest an approach to identify the present-day SMTZ from sedimentary records. Systematically testing this hypothesis with a larger selection of gravity cores and a dataset consisting of porewater profiles, foraminiferal $\delta^{13}C$ records, and sediment XRF records may help validating this premise.

In order answer the question if the seepage chronology of Vestnesa Ridge extends over several glacial cycles, foraminiferal records and authigenic carbonates from longer sediment cores are essential. Promising advances have been made in 2016 when authigenic carbonate crusts were collected from the seafloor, and two long sediment cores were recovered from pockmarks using the MARUM-MeBo seafloor drilling rig. Additional records may also unravel if seepage between the active and inactive Vestnesa Ridge segment differs, and what the reasons for such spatial variability are.

The main goal of methane seep research is to advance our understanding of its impact on the carbon cycle and the climate system (Dickens 2003, Schrag et al. 2013). Therefore, it is crucial to estimate how much methane is leaking from marine reservoirs, and to constrain the amount of methane-derived carbonate that is sequestered before it may enter the water column or the atmosphere. Important factors that are driving diagenesis are methane flux, microbial consumption of the methane, and rates of authigenic carbonate precipitation. Although seepage monitoring studies are challenging to conduct and are therefore scarce, they are the best methods to further constrain methane flux, to inform models, and to provide an improved overview over heterogeneous seepage areas (Torres et al. 2002, Luff and Wallmann 2003, Hong et al. 2016 and references therein). Monitoring and modelling approaches are promising tools to measure present-day methane flux, while geological records may help to estimate past methane flux. For example, high concentrations of $\delta^{13}C$-depleted biomarkers have been interpreted to indicate strong and/or relatively long lasting methanotrophic activity (Cook et al. 2001, Hinrichs et al. 2003, Zhang et al. 2003). Quantifying AOM rates from biomarker abundance and combining such information with the amount of methane-derived carbon in authigenic carbonate may allow estimating how much methane is sequestered in microbial biomass and authigenic carbonates. Such information may aid investigating the feedbacks between methane seepage, the carbon cycle, and the climate system.

References

Aagaard, K., Foldvik, A., Hillman, S.R., 1987. The west Spitsbergen current: disposition and water mass transformation. J. Geophys. Res. 92, 3778–3784.

Akimoto, K., Tanaka, T., Hattori, M., Hotta, H., 1994. Recent benthic foraminiferal assemblages from the cold seep communities- a contribution to the methane gas indicator, in Pacific Neogene Events in Time and Space, edited by R. Tsuchi, pp. 11–25, Univ. of Tokyo Press.

Aloisi, G., Pierre, C., Rouchy, J.M., Foucher, J.P., Woodside, J., 2000. Methane-related authigenic carbonates of Eastern Mediterranean Sea mud volcanoes and their possible relation to gas hydrate destabilisation. Earth Planet. Sci. Lett. 184, 321–338. http://dx.doi.org/10.1016/S0012-821X(00)00322-8.

Ambrose, W.G., Jr., Panieri, G., Schneider, A., Plaza-Faverola, A., Carroll, M.L., Aström, E.K.L., Locke. V., W.L., Carroll, J., 2015. Bivalve shell horizons in seafloor pockmarks of the last glacial interglacial transition: a thousand years of methane emissions in the Arctic Ocean. Geochem. Geophys. Geosyst. 16, 4108–4129. http://dx.doi.org/10.1002/2015GC005980.

Armstrong, H.A. and Brasier, M.D., 2005. Microfossils. 2nd Edition. pp. 142-187. Blackwell Publishing.

Åström, E. K. L*.,* M. L. Carroll*,* W. G. Ambrose*,* Carroll, J., 2016*.* Arctic cold seeps in marine methane hydrate environments: Impacts on shelf macrobenthic community structure offshore Svalbard. Mar. Ecol. Prog. Ser. 552*:* 1–18*. doi:*10.3354/meps11773.

Barnes, R.O. and Goldberg, E.D., 1976. Methane production and consumption in anaerobic marine sediments. Geology 4: 297–300.

Bayon, G., Henderson, G.M. Bohn, M., 2009. U–Th stratigraphy of a cold seep carbonate crust. Chemical Geology 260, 47–56. doi:10.1016/j.chemgeo.2008.11.020.

Beaudoin, Y.C., Boswell, R., Dallimore, S.R., Waite, W. (Eds.), 2014. Frozen Heat: A UNEP Global Outlook on Methane Gas Hydrates. United Nations Environment Programme, GRID-Arendal.

Beer, C.J., Schiebel, R., Wilson, P.A., 2010. Technical Note: On methodologies for determining the size-normalised weight of planktic foraminifera. Biogeosciences 7, 2193-2198. doi:10.5194/bg-7-2193-2010.

Berndt, C., Feseker, T., Treude, T., Krastel, S., Liebetrau, V., Hiemann, H., Bertics, V.J., Dumke, I., Dunnbier, K., Ferré, B., Graves, C., Gross, F., Hissmann, K., Huhnerback, V., Krause, S., Lieser, K., Schauer, J., Steinle, L., 2014. Temporal constraints on hydrate-controlled methane seepage off Svalbard, Science 343, 284–287. doi: 10.1126/science.1246298.

Bernhard, J.M., J.B. Martin, Rathburn, A.E., 2010. Combined carbonate carbon isotopic and cellular ultrastructural studies of individual benthic foraminifera: 2. Toward an understanding of apparent disequilibrium in hydrocarbon seeps, Paleoceanography, 25, PA4206, doi:10.1029/2010PA001930.

Bernhard, J.M., Buck, K.R., Barry, J.P., 2001. Montery Bay cold-seep biota: Assemblages, abundance and ultrastructure pf living foraminifera. Deep Sea Research Part I, 48, 2233.2249.

Bernhard, J.M. and Bowser, S.S., 2008. Peroxisome Proliferation in Foraminifera Inhabiting the Chemocline: An Adaptation to Reactive Oxygen Species Exposure? J. Eukaryot. Microbiol., 55. 135–144.

Bernardino, A.F., Levin, L.A., Thurber, A.R., Smith, C.R., 2012. Comparative Composition, Diversity and Trophic Ecology of Sediment Macrofauna at Vents, Seeps and Organic Falls. PLoS ONE 7(4): e33515. doi:10.1371/journal.pone.0033515.

Beszczynska-Möller, A., Fahrbach, E., Schauer, U., Hansen, E., 2012. Variability in Atlantic water temperature and transport at the entrance to the Arctic Ocean, 1997–2010. ICES Journal of Marine Science 69, 852–863. doi:10.1093/icesjms/fss056.

Birgel, D., Thiel, V., Hinrichs, K.-U., Elvert, M., Campbell, K.A., Reitner, J., Farmer, J.D., Peckmann, J., 2006. Lipid biomarker patterns of methane-seep microbialites from the Mesozoic convergent margin of California. Organic Geochemistry 37, 1289–1302.

Birgel, D. and Peckmann, J., 2008. Aerobic methanotrophy at ancient marine methane seeps: A synthesis. Organic Geochemistry 39, 1659-1667.

Boetius, A., Ravenschlag, K., Schubert, C.J., Rickert, D., Widdel, F., Giesecke, A., Amann, R., Jørgensen, B.B., Witte, U., Pfannkuche, O., 2000. A marine microbial consortium apparently mediating anaerobic oxidation of methane. Nature 407, 623–626. doi:10.1038/35036572.

Boetius A. and Wenzhoefer F., 2013. Seafloor oxygen consumption fuelled by methane from cold seeps. Nature Geosciences 6, 725-734. doi:10.1038/NGEO1926.

Borowski, W., Paull, C. K., Ussler, W., 1996. Marine pore-water sulphate profiles indicate in situ methane flux from underlying gas hydrate. Geology 24, 655–658.

Bohrmann, G., Greinert, J., Suess, E., Torres, M., 1998. Authigenic carbonates from the Cascadia subduction zone and their relation to gas hydrate stability. Geology 26, 647–650.

Bohrmann, G., Suess, E., Greinert, J., Teichert, B., Naehr, T., 2002. Gas hydrate carbonates from Hydrate Ridge, Cascadia Convergent Margin: Indicators of near-seafloor clathrate deposits. Proc. Fourth Int. Conf. Gas Hydrates, pp. 102–107.

Bowden, D.A., Rowden, A.A., Thurber, A.R., Baco, A.R., Levin, L.A., et al., 2013. Cold Seep Epifaunal Communities on the Hikurangi Margin, New Zealand: Composition, Succession, and Vulnerability to Human Activities. PLoS ONE 8(10): e76869. doi:10.1371/journal.pone.0076869.

Bradley, R. 2015. Paleoclimatology. 3rd Edition. p. 195-277. Academic Press, Harcourt Brace and Company, San Diego, California.

Burton, E.A., 1993. Controls on marine carbonate cement mineralogy: review and reassessment. Chemical Geology 105, 163-179.

Bünz, S., Polyanov, S., Vadakkepuliyambatta, S., Consolaro, C., Mienert, J., 2012. Active gas venting through hydrate-bearing sediments on the Vestnesa Ridge, offshore W Svalbard. Mar. Geol. 332–334, 189–197. http://dx.doi.org/10.1016/j.margeo.2012.09.012.

Campbell, K.A., 2006. Hydrocarbon seep and hydrothermal vent paleoenvironments and paleontology: Past developments and future research directions. Palaeogeography, Palaeoclimatology, Palaeoecology 232, 362– 407.

Canfield D.E., Berner R.A., 1987. Dissolution and pyritization of magnetite in anoxic marine sediments. Geochim. Cosmochim. Acta 51, 645-659.

Claypool, G.E., and Kaplan, I.R., 1974. The origin and distribution of methane in marine sediments. In: Kaplan, I.R. (Ed.), Natural Gases in Marine Sediments. Plenum Press, New York, London, pp. 99–139.

Cook, M.S., Keigwin, L.D., Birgel, D., Hinrichs, K.U., 2011. Repeated pulses of vertical methane flux recorded in glacial sediments from the southeast Bering Sea, Paleoceanography, 26, PA2210, doi:10.1029/2010PA001993.

Cokelet, E.D., Tervalon, N., Bellingham, J.G., 2008. Hydrography of the West Spitsbergen Current, Svalbard Branch: Autumn 2001, J. Geophys. Res. 113, C01006, doi:10.1029/2007JC004150.

Consolaro, C., Rasmussen, T.L., Panieri, G., Mienert, J., Bünz, S., Sztybor, K., 2015. Carbon isotope ($\delta^{13}C$) excursions suggest times of major methane release during the last 14 kyr in Fram Strait, the deep-water gateway to the Arctic. Clim. Past 11, 669–685. http://dx.doi.org/10.5194/cp-11-669-2015.

Conti, S., Fontana, D., Mecozzi, S., Panieri, G., Pini, G.A., 2010. Late Miocene seep-carbonates and fluid migration on top of the Montepetra intrabasinal high (Northern Apennines, Italy): Relations with synsedimentary folding. Sedimentary Geology 213, 41-54.

Crémière, A., Bayon, G., Ponzevera, E., Pierre, C., 2013. Paleo-environmental controls on cold seep carbonate authigenesis in the Sea of Marmara. Earth and Planetary Science Letters 376, 200-211.

Crémière, A., Lepland, A., Chand, S., Sahy, D., Condon, D., Noble, S.R., Martma, T., Thorsnes, T., Sauer, S., Brunstad, H., 2016. Timescales of methane seepage on the Norwegian margin following collapse of the Scandinavian Ice Sheet. Nature Communication 7, 11509. doi: 10.1038/ncomms11509.

Crémière, A., Chand, S., Sahy, D., Thorsnes, T., Martma, T., Noble, S.R., Pedersen, J.H., Brunstad, H., Lepland, A., Structural controls on seepage of thermogenic and microbial methane since the last glacial maximum in the Harstad Basin, southwest Barents Sea. Submitted manuscript.

Dewangan, P., Basavaiah, N., Badesab, F.K., Usapkar, A., Mazumdar, A., Joshi, R., Ramprasad, T., 2013. Diagenesis of magnetic minerals in a gas hydrate/cold seep environment off the Krishna–Godavari basin, Bay of Bengal. Marine Geology 340, 57–70. http://dx.doi.org/10.1016/j.margeo.2013.04.016.

Dickens, G.R., 2003. Rethinking the global carbon cycle with a large, dynamic and microbially mediated gas hydrate capacitor. Earth Planet. Sci. Lett. 213, 169–183.

Dickens, G. R., 2011. Down the Rabbit Hole: toward appropriate discussion of methane release from gas hydrate systems during the Paleocene-Eocene thermal maximum and other past hyperthermal events, Clim. Past 7, 831-846. https://doi.org/10.5194/cp-7-831-2011.

Dubilier, N*.,* C. Bergin*,* Lott*, C.,* 2008*.* Symbiotic diversity in marine animals: The art of harnessing chemosynthesis*.* Nat. Rev. Microbiol. 6*:* 725–740*. doi:*10.1038/nrmicro1992*.*

Eiken, O. and Hinz, K., 1993. Contourites in the Fram Strait. Sediment. Geol. 82, 15–32.

Edgar, K.M., Pälike, H., Wilson, P.A., 2013. Testing the impact of diagenesis on the δ18O and δ13C of benthic foraminiferal calcite from a sediment burial depth transect in the equatorial Pacific. Paleoceanography 28, 468–480. doi:10.1002/palo.20045.

Engen, Ø., J. I. Faleide, Dyreng, T.K., 2008. Opening of the Fram Strait gateway: A review of plate tectonic constraints, Tectonophysics 450, 51-69.

Etiope, G., 2015. Natural Gas Seepage. The Earth`s Hydrocarbon Degassing. 199pp. Springer.
Ferrell R.E. and Aharon, P., 1994. Mineral assemblages occurring around hydrocarbon vents in the northern Gulf of Mexico. Geo-Marine Letters 14, 74-80.
Goldsmith, J. and Graf, D., 1958. Relation between lattice constants and composition of the Ca-Mg carbonates. Am. Mineral. 43, 84–101.
Goswami, B.K., Weitemeyer, K.A., Minshull, T.A., Sinha, M.C., Westbrook, G.K., Chabert, A., Henstock, T.J., Ker, S., 2015. A joint electromagnetic and seismic study of an active pockmark within the hydrate stability field at the Vestnesa Ridge, West Svalbard margin, J. Geophys. Res., 120, 6797–6822, doi:10.1002/2015JB012344.
Greinert, J., 1999. Rezente submarine Mineralbildungen: Abbild geochemischer Prozesse an aktiven Fluidaustrittsstellen im Aleuten- und Cascadia-Akkretionskomplex, Ph.D. dissertation, GEOMAR Rep. 87, 21 pp., Univ. of Kiel, Kiel, Germany.
Greinert, J., Bohrmann, G., Suess, E., 2001. Gas Hydrate-Associated Carbonates and Methane-Venting at Hydrate Ridge: Classification, Distribution, and Origin of Authigenic Lithologies. In: Natural Gas Hydrates: Occurrence, Distribution, and Detection. Geophysical Monograph 124. 15 pp.
Gross, O., 2004. *Melonis barleeanus* (Williamson, 1858). In: Hayward, B.W.; Cedhagen, T.; Kaminski, M.; Gross, O., 2017. World Foraminifera Database. Accessed through: World Register of Marine Species at http://www.marinespecies.org/aphia.php?p=taxdetails&id=113563 on 2017-07-12.
Heinz, P., Sommer, S., Pfannkuche, O., Hemleben, C., 2005. Living benthic foraminifera in sediments influenced by gas hydrates at the Cascadia convergent margin, NE Pacific. Marine Ecology. Progress Series 304, 77–89.
Herguera, J.C., Paull, C.K., Perez, E., Ussler W., Peltzer, E.,2014. Limits to the sensitivity of living benthic foraminifera to pore water carbon isotope anomalies in methane vent environments, Paleoceanography, 29, 273–289, doi:10.1002/2013PA002457.
Hill, T. M., Kennett, J.P., Spero, H.J., 2003. Foraminifera as indicators of methane-rich environments: A study of modern methane seeps in Santa Barbara Channel, California. Marine Micropaleontology 49, 123-138.
Hill, T.M., Kennett, J.P., Valentine, D.L., 2004. Isotopic evidence for the incorporation of methane-derived carbon into foraminifera from modern methane seeps, Hydrate Ridge, Northeast Pacific. Geochim. Cosmochim. Acta 68, 4619–4627. http://dx.doi.org/10.1016/j.gca.2004.07.012.
Hinrichs, K.-U., Hayes, J.-M., Sylva, S.P., Brewer, P.G., DeLong, E.F., 1999. Methane-consuming archaebacteria in marine sediments. Nature 398, 802-805.
Hinrichs, K-U., 2001. A molecular recorder of methane hydrate destabilisation. Geochemistry, Geoshysics, Geosystems. Doi: 10.1029/2000GC000118.
Hinrichs, K-U., Hmelo, L.R., Sylva, P., 2003. Molecular Fossil Record of Elevated Methane Levels in Late Pleistocene Coastal Waters. Nature 299, 1214-1217.
Hong, W.-L., Sauer, S., Panieri, G., Ambrose, W., James, R., Plaza-Faverola, A., Schneider, A., 2016. Removal of methane through hydrological, microbial, and geochemical processes in the shallow sediments of pockmarks along eastern Vestnesa Ridge (Svalbard). Limnol. Oceanogr. 61, 324–343. http://dx.doi.org/10.1002/lno.10299.
Howe, J.A., Shimmield, T.M., Harland, R., 2008. Late quaternary contourites and glaciomarine sedimentation in the Fram Strait. Sedimentology 55, 179–200. http://dx.doi.org/10.1111/j.1365-3091.2007.00897.x.
Hustoft, S., Bünz, S., Mienert, J., Chand, S., 2009. Gas hydrate reservoir and active methane-venting province in sediments on < 20 Ma young oceanic crust in the Fram Strait, offshore NW-Svalbard. Earth Planet. Sci. Lett. 284, 12–24. http://dx.doi.org/10.1016/j.epsl.2009.03.038.
IPCC, 2013. Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Chapter 8 – Anthropogenic and Natural Radiative Forcing. 82 pp, Cambridge University Press. doi:10.1017/CBO9781107415324.
Iwasaki, S., K. Kimoto, O. Sasaki, H. Kano, M. C. Honda, Okazaki, Y., 2015. Observation of the dissolution process of *Globigerina bulloides* tests (planktic foraminifera) by X-ray microcomputed tomography, Paleoceanography, 30, 317–331, doi:10.1002/2014PA002639.
Jakobsson, M. et al. 2012. The International Bathymetric Chart of the Arctic Ocean (IBCAO) Version 3.0, Geophys. Res. Lett. doi: 10.1029/2012GL052219. Available online at: https://www.ngdc.noaa.gov/mgg/bathymetry/arctic/arctic.html.
Jessen, S.P., Rasmussen, T.L., Nielsen, T., Solheim, A., 2010. A new Late Weichselian and Holocene marine chronology for the western Svalbard slope 30,000–0 cal years BP. Quat. Sci. Rev. 29, 1301–1312. http://dx.doi.org/10.1016/j.quascirev.2010.02.020.

Johnson, J.E., Mienert, J., Plaza-Faverola, A., Vadakkepuliyambatta, S., Knies, J., Bünz, S., Andreassen, K., Ferré, B., 2015. Abiotic methane from ultraslow-spreading ridges can charge Arctic gas hydrates. Geology 43, 371–374. http://dx.doi.org/10.1130/G36440.1.

Judd, A., Hovland, M., 2007. Seabed Fluid Flow: The Impact on Geology, Biology and the Marine Environment. Cambridge University Press pp. 475.

Jørgensen, B.B., Kasten, S., 2006. Sulfur cycling and methane oxidation. In: Marine Geochemistry. 2nd Ed. Schultz, H.D., Zabel, M. (Eds.) Springer. 271-310.

Kiel, S., 2010. On the potential generality of depth-related ecologic structure in cold-seep communities: Evidence from Cenozoic and Mesozoic examples. Palaeogeogr. Palaeoclimatol. Palaeoecol. 295 (1–2), 245–257. http://dx.doi.org/10.1016/j.palaeo.2010.05.042.

Kennett, J.P., Cannariato, K.G., Hendy, I.L., Behl, R.J., 2000. Carbon Isotopic Evidence for Methane Hydrate Instability During Quaternary Interstadials. Science 288, 128-133.

Knies, J. and Stein, R., 1998. New aspects of organic carbon deposition and its paleoceanographic implications along the northern Barents Sea margin during the last 30,000 years. Paleoceanography 13/4, 384-394.

Knies, J., Damm, E., Gutt, J., Mann, U., Pinturier, L., 2004. Near-surface hydrocarbon anomalies in shelf sediments off Spitsbergen: Evidences for past seepages. Geochemistry, Geophysics, Geosystems 5/6, Q06003. doi:10.1029/2003GC000687.

Knies, J., Matthiessen, J., Vogt, C., Laberg, J.S., Hjelstuen, B.O., Smelror, M., Larsen, E., Andreassen, K., Ridvin, T., Vorren, T.O., 2009. The Plio-Pleistocene glaciation of the Barents Sea–Svalbard region: a new model based on revised chronostratigraphy. Quaternary Science Reviews 28, 812-829.

Knies, J., Daszinnies, M. C., Plaza-Faverola, A., Chand, S., Sylta, Ø., Bünz, S., Johnson, L. E., Mattingsdal, R., Mienert, J., 2018. Modelling persistent methane seepage offshore western Svalbard since early Pleistocene. Marine and Petroleum Geology. ISSN 0264-8172.s doi: 10.1016/j.marpetgeo.2018.01.020.

Knittel, K. and Boetius, A., 2009. Anaerobic Oxidation of Methane: Progress with an Unknown Process. Annual Review of Microbiology 63, 311-334. doi: 10.1146/annurev.micro.61.080706.093130.

Lambeck, K. and Chappell, J., 2001. Sea Level Change Through the Last Glacial Cycle. Science 292, 679–686.

Le Coze, F.; Gross, O., 2017. *Neogloboquadrina pachyderma* (Ehrenberg, 1861). In: Hayward, B.W., Cedhagen, T., Kaminski, M., Gross, O., 2017. World Foraminifera Database. Accessed through: World Register of Marine Species at http://www.marinespecies.org/aphia.php/aphia.php?p=taxdetails&id=113458 on 2017-07-12.

Levin, L.A., 2005. Ecology of cold seep sediments: Interactions of fauna with flow, chemistry and microbes. Oceanography and Marine Biology: An Annual Review 43, 1-46.

Levin, L.A. et al., 2016. Hydrothermal Vents and Methane Seeps: Rethinking the Sphere of Influence. Front. Mar. Sci. 3, 1–23. http://dx.doi.org/10.3389/fmars.2016.00072.

Luff, R. and Wallmann, K. 2003. Fluid flow, methane fluxes, carbonate precipitation and biogeochemical turnover in gas hydrate-bearing sediments at Hydrate Ridge, Cascadia Margin: numerical modeling and mass balances. Geochim. Cosmochim. Acta 67, 3403–3421.

Lund, B., 2015. Plaeoseismology of glaciated terrain. Encyclopedia of Earthquake Engineering. 1-16. doi: 10.1007/978-3-642-36197-5_25-1.

Mackensen, A., S. Schumacher, J. Radke, Schmidt, D., 2000. Microhabitat preferences and stable carbon isotopes of endobenthic foraminifera: Clue to quantitative reconstruction of oceanic new production?, Mar. Micropaleontol., 40, 233– 258.

Mackensen, A., Wollenburg, J., Licari, L., 2006. Low $\delta^{13}C$ in tests of live epibenthic and endobenthic foraminifera at a site of active methane seepage. Paleoceanography 12, PA2022. doi:10.1029/2005PA001196.

Mau, S., Römer, M., Torres, M.E., Bussmann, I., Pape, T., Damm, E., Geprägs, P., Wintersteller, P., Hsu, C.-W., Loher, M., Bohrmann, G., 2017. Widespread methane seepage along the continental margin off Svalbard - from Bjørnøya to Kongsfjorden. Nature. Scientific Reports 7, 42997. doi: 10.1038/srep42997.

Marshall, B. J., R. C. Thunell, M. J. Henehan, Y. Astor, Wejnert, K. E., 2013. Planktic foraminiferal area density as a proxy for carbonate ion concentration: A calibration study using the Cariaco Basin ocean time series. Paleoceanography 28, 363-376. doi:10.1002/palo.20034.

Martin, R.A., Nesbitt, E.A., Campbell, K.A., 2007. Carbon stable isotopic composition of benthic foraminifera from Pliocene cold methane seeps, Cascadia accretionary margin. Palaeogeography, Palaeoclimatology, Palaeoecology 246, 260–277.

Martin, R.A., Nesbitt, E.A., Campbell, K.A., 2010. The effects of anaerobic methane oxidation on benthic foraminiferal assemblages and stable isotopes on the Hikurangi Margin of eastern New Zealand. Marine Geology 272, 270–284. doi:10.1016/j.margeo.2009.03.024.

März, C., Hoffmann, J., Bleil, U., de Lange, G. J., Kasten, S., 2008. Diagenetic changes of magnetic and geochemical signals by anaerobic methane oxidation in sediments of the Zambezi deep-sea fan (SW Indian Ocean): Marine Geology 255, 118-130.

McCorkle, D.C., Keigwin, L.D., Corliss, B.H., Emerson, S.R., 1990. The influence of microhabitats on the carbon isotopic composition of deep-sea benthic foraminifera. Paleoceanography 5, 161–185.

Meister, P., Liu, B., Ferdelman, T., Jørgensen, B. B., Khalili, A. 2013. Control of sulphate and methane distributions in marine sediments by organic matter reactivity. Geochim. Cosmochim. Acta 104, 183–193 .

Millo, C., Sarnthein, M., Erlenkeuser, H., Grootes, P.M., Andersen, N., 2005. Methane induced early diagenesis of foraminiferal tests in the south-western Greenland Sea. Mar. Micropaleontol. 58, 1–12. http://dx.doi.org/10.1016/j.marmicro.2005.07.003.

Morris, A. W., and Riley, J. P., 1966. The bromide/chlorinity and sulphate/chlorinity ratio in sea water. Deep-Sea Res. 13: 699-705.

Naehr, T.H., Eichhubl, P., Orphan, V.J., Hovland, M., Paull, C.K., Ussler, W., Lorenson, T.D., Greene, H.G., 2007. Authigenic carbonate formation at hydrocarbon seeps in continental margin sediments: A comparative study. Deep. Res. Part II Top. Stud. Oceanogr. 54, 1268–1291. http://dx.doi.org/10.1016/j.dsr2.2007.04.010.

Niemann, H., Lösekann, T., de Beer, D., Elvert, M., Nadalig, T., Knittel, K., Amann, R., Sauter, E.J., Schlüter, M., Klages, M., Foucher, J.P., Boetius, A., 2006. Novel microbial communities of the Håkon Mosby mud volcano and their role as a methane sink. Nature 443, 854–858. doi:10.1038/nature05227.

Niemann, H. and Elvert, M., 2008. Diagnostic lipid biomarker and stable carbon isotope signatures of microbial communities mediating the anaerobic oxidation of methane with sulphate. Organic Geochemistry 39, 1668-1677.

Niemann, H., Linke, P., Knittel, K., MacPherson, E., Boetius, A., et al. 2013. Methane-Carbon Flow into the Benthic Food Web at Cold Seeps – A Case Study from the Costa Rica Subduction Zone. PLoS ONE 8(10): e74894. doi:10.1371/journal.pone.0074894.

Nisbet, E., Dlugokencky, E., Manning, M., Lowry, D., Fisher, R., France, J., Michel, S., et al., 2016. Rising atmospheric methane: 2007-2014 growth and isotopic shift. Global Biogeochemical Cycles, 30 (9), 1356-1370. https://doi.org/10.1002/2016GB005406.

Novosel, I., Spence, G.D., Hyndman, R.D., 2005. Reduced magnetization produced by increased methane flux at a gas hydrate vent. Marine Geology 216, 265– 274. doi:10.1016/j.margeo.2005.02.027.

Orphan, V.J., House, C.H. Hinrichs, K.-U., McKeegan, K.D., DeLong, E.F., 2001. Methane-consuming archaea revealed by directly coupled isotopic and phylogenetic analysis. Science, 293: 484-487.

Panieri, G., 2003. Benthic foraminifera response to methane release in an Adriatic Sea pockmark. Rivista Italiana di Paleontologia e Stratigrafia 109, 549–562.

Panieri, G., 2006. Foraminiferal response to an active methane seep environment: A case study from the Adriatic Sea. Mar. Micropaleontol. 61, 116–130. http://dx.doi.org/10.1016/j.marmicro.2006.05.008.

Panieri, G. and Sen Gupta, B.K., 2008. Benthic Foraminifera of the Blake Ridge hydrate mound, Western North Atlantic Ocean. Mar. Micropaleontol. 66, 91–102. http://dx.doi.org/10.1016/j.marmicro.2007.08.002.

Panieri, G., Camerlenghi, A., Conti, S., Pini, G.A., Cacho, I., 2009. Methane seepages recorded in benthonic foraminifera from Miocene seep carbonates, Northern Apennines (Italy). Palaeogeogr. Palaeoclimatol. Palaeoecol. 284, 271–282.

Panieri, G., James, R.H., Camerlenghi, A., Cesari, V., Cervera, C.S., Cacho, I., Westbrook, G.K., 2014. Record of methane emissions from the West Svalbard continental margin during the last 16,000 years revealed by $\delta^{13}C$ of benthic foraminifera. Glob. Planet. Change 122, 151–160. http://dx.doi.org/10.1016/j.gloplacha.2014.08.014.

Panieri, G., Lepland, A., Whitehouse, M.J., Wirth, R., Raanes, M.P., James, R.H., Graves, C.A., Crémière, A., Schneider, A., 2017a. Diagenetic Mg-calcite overgrowths on foraminiferal tests in the vicinity of methane seeps. Earth Planet. Sci. Lett. 458, 203–212. http://dx.doi.org/10.1016/j.epsl.2016.10.024.

Panieri, G., Bünz, S., Fornari, D.J., Escartin, J., Serov. P., Jansson, P., Torres, M.E., Johnson, J.E., Hong, W.L., Sauer, S., Garcia, R., Gracias, N., 2017b. An integrated view of the methane system in the pockmarks at Vestnesa Ridge, 79°N. Marine Geology 390, 282-300. http://dx.doi.org/10.1016/j.margeo.2017.06.006.

Patton, H., Andreassen, K., Bjarnadóttir, L.R., Dowdeswell, J.A., Winsborrow, M.C.M., Noormets, R., Polyak, L., Auriac, A., Hubbard, A., 2015. Geophysical constraints on the dynamics and retreat of the Barents Sea ice sheet as a paleo-benchmark for models of marine ice sheet deglaciation. Rev. Geophys. 53, 1051–1098. doi:10.1002/2015RG000495.

Paull, C.K., Hecker, B., Commeau, R., Freeman-Lynde, R.P., Neumann, C., Cprso, W.P., Golubic, S., Hook, J.E., Sikes, E., Curray, J., 1984. Biological Communities at the Florida Escarpment Resemble Hydrothermal Vent Taxa. Science 226, 965-967.

Paull, C.K., Chanton, J.P., Neumann, A.C., Coston, J.A., Martens, C.S., Showers, W., 1992. Indicators of Methane-Derived Carbonates and Chemosynthetic Organic Carbon Deposits: Examples from the Florida Escarpment. Palaios 7/4, 361-375.

Peckmann, J., Reimer, A., Luth, U., Luth, C., Hansen, B.T., Heinicke, C., Hoefs, J., Reitner, J., 2001. Methane-derived carbonates and authigenic pyrite from the north-western Black Sea. Marine Geology 177, 129-150.

Peckmann, J., Thiel, V., Michaelis, W., Clari, P., Gaillard, C., Martire, L, Reitner, J., 1999. Cold seep deposits of Beauvoisin (Oxfordian; southeastern France) and Marmorito (Miocene; northern Italy): Microbially induced authigenic carbonates. International Journal of Earth Sciences 88, 60-75.

Peltier, W.R., 2001. Global glacial isostatic adjustment and modern instrumental records of relative sea level history. International Geophysics 75, 65-95. https://doi.org/10.1016/S0074-6142(01)80007-3.

Petersen, C.J., Bünz, S., Hustoft, S., Mienert, J., Klaeschen, D., 2010. High-resolution P-Cable 3D seismic imaging of gas chimney structures in gas hydrated sediments of an Arctic sediment drift. Mar. Pet. Geol. 27, 1981–1994. http://dx.doi.org/10.1016/j.marpetgeo.2010.06.006.

Pignatti, J., 2010. *Cassidulina neoteretis* Seidenkrantz, 1995. In: Hayward, B.W., Cedhagen, T., Kaminski, M., Gross, O., 2017. World Foraminifera Database. Accessed through: World Register of Marine Species at http://www.marinespecies.org/aphia.php?p=taxdetails&id=556408 on 2017-07-12.

Plaza-Faverola, A., Bünz, S., Johnson, J.E., Chand, S., Knies, J., Mienert, J., Franek, P., 2015. Role of tectonic stress in seepage evolution along the gas hydrate-charged Vestnesa Ridge. Fram Strait Geophys. Res. Lett. 42, 733–742. http://dx.doi.org/10.1002/2014GL062474.

Rathburn, A.E., Levin, L.A., Held., Z., Lohmann, K.C. 2000. Benthic foraminifera associated with cold methane seeps on the northern California margin: Ecology and stable isotopic composition. Marine Micropaleontology 38, 247–266.

Rathburn, A.E., Perez, E.M., Martin, J.B., Day, S.A., Mahn, C., Gieskes, J., Ziebis, W., Williams, D., Bahls, A., 2003. Relationships between the distribution and stable isotopic composition of living benthic foraminifera and cold methane seep biogeochemistry in Monterey Bay, California. Geochem. Geophys. Geosyst 4. http://dx.doi.org/10.1029/2003GC000595.

Rebesco, M., Wahlin, A., Laberg, J.S., Schauer, U., Beszczynska-Möller, A., Lucchi, A., Noormets, R., Accettella, D., Zarayskaya, Y., Diviacco, P., 2013. Quaternary contourite drifts of the Western Spitsbergen margin. Deep Sea Research Part I, 79, 156-168. doi: 10.1016/j.dsr.2013.05.013.

Reeburgh, W.S., 1976. Methane consumption in Cariaco Trench waters and sediments. Earth Planet. Sci. Lett., 28, 337-344.

Reeburgh, W.S., 2007. Oceanic methane biogeochemistry. Chemical Reviews 107, 486-513.

Regenberg, M., Nürnberg, D., Schönfeld, J., Reichart, G.-J., 2007. Early diagenetic overprint in Caribbean sediment cores and its effect on the geochemical composition of planktonic foraminifera. Biogeosciences Discuss. 4, 2179–2213. doi:10.5194/bgd-4-2179-2007.

Riedinger, N., Pfeifer, K., Kasten, S., Garming, J.F.L., Vogt, C., Hensen, C., 2005. Diagenetic Alteration of Magnetic Signals by Anaerobic Oxidation of Methane Related to a Change in Sedimentation Rate. Geochim. Cosmochim. Acta 69/16, 4117–4126. doi:10.1016/j.gca.2005.02.004.

Ritger, S., Carson, B., Suess, E., 1986. Methane-derived authigenic carbonates formed by subduction-induced pore-water expulsion along the Oregon/Washington margin. Geological Society of America Bulletin 98, 147-156.

Robinson, C.A., Bernhard, J.M., Levin, L.A., Mendoza, G.F., Blanks, J., 2004. Surficial hydrocarbon seep infauna from the Blake Ridge (Atlantic Ocean, 2150 m) and the Gulf of Mexico (690–2240 m). Marine Ecology 25 (4), 313–336.

Roy, S., Hovland, M., Noormets, R., Olaussen, S., 2015. Seepage in Isfjorden and its tributary fjords, West Spitsbergen. Marine Geology 363, 146-159.

Sahling, H., Rickert, D., Lee, R.W., Linke, P., Suess, E., 2002. Macrofaunal community structure and sulfide flux at gas hydrate deposits from the Cascadia convergent margin, NE Pacific. Mar. Ecol. Prog. Ser. 231, 121–138. http://dx.doi.org/10.3354/meps231121.

Sauer, S., Crémière, A., Knies, L., Lepland, A., Sahy, D., Martmad, T., Noble, S.R., Schönenberger, J., Klug, M., Schubert. C.J., 2017. U-Th chronology and formation controls of methane-derived authigenic carbonates from the Hola trough seep area, northern Norway. Chemical Geology 470, 164-179.

Saunois, M., Jackson, R.B., Bousquet, P., Poulter, B., Canadell, J.G. 2016. The growing role of methane in anthropogenic climate change. Environmental research letters 11, 120207. doi:10.1088/1748-9326/11/12/120207.

Schneider, A., Crémière, A., Panieri, G., Lepland, A., Knies, J., 2017. Diagenetic alteration of benthic foraminifera from a methane seep site on Vestnesa Ridge (NW Svalbard). Deep-Sea Research I 123, 22-34. http://dx.doi.org/10.1016/j.dsr.2017.03.001.

Schneider, A., Panieri, G., Lepland, A., Consolaro, C., Crémière, A., Forwick, M., Johnson, J.E., Plaza-Faverola, A., Sauer, S., Knies, J. Seafloor methane seepage at Vestnesa Ridge (NW Svalbard) since the Last Glacial Maximum. Manuscript in review at Quaternary Science Reviews.

Schneider., A, Hong., W.-L., Panieri, G. Diagenetic alteration of foraminifera reveals minimum methane seepage duration. Manuscript in preparation for submission to Geology.

Schrag, D.P., Higgins, J.A., MacDonald, F.A., Johnston, D.T., 2013. Authigenic Carbonate and the History of the Global Carbon Cycle. Science 339, 540-543.

Sen Gupta, B.K., and Aharon, P., 1994. Benthic Foraminifera of bathyal hydrocarbon vents of the Gulf of Mexico: Initial report on communities and stable isotopes. Geo-Marine Letters 14, 88-96.

Sen Gupta, B.K., Platon, E., Bernhard, J.M., Aharon, P., 1997. Foraminiferal colonization of hydrocarbon-seep bacterial mats and underlying sediment, Gulf of Mexico slope. Journal of Foraminiferal Research 27, 292–300.

Sen Gupta, B.K. 2002. Modern Foraminifera. Kluwer Academic Publishers. 371 pp. ISBN 978-1-4020-0598-5.

Sexton, P.F. and Wilson, P.A., 2009. Preservation of benthic foraminifera and reliability of deep-sea temperature records: Importance of sedimentation rates, lithology, and the need to examine test wall structure. Paleoceanography 24. doi:10.1029/2008PA001650.

Sexton, P.F., Wilson, P.A., Pearson, P.N., 2006. Microstructural and geochemical perspectives on planktic foraminiferal preservation: “glassy” versus “frosty.” Geochemistry, Geophys. Geosystems 7. doi:10.1029/2006GC001291.

Sibuet, M. and Olu, K., 1998. Biogeography, biodiversity and ßuid dependence of deep-sea cold-seep communities at active and passive margins. Deep-Sea Research II 45, 517-567.

Smith, A.J., Mienert, J., Bünz, S., Greinert, J., 2014. Thermogenic methane injection via bubble transport into the upper Arctic Ocean from the hydrate-charged Vestnesa Ridge, Svalbard. Geochem. Geophys. Geosyst. 15, 1945–1959. http://dx.doi.org/10.1002/2013GC005179.

Sommer, S., Pfannkuche, O., Linke, P., Luff, R., Greinert, J., Drews, M., Gubsch, S., Pieper, M., Poser, M., Viergutz, T., 2006. Efficiency of the benthic filter: Biological control of the emission of dissolved methane from sediments containing shallow gas hydrates at Hydrate Ridge, Global Biogeochem. Cycles, 20, GB2019, doi:10.1029/2004GB002389.

Stott, L.D., Bunn, T., Prokopenko, M., Mahn, C., Gieskes, J., Bernhard, J.M. 2002. Does the oxidation of methane leave an isotopic fingerprint in the geologic record?, Geochem. Geophys. Geosyst., 3. Doi: 10.1029/2001GC000196, 2002.

Suess, E., Carson, B., Ritger, S.D., Moore, C.J., Jones, M.L., Kulm, L.D., Cochrance, G.R., 1985. Biological communities at vent sites along the subduction zone off Oregon. Bull. Biol. Soc. Washington 6, 475-484.

Sztybor, K. and Rasmussen, T.L., 2017a Diagenetic disturbances of marine sedimentary records from methane-influenced environments in the Fram Strait as indications of variation in seep intensity during the last 35 000 years. Boreas. doi:10.1111/bor.12202.

Talwani, M. and Eldholm, O., 1977, Evolution of the Norwegian-Greenland Sea: Geological Society of America Bulletin 88, 969–999. doi: 10.1130 /0016-7606(1977)88<969:EOTNS>2.0 .CO;2.

Teichert, B., Eisenhauer, A., Bohrmann, G., Haase-Schramm, A., Bock, B., Linke, P., 2003. U/Th Systematics and ages of authigenic carbonates from Hydrate Ridge, Cascadia Margin: Recorders of fluid flow variations. Geochim. Cosmochim. Acta 67/20, 3845–3857. doi:10.1016/S0016-7037(03)00128-5.

Teichert, B., Bohrmann, G., Suess, E., 2005. Chemoherms on Hydrate Ridge — Unique microbially-mediated carbonate build-ups growing into the water column. Palaeogeography, Palaeoclimatology, Palaeoecology 227, 67– 85.

Thiel, V., Peckmann, J., Seifert, R., Wehrung, P., Reitner, J., Michaelis, W., 1999. Highly isotopically depleted isoprenoids: molecular markers for ancient methane venting. Geochimica et Cosmochimica Acta 63, 3959–3966.

Thomas, D.J., Zachos, J.C., Bralower, T.J., Thomas, E., Bohaty, S., 2002. Warming the fuel for the fire: evidence for the thermal dissociation of methane hydrate during the Paleocene–Eocene thermal maximum. Geology 30, 1067–1070. doi:10.1130/0091-7613(2002)030!1067:WTFFTFO2.0.CO;2.

Torres, M., McManus, J., Hammond, D., De Angelis, M., Heeschen, K., Colbert, S., Tryon, M., Brown, K., Suess, E., 2002. Fluid and chemical fluxes in and out of sediments hosting methane hydrate deposits on Hydrate ridge, OR, I: hydrological provinces. Earth Planet. Sci. Lett. 201, 525-540.

Torres, M. E., A. C. Mix, K. Kinports, B. Haley, G. P. Klinkhammer, J. McManus, de Angelis, M. A., 2003. Is methane venting at the seafloor recorded by $\delta^{13}C$ of benthic foraminifera shells? Paleoceanography, 18(3), 1062, doi:10.1029/2002PA000824.

Torres, M. and Bohrmann, G., 2006. Gas Hydrates in Marine Sediments. In: Marine Geochemistry. 2nd Ed. Schultz, H.D., Zabel, M. (Eds.) Springer. pp. 482-512.

Torres, M.E. Martin, R.A., Klinkhammer, G., Nesbitt, E.A., 2010. Post depositional alteration of foraminiferal shells in cold seep settings: New insights from flow-through time-resolved analyses of biogenic and inorganic seep carbonates. Earth Planet. Sci. Lett. 299, 10–22. doi:10.1016/j.epsl.2010.07.048.

Uchida, M., Ohkushi, K., Kimoto, K., Inagaki, F., Ishimura, T., Tsunogai, U., TuZino, T., Shibata, Y., 2008. Radiocarbon-based carbon source quantification of anomalous isotopic foraminifera in last glacial sediments in the western North Pacific. Geochemistry, Geophysics, Geosystems 9, Q04N14. doi:10.1029/2006GC001558.

Urey, H.C., Lowenstam, H.A., Epstein S., 1951. Measurement of paleotemperatures and temperatures of the Upper Cretaceous of England, Denmark, and the southeastern United States. GSA Bulletin 62, 399-416.

Van Dover, C.L., German, C.R., Speer, K.G., Parson, L.M., Vrijenhoek, R.C. 2002. Evolution and Biogeography of Deep-Sea Vent and Seep Invertebrates. Science 295, 1253-1257.

Valentine, D.L., 2002. Biogeochemistry and microbial ecology of methane oxidation in anoxic environments: a review. Antonie van Leeuwenhoek 81, 271–282.

Vogt, P.R., Crane, K., Sundvor, E., Max, M.D., Pfirman, S.L., 1994. Methane-generated (?) pockmarks on young, thickly sedimented oceanic crust in the Arctic: Vestnesa Ridge, Fram Strait. Geology 22, 255–258.

Vogt, P.R., Gardner, J., Crane, K., Sundvor, E., Bowles, F., Cherkashev, G., 1999. Ground truthing 11- to 12-kHz side-scan sonar imagery in the Norwegia–Greenland Sea: Part I: pockmarks on the Vestnesa Ridge and Storegga slide margin. Geo Mar. Lett. 19, 97–110.

Whitehouse, P., 2009. Glacial isostatic adjustment and sea-level change. SKB Technical Report TR-09-11. 100pp.

Whiticar, M.J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. Chemical Geology 161, 291–314.

Winkelmann, D., Geissler, W., Schneider, J., Stein, R., 2008. Dynamics and timing of the Hinlopen/Yermak Megaslide north of Spitsbergen. Arctic Ocean. Mar. Geol. 250, 34–50. http://dx.doi.org/10.1016/j.margeo.2007.11.013.

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

Wollenburg, J. E., Raitzsch, M., Tiedemann, R. 2015. Novel high-pressure culture experiments on deep-sea benthic foraminifera – Evidence for methane seepage-related $\delta^{13}C$ of Cibicides wuellerstorfi. Marine Micropaleontology 117, 47-64. doi:10.1016/j.marmicro.2015.04.003.

Woodgate, R.A., Fahrbach, E., Rohardt, G., 1999. Structure and transports of the East Greenland Current at 75°N from moored current meters. J. Geophys. Res. 104/8, 18,059-18,072.

Zhang, C.L., Pancost, R.D., Sassen, R., Qian, Y., Macko, S.A., 2003. Archaeal lipid biomarkers and isotopic evidence of anaerobic methane oxidation associated with gas hydrates in the Gulf of Mexico. Organic Geochemistr 34, 827-836.

Paper I

Diagenetic alteration of benthic foraminifera from a methane seep site on Vestnesa Ridge (NW Svalbard)

Schneider A, Crémière A, Panieri G, Lepland A, Knies J

Deep Sea Research Part I: Oceanographic Research Papers 123, 22-34.

Paper II

Seafloor methane seepage at Vestnesa Ridge (NW Svalbard) since the Last Glacial Maximum

Schneider A, Panieri G, Lepland A, Consolaro C, Crémière A, Forwick M, Johnson JE, Plaza-Faverola A, Sauer S, Knies J

Manuscript in review at Quaternary Science Reviews.

Paper III

Diagenetic alteration of foraminifera reveals minimum methane seepage duration

Schneider A, Hong W-L, Panieri G

Manuscript in preparation for submission to Geology.