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THE ARCTIC UNIVERSITY OF NORWAY

Faculty of Science and Technology

Department of Geosciences

Reconstruction of past and present methane emission in the Arctic cold seeps using biogeochemical proxies

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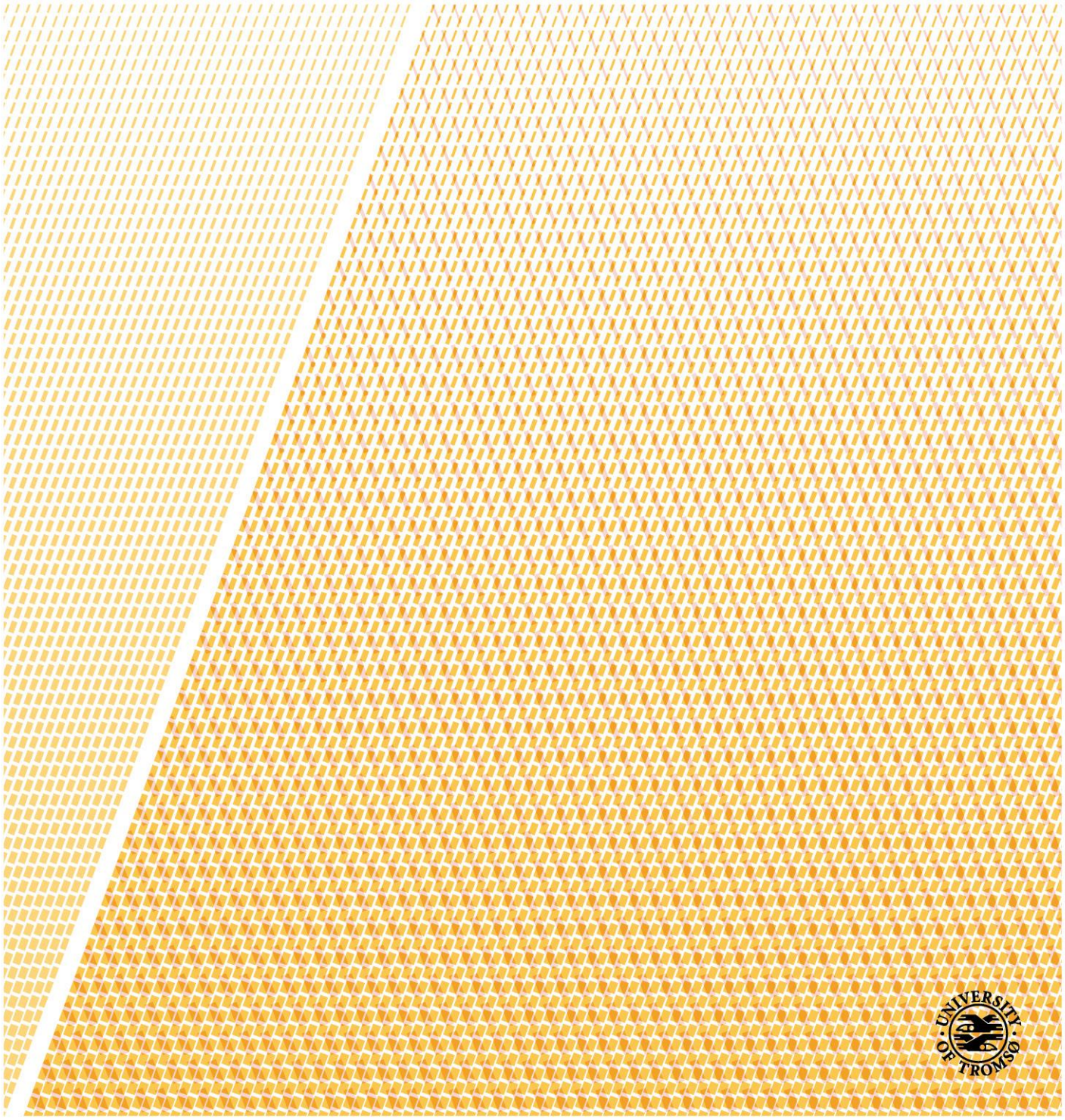
Haoyi Yao

A dissertation for the degree of Philosophiae Doctor – March 2020



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Reconstruction of past and present methane emission in the Arctic cold seeps using biogeochemical proxies

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Abstract

Global warming is now highly concerned by society as extreme weather is more often than ever, and the Arctic is experiencing warming twice as fast as the global mean. A large amount of carbon is stored in the forms of methane and methane hydrate in the continental margins worldwide. Methane is the most predominant gaseous compound in natural gas hydrate, which is stable under low temperature and high pressure. With the warming Arctic, methane from gas hydrate dissociation may release into the water column and atmosphere in the future and have positive feedback to the warming as methane is one of the most potent greenhouse gases. Therefore, it is crucial to study and understand the state, the drivers, and the fate of methane hydrate in the Arctic marine sediment.

In this thesis, I study the methane seepage events in both modern and paleo settings. The methane seepage history was studied using authigenic carbonates, foraminifera, molecular fossils such as lipid biomarkers and sedimentary properties. I focus on two methane seepage sites in the Arctic Ocean, Vestnesa Ridge (1200m water depth), and Storfjordrenna (380 meters water depth). The former is characterized by numerous seafloor pockmarks, subseafloor fluid flow system, and gas flares in the water column whereas the latter is characterized by mound features at the seafloor, and gas flares in the water column.

The thesis focused primarily on lipid biomarkers from the anaerobic oxidation of methane (AOM) microbial communities to reconstruct the history of methane seepage. The main research goal is to understand first the cold seep system at the study sites, then the current and paleo drivers of the methane emissions in the Arctic Ocean sediments, whether the discharge was triggered by the warming Arctic or it was a natural process that persists over a long time. Lipid biomarkers is a useful molecular tool to study methane seepage. They are stable over geological time scales and reflect the size as well as the source of the carbon pool based on its concentrations and isotopic signatures. Through these characteristics, they can trace the paleo methane seepage in combination with other methane proxies such as foraminifera and authigenic carbonates. These proxies unravel the history of methane seepage. Lipid biomarkers can also indicate the methane transport modes, diffusion vs. advection when used in combination with other geochemical data in modern settings.

Preface

This doctoral thesis was carried out between June 2015 and February 2020 at the Department of Geosciences at UiT with a nine-month leave. The PhD project was funded by the Research Council of Norway (grant no. 223259) for CAGE, and it is integrated into the methane history working package (WP5) at CAGE. My main supervisor is Prof. Dr. Giuliana Panieri and co-supervised by Prof. Helge Dr. Niemann (NIOZ).

The project aims to use lipid biomarkers from the microbial communities with foraminifera and other geochemical evidence to identify the methane seeping events in modern days and past together. As part of the thesis work, I participated in three CAGE cruises (CAGE 15-6, 16-5 and 17-2), two NORCRUST cruises (P1606 and P1707), and two international cruises together with MARUM (HE450 and MSM57). In these cruises, I have taken roles not only in sampling sediments for my project, but also helping in sampling pore water and onboard analysis, headspace sampling and onboard analysis, and have gained fruitful experience to prepare for and participate in research expeditions.I have participated and presented my research work and findings at several international conferences, including Gordon Research conference for gas hydrate in 2016, Goldschmidt conference in 2017 and 2019, and EGU18 General Assembly. For some of the meetings, I have received travel grants from the Ph.D. school ResClim and UiT. For Goldschmidt 2017, I was the volunteer for the conference for the entire week working on different positions (e.g., in charge of the large lecture room, runners for smaller lecture rooms).

In 2017, I received a ten-month travel grant from UiT, and I visited the University of Plymouth, School of Geography, Earth and Environmental Sciences to learn and apply the sea ice proxy IP_{25}, the rest of the time I visited the University of Basel, Department of Environmental Sciences to finish up the lipid biomarker analyses there.

During the Ph. D., I have duty works in assisting Geo 2008 for three semesters, helping the installation and startup of the stable isotope lab with the new mass spectrometer at UiT. I have served as a reviewer for Eurofleets Plus.

In addition to my thesis project, I have set up a project between CAGE and Oregon State University, Department of Chemistry, Loesgen group to extract and screen natural products from the marine environment for anti-bacterial, anti-cancer activities.

Acknowledgment

I am very grateful to my main supervisor, Giuliana Panieri, for opening up the opportunity for me to start this Ph.D. project. And through all these years, Giuliana was very supportive, providing all she can for me to be able to participate more research cruises, to get the travel grant from the university, to guide me on my research. I started as someone who could not recognize any species in foraminifera, and can pick only eight foraminifera in a day, and finished with identifying the common Arctic species and can pick up to hundreds of foraminifera in a day. Also, my co-supervisor, Helge Niemann, I truly appreciated all the support, guidance, and knowledge you gave me. The dedication and carefulness are something I should always remember to learn from. You are both very engaging and inspiring scientists to work with and to learn from.

I want to thank all the colleagues in CAGE and NGU. Andrea has always been a pioneer in the group to ask experience and advice from. Pierre-Antoine always seems hilarious and can release the pressure. Kasia always has surprising new ideas. Jochen and Aivo at NGU always ask about the progress and share their time to provide guidance and suggestions.

Marta is always there to support and help. I had my first research cruise with Marta and learned all the sampling techniques from you. Also, I would thank Helge and Moritz for hosting the lab use in Basel. The IG lab managers, Trine, Ingrid, and Karina, for providing numerous help on the lab use, equipment, and technical problems. Moreover, all my co-authors providing valuable insights to the manuscripts, and giving me the chance to share my data/knowledge with you.

Last but not least, to my family. Wei-Li, I would not come to Norway without you. I would not get so far in geosciences without you. Helping me to start from scratch in geosciences and taking responsibility for our daughter when I am under stress. It has been eight years since I finished my master thesis, it has been two doctoral programs we have been through, and I thank my parents and my in-laws for understanding the decision and being supportive along the way.

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1 Introduction

1.1 Methane in marine sediments

It is globally recognized that the Arctic is warming faster than anywhere on our planet. Global warming is now of serious concern by society as we are experiencing extreme weather more often than ever (Trenberth and Fasullo, 2007; Cohen et al., 2014). A huge amount of carbon is stored in the forms of methane and methane hydrate in the continental margins worldwide (Judd and Hovland, 2007). Gas hydrate is an ice-like substance formed primarily with methane gas and water in a clathrate structure. It is stable under low temperature and high pressure. With the continuous warming in the Arctic Ocean, methane may release into the water column and atmosphere in the future and then have further positive feedback to the warming.

Methane is concerned as a powerful greenhouse gas; the greenhouse effect is 25 times stronger (traps 25 times more heat per mass unit) than that of carbon dioxide in a 100-year time frame (Lelieveld et al., 1998). The atmospheric chemistry of methane: as it controls the concentration of tropospheric hydroxyl radicals, adds to the methane radiative forcing thus amplify the impact of methane emissions (Dlugokencky et al., 2011, Holmes, 2018). The contribution of methane in the atmosphere to the current global warming is estimated to be around 15% (Badr et al., 1991). All these factors make methane plays an essential role in the future climate modeling. At the same time, methane from the methane hydrate reservoirs is also a potential energy source. Marine sediments in the Arctic contain three times more energy-equivalent gas than oil (Gautier et al., 2009).

1.1.1 Methane sources

Methane in marine sediment can be produced by three different processes: thermogenic, microbial, and abiotic. Thermogenic methane formation occurs where complex organic molecule kerogen breaks down by a thermocatalytic reaction, which is part of the petroleum generating process. This thermocatalytic reaction develops deep within the sedimentary basins usually at subbottom depths exceeding 1000 m (Floodgate and Judd, 1992; Judd, 2004). Thermogenic methane formation requires temperatures above 80 °C and is the dominant process at temperatures above 150 °C (Clayton, 1991). Microbial methane is produced by methanogenic archaea biologically via methanogenesis (Kvenvolden and Rogers, 2005). Microbial methane formed by reducing CO_2 is the primary microbial process for most methane

formed in marine sediments, which is produced through the remineralization of sedimentary organic carbon (Whiticar, 1999). The rain of phytoplankton to the seafloor in highly productive areas and terrestrial sediment from the continents provide the organic carbon for methane formation to the sediment. The less common microbial methane production process utilizes acetate fermentation; because sulfate-reducing bacteria also use acetate as a substrate, so it is more competitive for acetate to be available for methanogenesis. The temperature for methanogenesis is between 35 °C and 45 °C and can be up to 60 °C (Ferry and Lessner, 2008). As a result, methanogenesis occurs at shallower sediment where organic matter is higher compared to the thermogenic formation in deeper subsurface (Judd, 2000). The least common way of methane formation is abiotic methane through magmatic and gas-water-rock reactions. This methane formation pathway is very rarely observed and poorly understood (Etiope and Sherwood Lollar, 2013). One of the known reactions for abiotic methane formation is Fischer-Tropsch reaction where CO_2 or CO with H_2 and metal catalysts are involved.

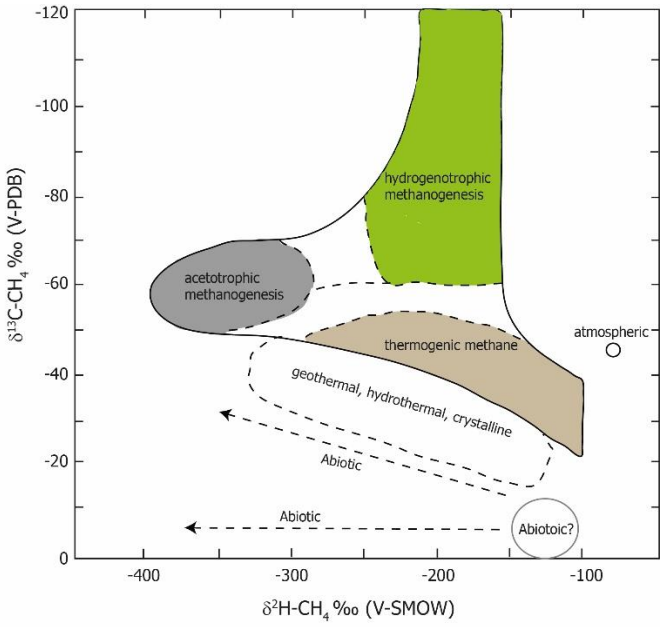

Figure 1. From Whiticar 1999 (modified). Schematic differences between carbon and hydrogen isotopes of different methane formation.

The efficient way to identify the sources of methane is through the isotopic signatures of the methane carbon and hydrogen (Figure 1). During the methane formation, the kinetic isotope effect changes the isotopic composition of the product methane (Judd and Hovland, 2007). The three known methane formation pathways can be differentiated by their stable carbon and hydrogen isotopic signatures, and the relative proportion of methane to other higher

hydrocarbons (i.e., ethane, propane, and butane) (Whiticar, 1999). Extensive isotope fractionation during the microbial methane formation process resulted in a very depleted value of the methane carbon isotope ranging from -100 to -50 ‰. Thermogenic methane carbon is generally enriched in ^{13}C compared to the microbial methane carbon; this is because the precursors are also more enriched in ^{13}C, a smaller isotope fractionation and a higher reaction temperature are involved. Abiotic methane is believed to be the most enriched in ^{13}C with $\delta^{13}C$ values above -25 ‰ (Etiope and Sherwood Lollar, 2013).

1.1.2 Methane sinks in the marine environment

Within the marine sediments, the most persistent biochemical sink of methane is through anaerobic oxidation of methane (AOM) (Barnes and Goldberg, 1976). AOM is carried out by a consortium between methanotrophic archaea and sulfate-reducing bacteria (Knittel and Boetius, 2009), which couple the methane oxidation strongly with sulfate reduction (Reeburgh, 2007). This AOM microbial consortia is estimated to consume up to 80-90 % of the methane produced in the sediment and is termed as the biofilter of methane (Figure 2).

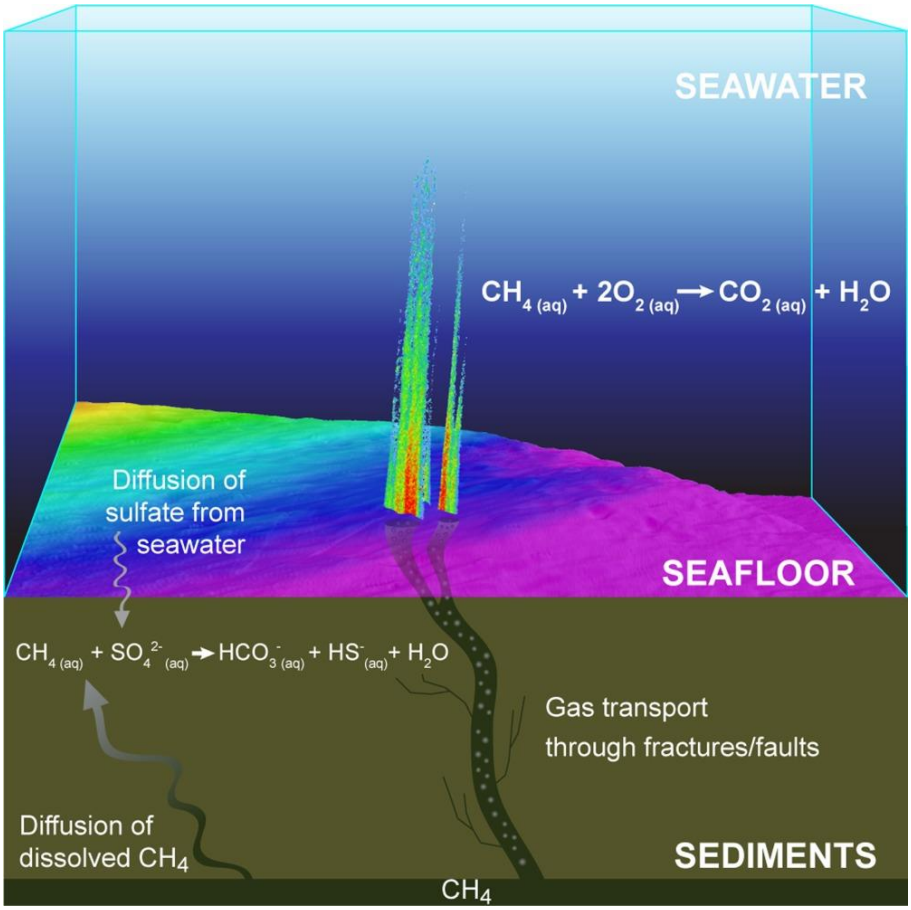

Figure 2. Methane sinks in marine sediments and water column. Figure from James et al., 2016.

AOM is highly efficient when methane is transported by diffusion (Joye et al., 2004). On the other hand, only about 20% of the methane is consumed by AOM at locations where methane migration is dominant by advection (Boetius and Wenzhöfer, 2013). The reduced efficiency of AOM in consuming methane at sites with high advective fluxes is due to that, during the advection, most methane is transported in the form of gas bubbles, which is able to bypass the sediment biofilter and eventually be released to the water column.

When AOM is coupled to sulfate reduction, the lower boundary of sulfate reduction zone is termed as sulfate methane transition zone (SMTZ), which can be centimeters (Fischer et al., 2012) to meters (D'Hondt et al., 2002) below the seafloor. The depth of SMTZ can be used to infer the upward methane flux (Borowski et al., 1996): a deeper SMTZ below the seafloor reflects a lower upward methane flux vs. a shallower SMTZ is translated to a high methane flux. Sometimes the SMTZ can be only centimeters below the seafloor (e.g., Treude et al., 2003; Fischer et al., 2012; Yao et al., 2019) that often indicate a very high methane flux.

After the discovery of AOM coupled to sulfate reduction, recent studies have also provided evidence for other electron acceptors coupled to methane oxidation such as Fe/Mn oxides (Beal et al., 2009; Sivan et al., 2014) and nitrite (Ettwig et al., 2010). However, the environmental significance of these novel electron acceptors in marine sediments is yet to be evaluated as the amount of sulfate is of magnitude higher than these other potential electron acceptors. Therefore, the biofilter efficiency of these newly discovered electron acceptors would be much lower than the sulfate-dependent AOM.

Once methane gas bypasses the sediment-water interface and enters the water column, methane can then be oxidized aerobically (MOx) as oxygen becomes available as the electron acceptor (Hanson and Hanson, 1996). There have been relatively fewer measurements of the strength of this sink compared to that of AOM (Valentine and Reeburgh, 2000; Kessler et al., 2011; Mau et al., 2013). In general, the oxidation rates are mostly affected by temperature, pressure, and methane concentration (Scranton and Brewer, 1978). The MOx studies inoculate seawater samples with radioisotope traces to measure the rate at specific sites and times of sampling. The stoichiometry of this reaction also remains unclear. Other than the methane that is consumed through chemical reactions, other physical processes such as bubble-stripping, a process that replaces methane with oxygen and nitrogen during the

bubble ascending in the water column, is another essential sink prevent methane from leaking to the atmosphere (McGinnis et al., 2006).

1.2 Study methane dynamics in marine sediments using proxies

Proxies or 'proxy variables' are sediment geochemical properties that have a close relationship to environmental parameters. Proxies can deliver useful information for reconstructing environmental parameters. They are measurable descriptors for those desired but unobservable environmental variables (Wefer et al., 1999). To reconstruct a past methane emission history, we must turn to proxies as one can no longer observe methane emission in the past. The figure below illustrated the well-established methane proxies we apply and their relationship with regard to the AOM process.

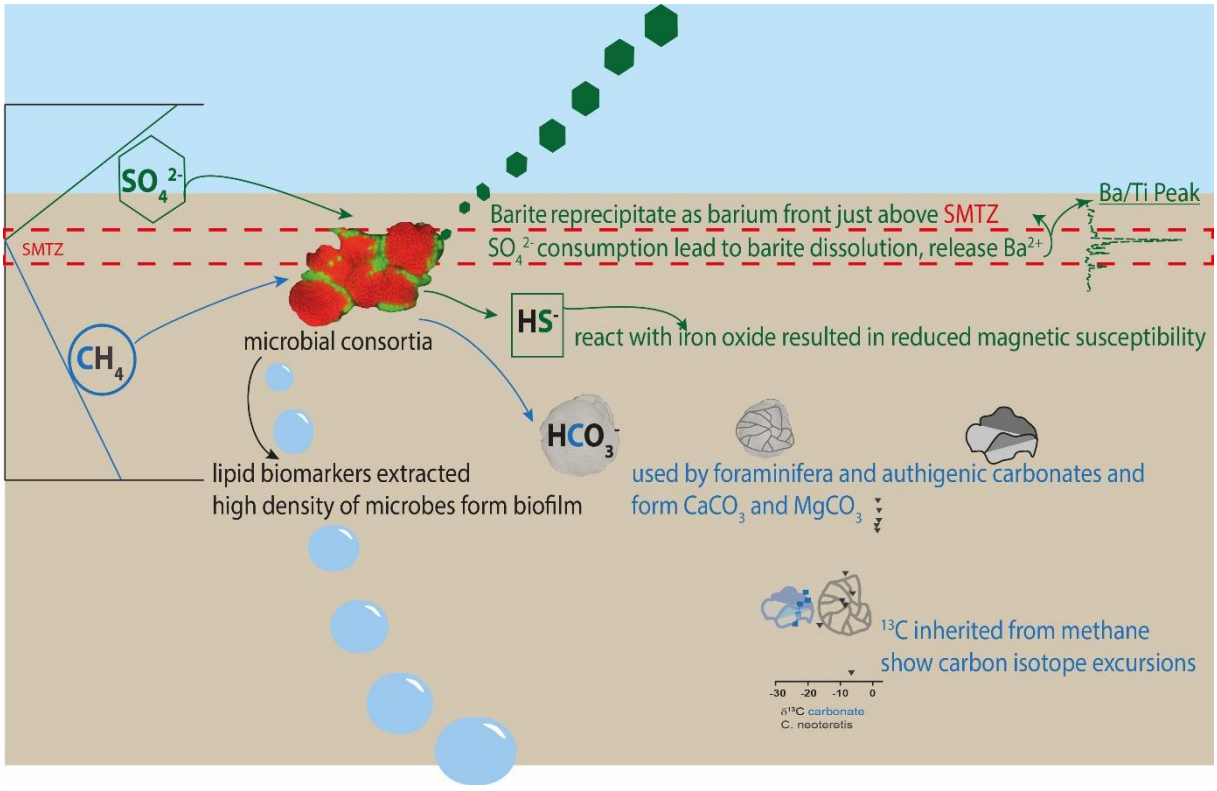

Figure 3. An illustration of proxies related to the AOM process used in my thesis.

1.2.1 Molecular fossils

Previous investigations of lipid biomarkers along with the phylogenetic affiliation of microbial communities revealed that specific biomarker patterns could help identify particular AOM communities (Blumenberg et al., 2004; Elvert et al., 2005; Niemann and Elvert, 2008). The AOM consortia consist of methanotrophic archaea and sulfate-reducing bacteria (SRB). Lipid

biomarkers come from the hydrophobic core of the cell membranes of the microbes. Archaeal cell membranes are mainly comprised of isopranyl glycerol ether lipids, which are contrasting different from the acyl ester lipids found in bacteria (Tornabene et al., 1979). At least three phylogenetically distinct groups of methanotrophic archaea, ANME-1, ANME-2 and ANME-3, have been identified that are qualified for AOM. The corresponding SRB partners of ANME-1 and ANME-2 are two different ecotypes of SRB related to the *Desulfosarcina/Desulfococcus* (DSS) cluster and Seep-1 SRB (Boetius et al., 2000; Knittel et al., 2005). The controlling factors for these different phylogenetic groups include varying sulfate and methane concentrations. It has been observed that at high flux seep sites with significantly higher cell-specific AOM rates are dominated by ANME-2 communities, whereas ANME-1 communities seem to be better adapted to low seepage fluxes and grow within a broader range of temperatures (Blumenberg et al., 2004; Elvert et al., 2005; Nauhaus et al., 2007; Stadnitskaia et al., 2008a; Rossel et al., 2011). Substantial isotopic fractionation occurs during the production of methanotrophic biomass, thus the biomass of methanotrophic archaea involved in AOM is strongly depleted in ^{13}C. In comparison, the corresponding SRB lipids are usually less depleted. It is believed that SRB assimilates methane derived CO_2 autotrophically, whereas archaea utilize methane and assimilate carbon directly from the ^{13}C-depleted source (Wegener et al., 2008). The exact mechanism of the AOM consortia is still in debate (Kellermann et al., 2012; Milucka et al., 2012; Wegener et al., 2015; Scheller et al., 2016).

Among the specific methanotrophic archaeal related lipid biomarkers, higher contents of *sn2*-hydroxyarchaeol relative to archaeol have been reported in most modern ANME-2 dominated seep sites, as well as investigation of lipid biomarkers on carbonates (Blumenberg et al., 2004; Elvert et al., 2005; Niemann and Elvert, 2008; Birgel et al., 2011; Himmler et al., 2015). Abundant strongly ^{13}C-depleted crocetane was also featured in most of the above-mentioned ANME-2 dominated habitats as well. Nearly no crocetane was found in the ancient ANME-1 dominated systems (Niemann and Elvert, 2008; Peckmann et al., 2009; Haas et al., 2010). Therefore, the *sn2*-hydroxyarchaeol/archaeol ratio together with the occurrence of crocetane have been used to contradistinguish the types of archaeal phylogenetic groups mediating AOM (Blumenberg et al., 2004; Niemann and Elvert, 2008). High contents of C16:1ω5 fatty acid and the presence of cyC17:0ω5 fatty acid along with a low ratio of *ai*C15:0 fatty acid relative to *i*-C15:0 fatty acid is attributed to the Seep-1 SRB partner associated with ANME-2

(Niemann and Elvert, 2008). Compound-specific isotopes of the specific archaeal lipid biomarkers can provide more information on the phylogenetical group, as ANME-1 shows less fractionation between the source methane and their lipid biomarkers' carbon isotope (Niemann and Elvert, 2008).

Therefore, the lipid biomarkers of the AOM microbial community can provide useful insight into both modern and paleo methane seepage. Lipid contents, distribution patterns, and compound-specific carbon isotopes of these archaeal and SRB molecular fossils, in combination with other proxies, can be used to differentiate engaged microbial communities and to constrain seepage intensity (Haas et al., 2010; Birgel et al., 2011).

1.2.2 Methane derived authigenic carbonates (MDAC)

AOM is also closely related to carbonate formation at shallow depths beneath the seafloor, as one product of the AOM process is bicarbonate. Bicarbonate can increase alkalinity and form authigenic carbonates as aragonite, calcite, and dolomite depending on the cation (i.e. Mg^{2+}, Ca^{2+}) concentrations. These three are the main carbonate phases associated with methane seeps; the mineralogy correlated to the predominant pore water cation composition at the depth of formation(Burton, 1993; Ferrell and Aharon, 1994; Bohrmann et al., 1998) and can also provide some insight into the precipitating environment. For example, the aragonites are believed to be formed at high sulfate concentrations while the high sulfate would inhibit calcite formation (Bohrmann et al., 1998; Aloisi et al., 2000). Seep carbonates serve as a good chemical archive for methane seepage. They are characterized by negative $\delta^{13}C$ values often below -30 ‰ (Peckmann and Thiel, 2004), which are inherited from ^{13}C-depleted methane, reflecting their light carbon sources (Claypool and Kaplan, 1974; Whiticar, 1999). The $\delta^{18}O$ of the seep carbonates can also reveal information about the precipitating environment. In the sediments containing gas hydrate, hydrate dissociation would produce an elevated $\delta^{18}O$ signature in the seep carbonate (Bohrmann et al., 1998; Aloisi et al., 2000; Bohrmann et al., 2002). Seep carbonate serves as suitable housing for the AOM microbial communities, lipid biomarkers extracted from the carbonates along with other biogeochemical information can shed some light on the methane seepage at the time of carbonate precipitation.

1.2.3 Foraminifera

Foraminifera are single-cell protists with calcified shells or tests. They have pseudopods, fine strands of cytoplasm, and live in the marine domain (Sen Gupta, 2003). Foraminifera are abundant as fossils for the last 540 Ma. Foraminifera can be found in all marine settings, from the cold seeps to hot vent. Some of them live in the water column floating freely, these are known as planktonic foraminifera. The others live on the seafloor (epibenthic) or in the sediments pore space (infaunal), these are known as benthic foraminifera. Their species assemblages, especially the benthic ones, can be very particular and provide information about the environment they live in (Horton, 1999; Todo et al., 2005). Depending on the species, foraminifera develop different chambers of their calcified shells (tests) when they grow. The shell can consist of calcite or aragonite and/or organic compounds (Bentov and Erez, 2006; de Nooijer et al., 2014). Because foraminifera are everywhere in the marine realm, they are one of the most essential biological proxies to study the paleoenvironment (Armstrong and Brasier, 2005).

Foraminifera have been used as geochemical proxies to reconstruct the paleo seepage at different locations such as Cascadian margin Pacific Ocean (Rathburn, 2000; Rathburn et al., 2003; Hill et al., 2003; Hill et al., 2004; Bernhard et al., 2010), Blake ridge Atlantic Ocean (Panieri and Sen Gupta, 2008), the Mediterranean (Panieri, 2006) and Vestnesa Ridge (Schneider et al., 2018). Foraminifera have also been studied in modern seep settings to explore their biological response to methane (Bernhard et al., 2010; Bernhard and Panieri, 2018), as well as the origination of changes in stable isotope composition of their tests (Rathburn et al., 2003; Torres et al., 2003b; Panieri et al., 2009).

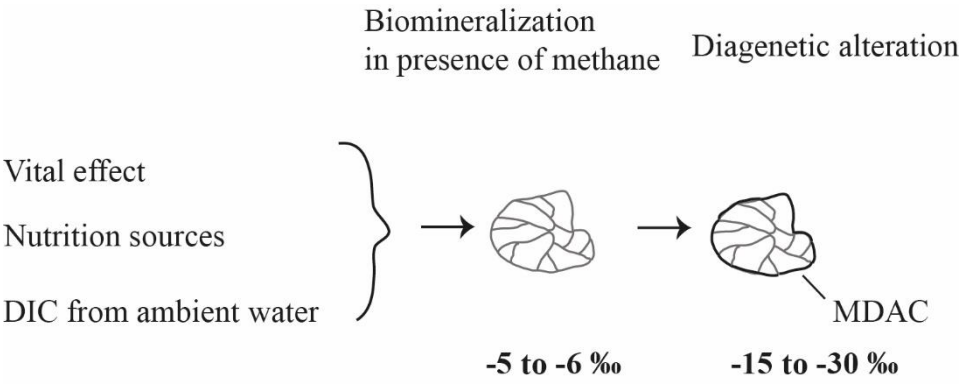

Figure 4. Modified from Schneider et al., 2019

The $\delta^{13}C$ of planktonic foraminifera in a standard marine setting without methane discharge range between -0.5 to 0.5 ‰ in the Barents sea (Knies and Stein, 1998). The $\delta^{13}C$ of benthic foraminifera, such as *C. neoteretis,* in a typical marine environment absent of methane seepage range between 0 to -1.15 ‰ (Wollenburg et al., 2001). More depleted carbon isotopic excursions in modern and fossil foraminiferal tests have been interpreted as a result of methane influence, and have been used to imply the strong ^{13}C-depletions in the tests are associated with ^{13}C-depleted methane. (Kennett, 2000; Hill et al., 2003; Panieri et al., 2009; Martin et al., 2010; Panieri et al., 2014).

The variations and extent of negative excursion in $\delta^{13}C$ of foraminiferal tests at the seep sites are likely the combined outcome of four aspects (Figure 4). Species-specific vital effects, nutrition sources as the ingestion of ^{13}C-depleted AOM microbes (archaea or bacteria) the foraminifera may feed on (Rathburn, 2000; Panieri, 2006; Bernhard and Panieri, 2018), calcification using a ^{13}C-depleted DIC (primary), and diagenetic alteration of the foraminiferal tests.

Vital effect based on the species differences can account for 1-2 ‰ of the carbon isotopic values of the foraminiferal shells (Urey et al., 1951; McCorkle et al., 1990; Mackensen et al., 2006). Foraminifera are attracted to rich organic and microbial food, and some foraminifera were found to prefer the seep-associated microbes (Panieri et al., 2009; Martin et al., 2010). Nonetheless, the nutrition sources can contribute only up to 5-6 ‰ of the negative $\delta^{13}C$ values (Hill et al., 2003).

Primary biomineralization, foraminifera developing their shells with the depleted DIC produced by AOM is suggested to be another factor that may contribute to the negative values of foraminiferal tests. Some research show that living *Cibicides wullerstorffi*'s test become depleted in a culturing experiment with methane-derived DIC, implying the test biomineralization takes place in the presence of methane-derived DIC (Wollenburg et al., 2015). Others have doubts that biomineralization can not occur during seepage as the equilibrium between foraminifera and porewater DIC is not reached (Rathburn et al., 2003; Torres et al., 2003b; Herguera et al., 2014).

The most substantial influence on the negative carbon excursion of foraminiferal test is the diagenetic alteration of the tests under the methane influence (Rathburn, 2000; Rathburn et

al., 2003; Hill et al., 2003; Torres et al., 2003b; Panieri, 2006; Panieri et al., 2009; Panieri et al., 2014; Panieri et al., 2017b; Schneider et al., 2017; Schneider et al., 2018). The ^{13}C-depleted bicarbonate produced during AOM can precipitate not only as authigenic carbonates concretions (Aloisi et al., 2002; Reitner et al., 2005) but also on the foraminiferal shells. Once dead, both benthic and planktonic species can record the ^{13}C signature from the AOM process by acting as a 'template' for authigenic carbonate to precipitate coating layers on (Panieri et al., 2016; Panieri et al., 2017b; Schneider et al., 2017). Such coating carbonate precipitation at the SMTZ cumulatively added a second or third layer of ^{13}C-depleted carbon to the foraminiferal tests is termed as diagenetic alteration (Schneider et al., 2017). These coating layers usually exhibit different states of shell preservation and very depleted $\delta^{13}C$ values up to -20 ‰ (Panieri et al., 2016; Panieri et al., 2017b; Schneider et al., 2017). Both *C. neoteretis* and *N. pachyderma* are excellent templates for the authigenic carbonate formation (Panieri et al., 2017). As a result of multiple coating layers, the diagenetic alteration of foraminiferal tests can cause a much more profound depleted $\delta^{13}C$ signal (Torres et al., 2003b; Hill et al., 2004; Panieri et al., 2009; Martin et al., 2010; Schneider et al., 2017).

1.2.4 Sediment properties

The sediments experienced active methane seepage collect diagenetic overprints as a result of the AOM process. The products of AOM, bicarbonate (HCO_3^-) is consumed in ambient DIC, carbonate precipitation, and foraminifera shell. The other product of AOM is hydrogen sulfide (HS^-), which also increase alkalinity, and can react with iron (II) in the pore water and yield paramagnetic pyrite (FeS_2) (Canfield and Berner, 1987; Peckmann et al., 2001; Riedinger et al., 2006; Dewangan et al., 2013). At the same time, metastable greigite (Fe_3S_4) can form during the pyritization process as a precursor to pyrite (Hunger and Benning, 2007). Both the paramagnetic authigenic pyrite and ferromagnetic greigite can then reduce the magnetic susceptibility of the original sediment magnetic properties.

1.2.5 Others

Other common proxies such as barite formation at the base of SMTZ, dense benthic macrofaunal communities, and AOM biofilm appearance are also used for tracing the methane seepage in combination with the previously discussed proxies.

Briefly, in the sulfate depletion zone below the SMTZ, barite is destabilized and dissolved. Barite can re-precipitate above the SMTZ as sulfate become available again, as the fluid migrates upwards, the barite formation at the base of SMTZ is known as 'barite front' (Torres et al., 1996; Dickens, 2001; Torres et al., 2003a; Solomon and Kastner, 2012). The barite front can be detected with geochemical analysis of barium concentration in both sediment and pore water (Kasten et al., 2012), a simplified way of identifying barite front is from the Ba/Ti ratio or Ba counts of XRF scan of the sediment cores (Sauer et al., 2016). Discovery of a discrete shell bed dominated by Vesicomydae (Phreagena, Isorropodon) at Vestnesa Ridge was interpreted as a high flux seepage episode (Ambrose et al., 2015; Schneider et al., 2018). The seepage not only supports elevated macrofauna biomass, but high methane flux can also support elevated AOM microbial biomass (Yao et al., 2019). In unusual cases, the biomass accumulated so much that form biofilm, which is rarely observed (Briggs et al., 2011; Gründger et al., 2019), but the presence of biofilm is very reliable and serve as a direct piece of evidence for AOM and thus methane seepage.

1.3 Study areas

1.3.1 Vestnesa Ridge

Vestnesa Ridge (79 °N, 5-7 °E, Figure 5), northwest of Svalbard, is one of the northernmost hydrate reservoirs. The water depth is 1200 to 1300 meters, and the ridge is a 100 km long sediment drift on the eastern Fram Strait. Fram Strait was the only deep-water gate to the Arctic Ocean, and it was opened during the late Oligocene to Miocene. The final opening of Fram Strait during the late Miocene (Jakobsson et al., 2007; Knies et al., 2014) led to the development of over 2 km thick sediment accumulation at the eastern segment of the ridge. Moreover, the shallow stratigraphy consist of contourite, turbidite and hemipelagic sediments have been worked by the ocean bottom currents (Howe et al., 2008).

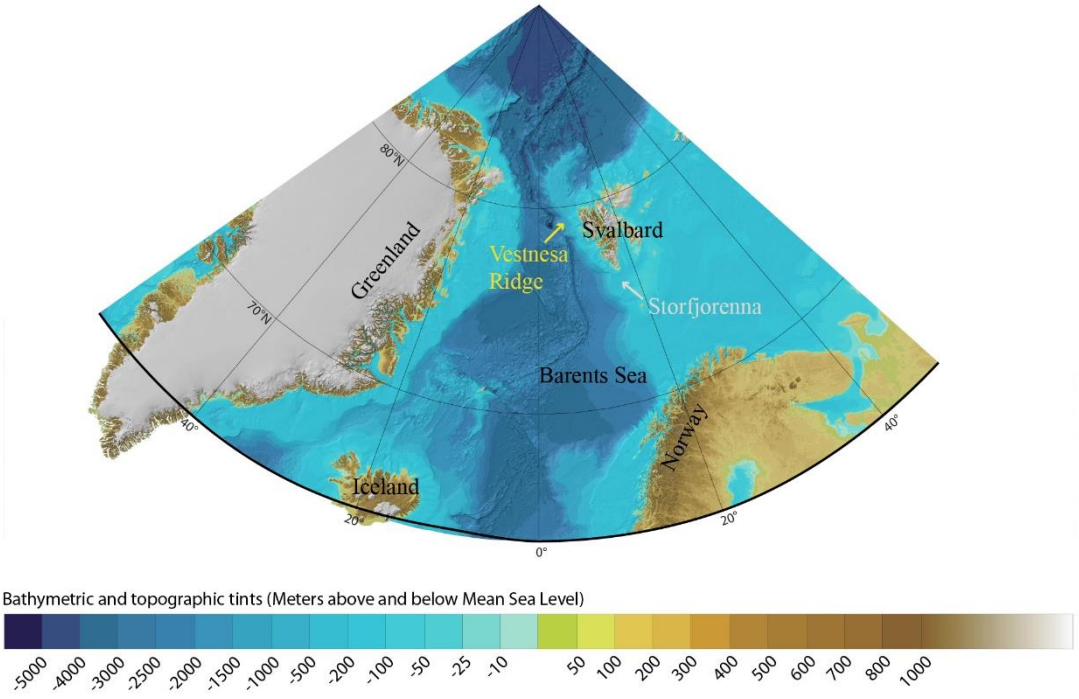

Figure 5. An overview map of the Arctic Ocean with the location of two study areas: Vestnesa Ridge and Storfjordrenna, image section from IBCAO3.0 (Jakobsson et al., 2012).

Since the discovery of pockmarks, the semi-circular seafloor depressions, by Vogt et al. (1994, 1999) in Vestnesa Ridge, the area was mapped thoroughly and well-studied by variously geophysical approaches. Pockmarks are formed under vigorous gas and fluid seepage in unconsolidated sediments (Judd and Hovland, 2007). In addition to the pockmarks as morphological evidence, the eastern segment of Vestnesa Ridge is also characterized by up to 900 m high gas bubble streams (or termed as hydroacoustic flares) in the water column (Smith et al., 2014; Panieri et al., 2017a) (Figure 6) and acoustic chimneys in the sediments from the seismic data as gas migration pathways. It is suggested the methane seepage in Vestnesa was driven by a rare bottom-up mechanism, where heat from the nearby mid-ocean ridge system perturbs the gas hydrate stability after the investigation of the local seismic (Bünz et al., 2012). The fluid and gas migration from deep hydrocarbon reservoirs toward the seafloor has occurred since the early Pleistocene (Knies et al., 2018).

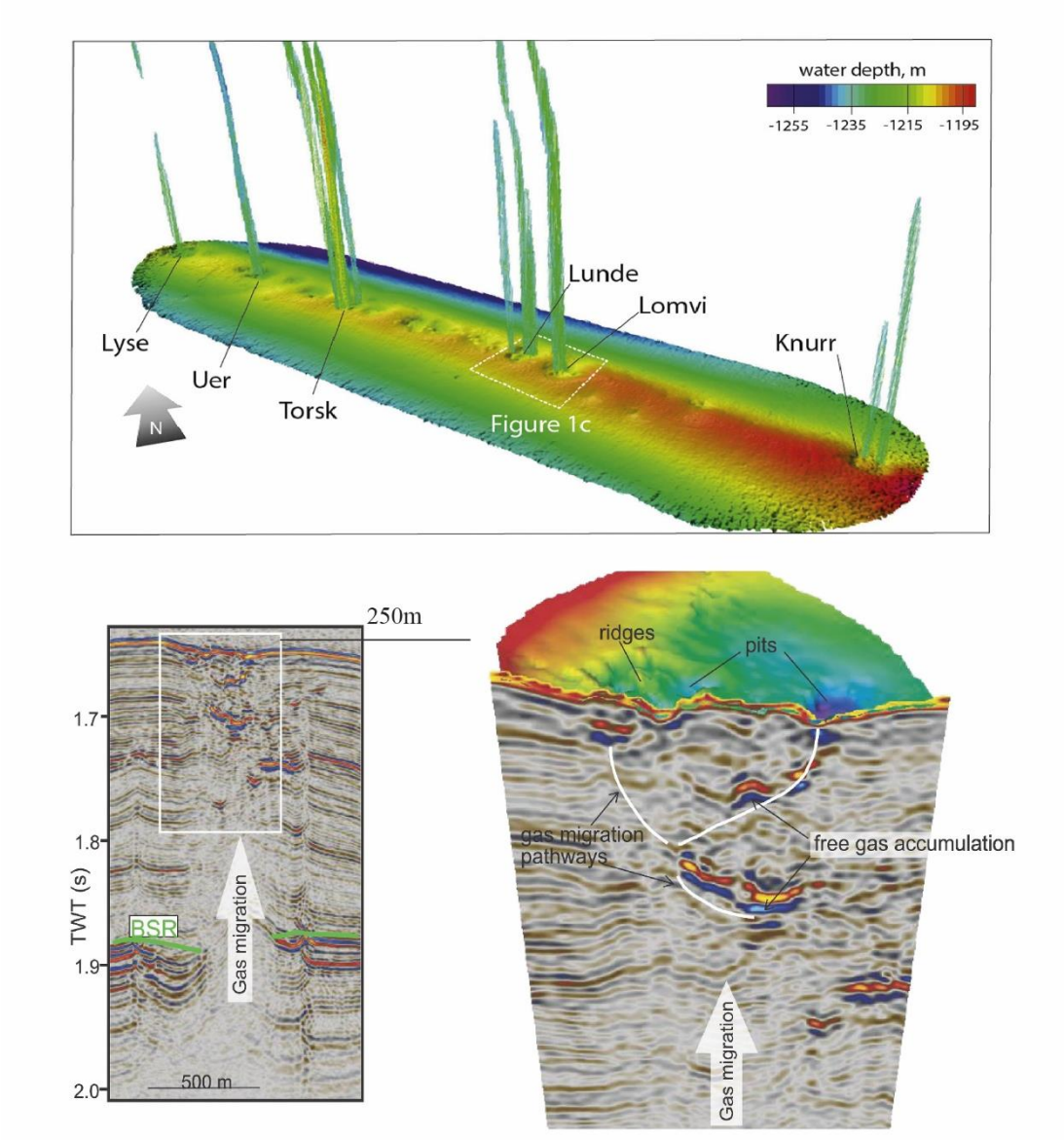

Figure 6. Seafloor bathymetry of the eastern section of Vestnesa Ridge, with gas flares emitting to the water column(above); gas migration pathway and BSR in the seismic data (left below); Seismic profile outlining vertical gas migration pathway and acoustic anomalies beneath Lomvi pockmark (right below). Figures from Panieri et al., 2017a.

Vestnesa Ridge hosts a very complex fluid system from the deep hydrocarbon reservoirs (Petersen et al., 2010; Bünz et al., 2012; Plaza-Faverola et al., 2015; Panieri et al., 2017a). The ridge actively releases methane from seafloor only along the eastern segment of the ridge (Bünz et al., 2012; Plaza-Faverola et al., 2015; Panieri et al., 2017a). It has also been suggested that tectonic stress field controls subsurface faulting and rifting which results in the observed seafloor methane seepage (Plaza-Faverola et al., 2015). Modeling indicated that the onset of the hydrocarbon discharge was the result of the rapid burial of hydrocarbon source after the

onset of Northern Hemisphere glaciations which lead to an increased sediment deposition (Knies et al., 2018). It is this hydrocarbon system from 2.7 Ma ago, that predominantly controls the deep thermogenic methane fluxes and seepage dynamics in Vestnesa Ridge over geological times (Knies et al., 2018).

Recent studies in the area on the $\delta^{13}C$ of foraminifera and methane derived authigenic carbonates correlated the past and ongoing methane seepage and subseafloor methane cycling to the glacio-isostatic adjustment (Schneider et al., 2018; Himmler et al., 2019). New evidence from U-Th dating of methane derived authigenic carbonates also shown that the seepage timing is linked with the wax and wane of the ice sheet (Himmler et al., 2019). Glacio-isostatic adjustments may have triggered the re-activation of tectonic faulting at Vestnesa Ridge and induced the fluid migration pathway for methane transport.

1.3.2 Storfjordrenna Gas hydrate mounds

Storfjordrenna or Storfjorden Trough (76 °N, 15- 16 °E), is located ~50 km south of Svalbard (Figure 5), and the water depth of around 380-400 m (Serov et al., 2017). Storfjorden trough is the second-largest trough in the western Barents Sea and is strongly affected by the ice sheet dynamics. The trough was developed by a dynamic ice stream draining substantial portions of the Barents Sea Ice sheet (BSIS) during the glaciation. Very different from Vestnesa Ridge, Storfjordrenna represents a shallow-water gas hydrate system, which can be directly affected by the bottom water warming and pressure changes induced by ice sheet retreatment (Serov et al., 2017). Indeed, ice sheet modeling suggests that Storfjordrenna was covered by grounded ice up to 2 km in thickness from 33 Ka to 19 Ka BP (Patton et al., 2017) After the deglaciation, relaxation of the underlying lithosphere leads to the glacio-isostatic adjustments which are still happening today (Auriac et al., 2016).

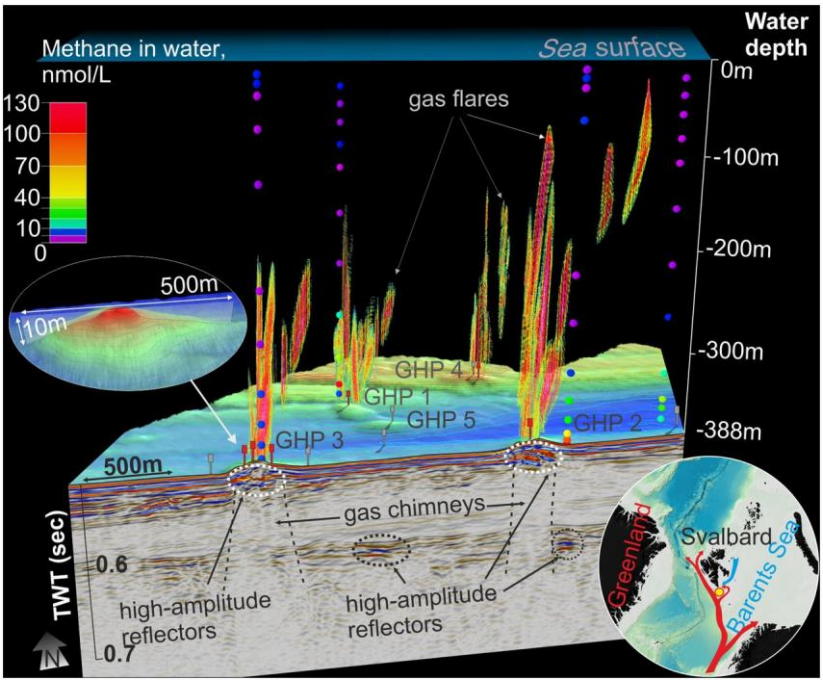

Figure 7. Seafloor morphology, gas chimneys in the seismic, and gas flares emitting to the water column in the Storfjordrenna gas hydrate mounds or gas hydrate pingo (GHP) as denoted in the figure. Figure from Serov et al. (2017).

Several mounds in Storfjordrenna were discovered during 2015 research cruises. These mounds with gas hydrate underneath were named gas hydrate mounds (GHMs) or gas hydrate pingos (GHP, Figure 7) were around 10 m in height and 500 m in width. They feature gas flares above the mounds, and hydrates were recovered from several of them (Hong et al., 2017; Serov et al., 2017). Earlier investigations and modeling suggest that the methane seepage in Storfjordrenna was linked with the ice sheet dynamic as the area was in the glaciated area, and the shallow water depth could be changed due to glacial isostatic adjustment. The gas hydrate stability zone (GHSZ) thickness change as the ice sheet advanced and retreated (Serov

et al., 2017, Figure 8 below).

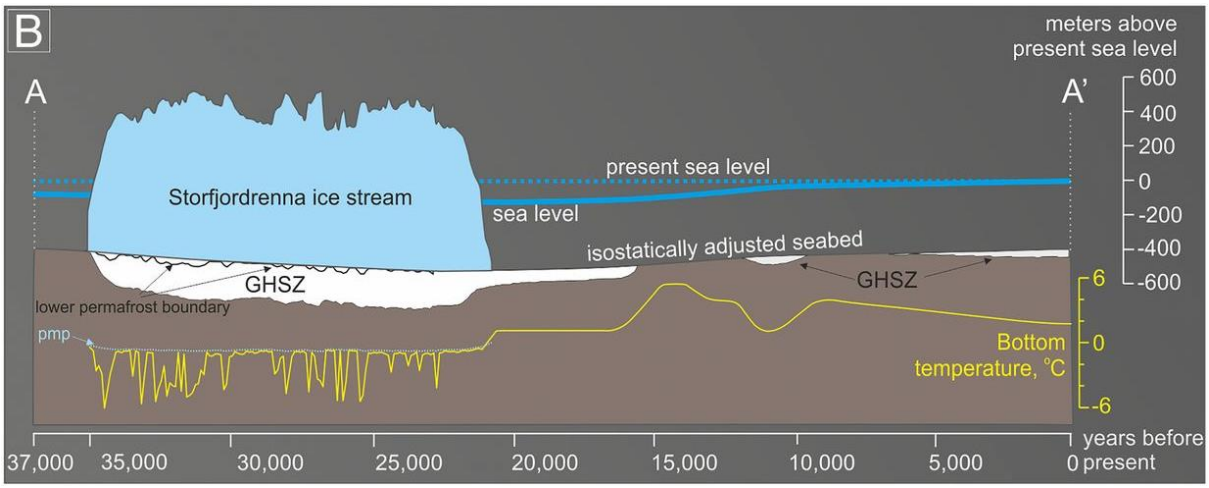

Figure 8. modeling of the relationship between the gas hydrate stability zone and ice sheet coverage in 37,000 year time frame. Figure from Serov et al. (2017).

Seismic data revealed sub-vertical amplitude masking zones beneath the GHMs as the fluid migration pathways (Waage et al., 2019). The upper Paleocene-Eocene and Pliocene-Pleistocene sedimentary rocks offer high-permeability zones for the gas and fluid migration. Waage et al (2019) observed a clear relationship between the thermogenic methane system in Storfjordrenna GHMs and the regional fault system, which could potentially establish a typical scenario of fault-controlled methane migration across the whole Svalbard- Barents Sea margin.

1.4 Methodology

1.4.1 Core collection and sediment properties

In this thesis, the sediment cores were collected from three CAGE cruises CAGE 15-2, CAGE 15-6, CAGE 16-5 (all cruise reports are accessible from the CAGE website)and an NGU cruise P1606. The gravity cores were collected in Storfjordrenna gas hydrate mounds 3 (active) and 5(inactive). Upon recovery of the cores, they were cut into 1m sections, split longitudinally into working and archive halves. Subsamples for stable isotope analyses of foraminifera and authigenic carbonates, lipid biomarker and radiocarbon dating were sampled onboard in the working half. The archive half was stored at 4 °C for sedimentary XRF and MSCL scanning onshore at UiT Geolab. The multi-cores from Vestnesa Ridge were collected by the multicorer system. The system was equipped with a MISO (Multidisciplinary Instrumentation in Support of Oceanography, Woods Hole Oceanographic Institution) towcam. Each deployment collect six paralleled cores at most (Panieri et al., 2015;Panieri et al., 2017a). Among the six cores, one was assigned for porewater analyses, and the two adjacent cores were subsampled for lipid biomarker and headspace gas analyses, respectively. A push core was collected during cruise P1606 using the remotely operated vehicle (ROV) Ægir with a video survey (Yao et al., 2019).

Sedimentary property measurements such as magnetic susceptibility, XRF, and X-ray scanning were done at UiT Geolab on the archive half. Magnetic susceptibility was acquired in 1 cm interval using a GeoTek Multi-Sensor Core Logger (MSCL) on all the gravity cores (except 1520GC). X-ray fluorescence (XRF) element-geochemical data were attained with an Avaatech XRF Core Scanner at 1 cm resolution. All the archived halves of the sediment cores and archiving multicores were scanned with a GEOTEK X-ray core imaging system (MSCL-XCT 3.0), using an X-ray intensity of 120 kV and a measuring resolution of 1 cm.

1.4.2 Stable isotope of foraminifera tests and carbonates

Foraminiferal and carbonates $\delta^{13}C$ and $\delta^{18}O$ analysis were done at the stable isotope laboratory at UiT using a Thermo Scientific MAT253 Isotope Ratio Mass Spectrometer (IRMS) coupled to a Gasbench II. Studies in this thesis were done on two benthic: *Cassidulina neoteretis* (Seidenkrants 1995), *Melonis barleeanu*s (Williamson 1858), and one planktonic (*Neogloboquadrina pachyderma* (Ehrenberg 1861)) foraminiferal species. These species were

picked due to their high abundance in the study areas after an overview survey of all the foraminiferal samples. Carbonate nodules/crusts were sieved out, grounded into homogeneous powder using a quartz mortar. Foraminiferal tests or carbonate powder were placed in specific vials and flushed with helium gas before five drops of water-free H_3PO_4 were added manually. After equilibration (>3 hours at 50°C), the samples were analyzed on the IRMS. Normalization to the Vienna Pee Dee Belemnite (VPDB) for carbon and oxygen isotopes were done using in-house standards. Analytical precision was better than 0.07 ‰ for $\delta^{13}C$ and 0.08 ‰ for $\delta^{18}O$ by measuring the certified standard NBS-19 repeatedly in the sequence queue.

Carbonate nodules/crusts were grounded and analyzed on a Bruker D8 Advanced diffractometer (Cu Ka radiation in 3-75 ° 2θ range) at NGU (Sauer et al., 2017) for mineralogy. The quantification of the carbonate mineralogical composition phases was modeled using the Rietveld algorithm-based code Topas-4 by Bruker. The correction of the spectrum was made on the main quartz peak, and the displacement of calcite d104 was used to estimate the amount of $MgCO_3$ mole percentage (Goldsmith et al., 1958).

1.4.3 Lipid biomarkers of sediment and carbonates

Sediment lipid biomarkers were extracted and analyzed according to previously reported protocols (Elvert et al., 2003). Briefly, a total lipid extract (TLE) was attained by ultrasonication of ~ 20 g wet sediment samples in four steps using solvents with decreasing polarity: dichloromethane (DCM) / methanol (MeOH) 1 : 2; DCM/MeOH 2 : 1; and only DCM for the last two steps. Carbonate lipid biomarkers were extracted similarly but were washed and acidified by 37% HCl before the TLE extraction.

The TLE was saponified with NaOH, the resulting neutral fraction was extracted with hexane prior to methylation to produce fatty acid methyl esters (FAMEs) for chromatographic analysis. The positions of the double bonds in FAMEs were determined by analyzing the corresponding dimethyl–disulfide adducts (DMDS) (Nichols et al., 1986; Moss and Lambert-Fair, 1989). With pipette column chromatography, the neutral fraction was further separated by solvents with increasing polarity into hydrocarbons, ketones, and alcohols. The alcohol fraction was derivatized to form trimethylsilyl (TMS) adducts for analysis.

The individual lipid compound was analyzed using gas chromatography (GC) (Thermo Scientific TRACE™ Ultra), equipped with a capillary column (Rxi-5ms, 50 m, 0.2mmID, 0.33 µm df), helium gas was used as a carrier gas at a constant flow rate of 1mL min^{-1}. The initial oven

temperature was set to be 50 °C, held for 2 min. Increased to 140 °C at a rate of 10 °C min^{-1}, and held for 1 min. Further increased to 300 °C at 4 °Cmin^{-1}. The final hold time was 63 min to analyze FAMEs and 160 min for the neutral hydrocarbon and alcohol fractions to analyze higher boiling points lipids. Concentrations of the lipids were determined by flame-ionization detection (FID) against internal standards. Unknown compounds were identified with a quadrupole mass spectrometry (QMS) unit (Thermo Scientific DSQ II) at the chromatography periphery. Using the same temperature program, compound-specific stable carbon isotope ratios were determined using a magnetic sector isotope ratio mass spectrometry (Thermo Scientific Delta V Advantage) coupled to a GC setup the same as the above-mentioned specification. $\delta^{13}C$ values are reported with an analytical error of ±1‰.

2 List of scientific contributions

- List of first author scientific paper and manuscripts:

Paper 1:

Yao, H., Hong, W. L., Panieri, G., Sauer, S., Torres, M. E., Lehmann, M. F., Gründger, F., and Niemann, H.: Fracture-controlled fluid transport supports microbial methane-oxidizing communities at Vestnesa Ridge, Biogeosciences, 16, 2221-2232, 10.5194/bg-16-2221-2019, 2019

Paper 2:

Yao, H., Niemann, H., and Panieri, G.: Multi-proxy approach to unravel methane emission history of an Arctic cold seep (submitted to Quaternary Science Reviews)

Paper 3:

Yao, H., Panieri, G., Lehmann, M., Himmer, T., and Niemann, H.: Biomarker and isotopic composition of seep carbonates record environmental conditions in two Arctic methane seeps (to be submitted to Deep Sea Research)

- List of co-authored papers:

Paper 4:

Hong, W. L., Torres, M. E., Carroll, J., Cremiere, A., Panieri, G., Yao, H., and Serov, P.: Seepage from an arctic shallow marine gas hydrate reservoir is insensitive to momentary ocean warming, Nat Commun, 8, 15745, 10.1038/ncomms15745, 2017.

Paper 5:

Köseoğlu, D., Belt, S. T., Smik, L., Yao, H., Panieri, G., and Knies, J.: Complementary biomarker-based methods for characterising Arctic sea ice conditions: A case study comparison between multivariate analysis and the PIP25 index, Geochimica et Cosmochimica Acta, 222, 406-420, 10.1016/j.gca.2017.11.001, 2018.

Paper 6:

Su, G., Zopfi, J., Yao, H., Steinle, L., Niemann, H., and Lehmann, M.F.: Manganese/iron-supported sulfate-dependent anaerobic oxidation of methane by archaea in lake sediments, Limnology and Oceanography, n/a, 10.1002/lno.11354,

Paper 7:

Pape, T., Bünz, S., Hong, W.-L., Torres, M. E., Riedel, M., Panieri, G., Lepland, A., Hsu, C.-W., Wintersteller, P., Wallmann, K., Schmidt, C., Yao, H., and Bohrmann, G.: Origin and Transformation of Light Hydrocarbons Ascending at an Active Pockmark on Vestnesa Ridge, Arctic Ocean, Journal of Geophysical Research: Solid Earth, 125, e2018JB016679, 10.1029/2018jb016679, 2020.

Paper 8:

Dessandier, P.-A., Borrelli, C., Yao, H., Sauer, S., Hong, W.-L., and Panieri, G.: Foraminiferal $\delta^{18}O$ reveals gas hydrate dissociation in Arctic and North Atlantic ocean sediments, Geo-Marine Letters, 10.1007/s00367-019-00635-6, 2020.

Paper 1 deals with the modern setting of the methane seep in Vestnesa Ridge. Three short sediment cores were compared for their methane concentrations, porewater geochemistry, and lipid biomarkers. The X-ray image revealed the presence of a mini-fracture in one of the cores. Our investigation revealed this fracture occurred rather recently and served as the methane gas migration pathway in the sediment.

Paper 2 reports the use of a multi-proxy approach to unravel the methane seepage history in another Arctic gas hydrate reservoir- Storfjordrenna gas hydrate mounds. We used the sedimentary Ba/Ti ratio, the carbon isotope of authigenic carbonates, foraminiferal test, and lipid biomarkers to reconstruct the methane history in Storfjordrenna in relation to the glacial-interglacial cycles. In addition to methane history, we also evaluate the use, the pros and cons of these various methane proxies.

Paper 3 is about the lipid biomarkers in methane derived authigenic carbonates. Herein, we studied the carbonates from both Vestnesa Ridge and Storfjordrenna. The studied carbonate samples were collected both from the seafloor and in the subsurface from drill cores. The mineralogy, stable carbon and oxygen isotopes, lipid biomarkers were investigated on these carbonates to reveal their dominant microbial community and the precipitating environment.

All three papers featured the use of lipid biomarkers from the AOM microbial communities in both modern and fossil settings in the Arctic Ocean. The usage of lipid biomarkers in sediments to refer to the methane seepage in non-Arctic marine sediment has a long history over about 20 years (Hinrichs et al., 1999). The lipid biomarker records in the Arctic are rare, mostly in Haakon Mosby mud volcano (Niemann et al., 2006;Chevalier et al., 2010) compare to other

known methane seep sites such as Gulf of Mexico (Zhang, 2002;Zhang et al., 2003;Pancost et al., 2005;Zhang et al., 2011;Kellermann et al., 2012), Black Sea (Peckmann et al., 2001;Blumenberg et al., 2005;Stadnitskaia et al., 2007;Sollai et al., 2019); and Hydrate Ridge (Birgel et al., 2006;Lipp and Hinrichs, 2009;Kaneko et al., 2013;Elvert et al., 2013).

Lipid biomarkers are a useful molecular tool to study methane seepage. They are stable over geological time scales and reflect the size and carbon source from the concentration and their isotopic signatures. Through these characteristics, they can trace the paleo methane seepage in combination with other methane proxies such as foraminifera and authigenic carbonates, as used in paper 2. It can indicate the transport modes of methane when used in combination with other geochemical data, as used in paper 1. The lipid biomarker pattern can provide information on the responsible AOM microbes as used in all three papers.

In comparison to other molecular tools used to investigate the microbes, lipid biomarkers are more stable than RNA and can indicate the recent lived or living microorganisms through intact polar lipid (Zink et al., 2003;Rossel et al., 2008;Lipp and Hinrichs, 2009)or some signature short-lived lipid biomarkers (Blumenberg et al., 2004;Stadnitskaia et al., 2008b). Lipid biomarkers have advantages such as less prone to degradation and contamination, higher detection limits, and the possibility of automating the whole extraction procedure. It is an excellent way to complement DNA detection in recognizing microbial communities.

The extent of the $\delta^{13}C$ of lipid biomarkers is the result of the carbon source and isotope fractionation (Wegener et al., 2008;Kellermann et al., 2012). That identification of specific lipid biomarkers provide means to identify not only the microbial communities, but also the $\delta^{13}C$ of the compound-specific isotope can indicate potential carbon source, and the process methane involved (methanogenic vs. methanotrophic).

Furthermore, the lipid biomarkers have applications beyond the methane seeps. In the co-authored paper list, paper 5 utilized the lipid biomarkers from diatoms living in the sea ice to reconstruct the sea ice coverage history.

3 Research papers

3.1 Fracture-controlled fluid transport supports microbial methane-oxidizing communities at Vestnesa Ridge (full text in the appendix)

3.2 Multi-proxy approach to unravel methane emission history of an Arctic cold seep (full text in the appendix)

3.3 Biomarker and isotopic composition of seep carbonates record environmental conditions in two Arctic methane seeps (full text in the appendix)

4 Summary and conclusion

The overall objective of this Ph.D. project was to investigate the Arctic Ocean sediment methane seepage history, timing, duration, and possible drivers using lipid biomarkers and foraminifera along with other geochemical data. With this goal, we set out to apply the methodology in two gas hydrate provinces in the Arctic: Vestnesa Ridge, one of the northernmost known active methane seep sites, and Storfjordrenna gas hydrate mounds, a shallow-water gas hydrate site. The main conclusions that draw from this Ph.D. project investigations are as follows:

Using lipid biomarkers and porewater data in the active pockmark at Vestnesa Ridge, we demonstrated a recently opened mini-fracture in the sediment that provides a pathway for methane gas transport in advective mode, and therefore facilitating the development of an active AOM community. Mini-fractures are rarely recognized because the detection is mostly incidental. We highlighted the importance of the mini-fracture network in sediment, their relevance for benthic methane dynamic, and benthic carbon cycling.

Reconstruction of methane seepage history in Storfjordrenna allows us to compare and evaluate the use of different proxies, such as sediment properties: magnetic susceptibility, Ba/Ti ratio from sediment XRF scan; $\delta^{13}C$ of foraminifera, $\delta^{13}C$ of authigenic carbonates, mineralogy of carbonates and $\delta^{13}C$ of lipid biomarkers, etc. The signals from these proxies indicate a relationship between the methane seepage and the glacial-interglacial cycles, as our study site is a shallow-water site where the gas hydrate stability zone can be sensitive to isostatic rebound.

The lipid biomarkers in the authigenic carbonates from both study sites further revealed a high methane flux period in the past as the carbonate formation close to the seafloor. The lipid biomarker patterns and the mineralogy of the carbonates are in agreement with the location where the carbonates were found (in core vs. on the seafloor). Lipid biomarkers for aerobic oxidation of methane were also found in these carbonates revealed the close distance between AOM and aerobic oxidation of methane indicate high methane discharge at the study site may release methane bubbles to the water column.

5 Outlook

Other than our main objectives achieved in the Ph.D. project, challenges in the research of methane seep remained. To identify the exact timing of a seepage event, U-Th dating of carbonate is one possible way. The accumulated diagenetic alterations on foraminiferal tests made the dating difficult, incubation of foraminifera (with methane and microbes) and modeling of the authigenic carbonate growth (by weighing the weight differences) from the incubation result could shed some light into the time frame of the diagenetic alteration, and degree of the diagenetic alteration.

In the lipid biomarkers line, as recently discovered, more electron acceptors such as nitrate/nitrite, manganese/iron oxides were able to couple to methane independently from sulfate, some of these microbes were identified by DNA analysis, yet the signature/specific lipid biomarkers have not been identified in these novel methane oxidation modes.

Furthermore, the main goal of methane seep research in the Arctic was to answer questions like, will the methane hydrate dissociation have positive feedback on climate- warming? Will the methane seepage far beneath the seafloor cause Ocean acidification? When will the Arctic methane hydrate dissociate? These questions require a more quantitative rather than qualitative investigation on the carbon storage and carbon cycling in the benthic system.

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Paper I

Fracture-controlled fluid transport supports microbial methane-oxidizing communities at Vestnesa Ridge

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Fracture-controlled fluid transport supports microbial methane-oxidizing communities at Vestnesa Ridge

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Abstract. We report a rare observation of a mini-fracture in near-surface sediments (30 cm below the seafloor) visualized using a rotational scanning X-ray of a core recovered from the Lomvi pockmark, Vestnesa Ridge, west of Svalbard (1200 m water depth). Porewater geochemistry and lipid biomarker signatures revealed clear differences in the geochemical and biogeochemical regimes of this core compared with two additional unfractured cores recovered from pockmark sites at Vestnesa Ridge, which we attribute to differential methane transport mechanisms. In the sediment core featuring the shallow mini-fracture at pockmark Lomvi, we observed high concentrations of both methane and sulfate throughout the core in tandem with moderately elevated values for total alkalinity, ^{13}C-depleted dissolved inorganic carbon (DIC), and ^{13}C-depleted lipid biomarkers (diagnostic for the slow-growing microbial communities mediating the anaerobic oxidation of methane with sulfate – AOM). In a separate unfractured core, recovered from the same pockmark about 80 m away from the fractured core, we observed complete sulfate depletion in the top centimeters of the sediment and much more pronounced signatures of AOM than in the fractured core. Our data indicate a gas advection-dominated transport mode in both cores, facilitating methane migration into sulfate-rich surface sediments. However, the moderate expression of AOM signals suggest a rather recent onset of gas migration at the site of the fractured core, while the geochemical evidence for a well-established AOM community at the second coring site suggest that gas migration has been going on for a longer period of time. A third core recovered from another pockmark along the Vestnesa Ridge Lunde pockmark was dominated by diffusive transport with only weak geochemical and biogeochemical evidence for AOM. Our study highlights that advective fluid and gas transport supported by mini-fractures can be important in modulating methane dynamics in surface sediments.

1 Introduction

Large-scale fractures are commonly observed on seismic profiles (Tobin et al., 2001; Weinberger and Brown, 2006; Plaza-Faverola et al., 2015) and can provide increased sediment permeability and conduits for fluid and gas transport. Macro-fractures were often observed in association with cold seep systems, where methane-rich fluids from greater sediment depth reach shallow sediments and may even be transported across the sediment–water interface (Berndt et al., 2014; Sahling et al., 2014). Prominent examples of fracture-controlled fluid migration at cold seep systems include locations such as Hydrate Ridge (Torres et al., 2002; Weinberger

and Brown, 2006; Briggs et al., 2011), Blake Ridge (Egeberg and Dickens, 1999), and the recently documented Storfjordrenna gas hydrate mounds in the Barents Sea (Hong et al., 2017b, 2018; Waage et al., 2019). Seepage at these locations can sustain high biomass levels of chemosynthetic communities that either directly oxidize methane or metabolize products of methane oxidation, such as sulfide (Boetius and Suess, 2004; Niemann et al., 2013). Fractures visible on seismic profiles often exceed 10 m in length (Gabrielsen et al., 1998). However, surface sediments may also feature smaller-scale, branched fracture networks (hereafter referred to as mini-fractures) which propagate from macro-fractures as the fluid pressure increases (Friedman, 1975; Briggs et al., 2011; Anders et al., 2014).

The role of small-scale fracture networks in routing methane upwards into the near-surface sediments is not well understood. In particular, the biogeochemical effects of mini-fractures in sediments with methane-dependent microbial communities is poorly constrained but is important for our understanding of how fracture networks influence microbial dynamics. Geochemically, fractures facilitate migration of deep fluids that are laden with electron donors from deeper sediments, which can then be used by sedimentary microbes as metabolic or bioenergetics substrates. To date, such mini-fractures have either been detected by X-ray images of cores under pressure (Riedel et al., 2006), or by the presence of macroscopic biofilms lining subseafloor fractures (Briggs et al., 2011). These biofilms were usually present at the sulfate–methane transition zone (SMTZ), where methane is oxidized by a consortium of anaerobic methanotrophic archaea (ANME) and sulfate-reducing bacteria (SRB) mediating the anaerobic oxidation of methane (AOM) with sulfate as the terminal electron acceptor (Knittel and Boetius, 2009):

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O. \quad \text{(R1)}$$

In contrast to large-scale transport pathways, mini-fractures are difficult to detect as they cannot be resolved with seismic tools (Emery and Myers, 1996; Gabrielsen et al., 1998) and may thus play an underappreciated but potentially important role in sediment methane dynamics, and the efficiency of the benthic microbial methane filter.

In this study, we report on the presence of a mini-fracture in the near-surface sediments of the active pockmark Lomvi, located on Vestnesa Ridge (79° N, 6° E), west of the Svalbard archipelago. Using an interdisciplinary approach that combines geochemical and organic geochemical methods, we investigate the effects that such mini-fractures may impose on benthic methane dynamics and associated microbial communities. Our data show that mini-fractures can provide conduits for advective gas migration fostering AOM, but the moderate expression of AOM-associated biogeochemical signals along the mini-fracture at the Lomvi pockmark suggest a rather recent opening of this particular fracture.

2 Material and methods

2.1 Study sites

Vestnesa Ridge is NW–SE trending, ∼ 100 km long, and covered with ∼ 1 km thick contourite drifted sediments. Vestnesa Ridge features numerous pockmark structures (see a more detailed description of the geological setting in Plaza-Faverola et al., 2015, and Panieri et al., 2017). This ridge is part of a submarine gas-hydrate system on the west Svalbard margin (1200 m water depth), where fluid and gas migration from deep hydrocarbon reservoirs towards the seafloor has potentially been ongoing since the early Pleistocene (Knies et al., 2018). Past investigations have shown that the ridge actively releases methane gas from the seafloor along the eastern segment of the structure (Bünz et al., 2012; Smith et al., 2014; Plaza-Faverola et al., 2015; Panieri et al., 2017), and seismic data suggest that seepage is related to intensive seabed faulting and rifting (Plaza-Faverola et al., 2015). The eastern part of Vestnesa Ridge features the pockmarks Lunde and Lomvi (Fig. 1), both belonging to the most active structures known in the area (Bünz et al., 2012; Panieri et al., 2017). Pockmarks are morphological expressions of fluid and/or gas eruptions from sediments, and are commonly observed in active hydrocarbon systems (Hovland et al., 2002). Pockmarks can be prominent in the seafloor bathymetry, ranging in shape from circular, crater-like edifices to "push-down" sediment features (Hovland et al., 2002). Enhanced reflections and "push-down" features observed in the seismic transects of Lunde and Lomvi were interpreted as chimney structures containing free gas, which originate from beneath the bottom of the gas-hydrate stability zone (Bünz et al., 2012; Smith et al., 2014). Excessive pore pressure at the summit of this gas column fractured the sediments and led to the presence of free gas in the hydrate stability zone (Weinberger and Brown, 2006; Bünz et al., 2012).

2.2 Sample collection

We investigated three sediment cores from Vestnesa Ridge: two were collected by a multicorer (MC) during cruise CAGE15-2 with R/V *Helmer Hanssen* in 2015 (core Lomvi 893MC and core Lunde 886MC), and an additional push core (core Lomvi 008PC) was recovered with the remotely operated vehicle (ROV) Ægir about 80 m away from core Lomvi 893MC during the P1606 cruise with R/V *G.O. Sars* in 2016 (Table 1). The MC system used during cruise CAGE15-2 can collect up to six parallel cores during every deployment, and a MISO (Multidisciplinary Instrumentation in Support of Oceanography, Woods Hole Oceanographic Institution) towcam was attached to the MC frame, allowing targeted video-controlled sampling (Panieri et al., 2015, 2017). Among the six cores, one was subsampled for porewater analyses, and two adjacent cores were used for lipid biomarker and headspace gas analyses, respectively. The cores for porewater

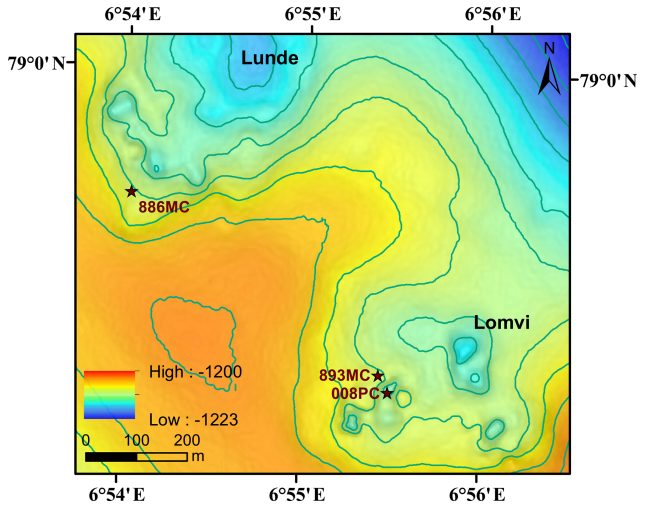

Figure 1. Regional multibeam bathymetric map of Vestnesa Ridge showing the Lunde and Lomvi pockmarks and sampling locations. Locations of multicores and push cores used in this paper are denoted as stars.

extraction were used for X-ray analysis. Core Lomvi 893MC was collected at a site with bacterial mats around outcropping carbonate crusts at the Lomvi pockmark, whereas core Lunde 886MC was collected at a soft sediment site with patchy bacterial mats and tubeworms at the Lunde pockmark (Figs. 1 and 2). The push core Lomvi 008PC was recovered from a large patch of bacterial mat at the Lomvi pockmark. This core was only sampled for the analysis of porewater and lipid biomarkers (limited sample material impeded the analysis of the gas composition from Lomvi 008PC).

Immediately upon recovery, we subsampled the cores for subsequent gas, porewater, and biomarker analyses. Details on headspace sampling and gas analysis in the multicores were described in Panieri et al. (2017) and references therein. Briefly, 5 mL of bulk sediments were sampled into a 20 mL headspace glass vial, containing 5 mL of 1M NaOH and two glass beads. The gas analysis was performed with a ThermoScientific Trace 1310 gas chromatograph (GC) equipped with a TG-BOND alumnia (Na_2SO_4) column (30 m × 0.53 mm × 10 µm). The methane headspace samples were obtained on a parallel core as the fractured core in the same set of the multicorer frame. Porewater was extracted at ambient temperature (ca. −1 °C), at a resolution of 2 cm, with either 10 cm (Lomvi 893MC and Lunde 886MC) or 5 cm rhizon samplers (Lomvi 008PC) attached to acid-cleaned syringes (Seeberg-Elverfeldt et al., 2005). Rhizon membranes were soaked in Milli-Q water before use. The first 0.5 mL of the recovered porewater was discarded to avoid dilution or contamination with residual Milli-Q water in the rhizons. Sediment samples for biomarker analyses were collected on board with a methanol pre-cleaned spatula at a resolution of 2 cm, wrapped in aluminum foil and subsequently stored frozen at −20 °C until analysis. Intact sediment cores were kept at 4 °C for further X-ray analysis in onshore laboratories using a Geotek MSCL-XCT at UiT.

2.3 Porewater analyses

Total alkalinity (TA) was measured on board using the Gran titration method (Grasshoff et al., 1999) within a few hours after the syringes were disconnected from the rhizon samplers. The HCl titrant (0.012 M) was checked daily on board with local surface seawater and 10 mM of borax to verify the acid concentration. The pH meter of the titrator was calibrated with pH standard solutions (pH of 4, 7, and 11) both before and during the cruise. Porewater aliquots (2 mL) for sulfate analysis were preserved with 3 mL zinc acetate solution (23 mM) to precipitate the dissolved sulfide (Gieske et al., 1991; Grasshoff et al., 1999) for CAGE 15-2 samples. All sulfate analyses were performed using a Dionex ICS-1100 Ion Chromatograph equipped with a Dionex IonPac AS23 column at the Geological Survey of Norway (NGU) (Sauer et al., 2016). For sulfide concentration measurements, the precipitated zinc sulfide was quantified in the onshore geology laboratory at UiT with a spectrophotometric method (Cline, 1969) using a UV-1280 UV–vis Spectrophotometer (Shimadzu). The amount of zinc acetate added to samples from core 008PC was too low to precipitate all dissolved sulfide; thus the measured sulfide concentrations are minimum values. For the subsequent measurement of $\delta^{13}C$ of dissolved inorganic carbon (DIC), 2 mL aliquots of porewater were fixed on board with saturated $HgCl_2$ (27 mM final concentration) (Grasshoff et al., 1999). The $\delta^{13}C$ DIC of CAGE 15-2 samples (Bernhard and Panieri, 2018) were analyzed using a Finnigan DELTA-Plus mass spectrometer coupled to a GasBench II as described in Torres et al. (2005). The $\delta^{13}C$ DIC in pore waters of core Lomvi 008PC was determined from the CO_2 liberated from the water after acidification with phosphoric acid. Measurements were carried out at EAWAG (The Swiss Federal Institute of Aquatic Science and Technology) using an IRMS (Isotope Ratio Mass Spectrometer, Isoprime) equipped with a Gilson 222XL Liquid Handler and a Multiflow unit (Isoprime). The standard deviation of the $\delta^{13}C$ DIC measurements from repeated measurements of standards was ±0.1 ‰ (1σ, $n = 27$). The stable carbon isotope values for DIC are reported in the conventional δ notation in per mill (‰) relative to V-PDB (Vienna Pee Dee Belemnite).

2.4 Lipid extraction, quantification, identification, and determination of compound-specific stable carbon isotope composition

Lipid biomarkers were extracted and analyzed according to previously reported protocols (Elvert et al., 2003) with modification for alcohol derivatization (Niemann et al., 2005) and instrument setup (Blees et al., 2014; Steinle et al., 2018). Briefly, a total lipid extract (TLE) was obtained by ultrasonication of ∼ 20 g wet sediment samples in four extraction

Table 1. Information on coring stations, coring coordinates, seafloor habitat information, and analyses performed at each site. DIC: dissolved inorganic carbon; TA: total alkalinity; conc.: concentration; NA – not available.

Pockmark (cruise)	Lomvi (CAGE15-2)	Lomvi (P1606)	Lunde (CAGE15-2)
Core	Lomvi 893MC	Lomvi 008PC	Lunde 886MC
Coordinates	79°0.180′ N	79°0.162′ N	79°0.366′ N
	6°55.434′ E	6°55.488′ E	6°54.030′ E
Habitat	bacterial mats and carbonate crusts	bacterial mats	tubeworms
Methane	methane headspace	NA	methane headspace
Porewater analyses	sulfate, sulfide, TA, δ^{13}C DIC	sulfate, sulfide, TA, δ^{13}C DIC	sulfate, sulfide, TA, δ^{13}C DIC
Lipid biomarkers	conc. and δ^{13}C	conc. and δ^{13}C	conc. and δ^{13}C

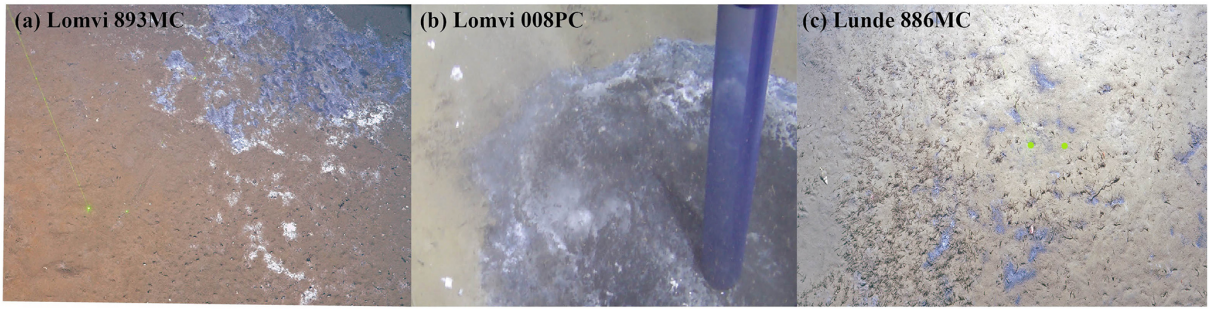

Figure 2. Still images of the seafloor before launching of the multicorer at coring site Lomvi 893MC **(a)** and coring site Lunde 886MC **(c)**, as well as during ROV guided push coring at coring site Lomvi 008PC **(b)**. Coring site Lomvi 893MC **(a)** and 008PC feature bacterial mats and reduced, black sediments, while the coring site Lunde 886MC **(c)** is characterized by soft sediments with tubeworms and small patchy bacterial mats. Green laser points **(a, c)** are 20 cm apart and the diameter of the push core **(b)** is 8.5 cm.

steps with solvents of decreasing polarity: dichloromethane (DCM) / methanol (MeOH) 1 : 2; DCM/MeOH 2 : 1; and DCM for the last two extraction steps. The TLE was then saponified, and a neutral lipid fraction was extracted prior to methylation of the remaining polar fraction (comprising free fatty acids) to yield fatty acid methyl esters (FAMEs) for chromatographic analysis. Double bond positions of FAMEs were determined by analyzing dimethyl–disulfide adducts (Nichols et al., 1986; Moss and Lambert-Fair, 1989). The neutral fraction was further separated into hydrocarbons, ketones, and alcohols, the latter of which was derivatized to form trimethylsilyl adducts for analysis.

Individual lipid compounds were analyzed using a GC (Thermo Scientific TRACE™ Ultra), equipped with a capillary column (Rxi-5ms, 50 m, 0.2 mm ID, 0.33 µm d_f), using helium gas as a carrier gas at a constant flow rate of 1 mL min^{-1}. The initial oven temperature was set to 50 °C, held for 2 min and then increased to 140 °C at a rate of 10 °C min^{-1}, held for 1 min, then further increased to 300 °C at 4 °C min^{-1}. The final hold time was 63 min to analyze FAMEs or 160 min to analyze larger (i.e., high boiling point) lipids in the hydrocarbon and alcohol fractions. Concentrations were determined by flame-ionization detection (FID) against internal standards. Unknown compounds were identified with a quadrupole mass spectrometry unit (Thermo Scientific DSQ II) at the chromatography periphery. Similarly, compound-specific stable carbon isotope ratios were determined using a magnetic sector isotope ratio mass spectrometry unit (Thermo Scientific Delta V Advantage) coupled to a gas chromatography setup with the above-outlined specification. δ^{13}C values are reported with an analytical error of ±1 ‰.

3 Results and discussion

3.1 Sediment X-ray imaging and porewater geochemistry

Our detailed X-ray imaging of cores retrieved from locations of known methane seepage in Vestnesa Ridge revealed a mini-fracture in the core Lomvi 893MC in the top 30 cm (Fig. 3) but not in any other core. However, it is important to note that X-ray imaging can only confirm the presence of a fracture while the size or expansion of the original fracture cannot be resolved. Upon recovery, core Lomvi 893MC showed extensive gas ebullition. Thus it is possible that the fracture expanded during core retrieval because of pressure-induced volume changes in sedimentary gases. Nevertheless, our analyses revealed a substantial increase in methane concentrations in the upper section of the core (Fig. 4), which is

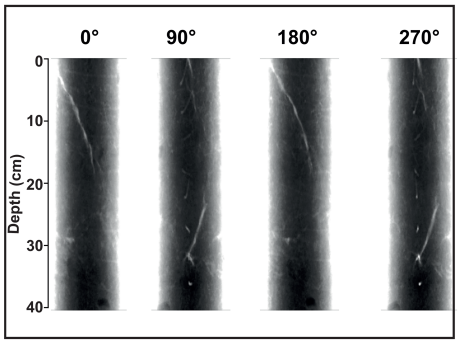

Figure 3. X-ray images of core Lomvi 893MC. The different rotational planes show a whitish X-ray transparency extending throughout the core. This zone is interpreted as a zone of weakness facilitating fluid and gas migration in situ. The void probably became gas filled after core recovery. A rotational video of this core is available in the Supplement.

an uncommon observation in marine settings where methane originates at greater sediment depth (i.e., methane concentrations typically increase downcore). We argue that the higher concentration at the surface of the core directly indicates an advective (fracture controlled) influx of methane into the top sediment section at the coring side of the core Lomvi 893MC. Typically, high methane concentrations in marine sediments lead to elevated rates of AOM, which in return lead to sulfate depletion and sulfide production, and thus the development of a sulfate methane transition zone (SMTZ). Furthermore, excess production of DIC during AOM leads to elevated sediment TA and low δ^{13}C DIC values. The marked methane increase at coring site Lomvi 893MC was not paralleled by changes in other parameters, which are commonly associated with AOM (Fig. 4a). Rather, the smooth porewater profiles of sulfate, sulfide, TA, and δ^{13}C of DIC in this core seem typical for locations with low methane input, as often found in settings characterized by diffusive transport regimes (Treude et al., 2003; Egger et al., 2018; Niemann et al., 2009). We attribute this apparently contradictory observation of enhanced methane concentrations on the one hand and the rather "inconspicuous" signals for AOM activity on the other to a recent genesis of the fracture (see additional discussion below). To further investigate the changes associated with the highly heterogeneous nature of the methane dynamics in this region, we compared this first core with two additional cores from contrasting settings at Vestnesa Ridge.

The push core Lomvi 008PC retrieved from an active venting site (ca. 80 m to the SE of core Lomvi 893MC) at the Lomvi pockmark showed sulfate depletion within the first 5 cm b.s.f. (below the sea floor) (Fig. 4b), indicating a high methane flux and a shallow SMTZ (Reeburgh, 2007). This shallow SMTZ is comparable to those typically observed at locations of high methane flux, such as the *Beggiatoa* fields at Hydrate Ridge (Treude et al., 2003), the Gulf of Mexico (Ussler and Paull, 2008), or Haakon Mosby Mud Volcano (Niemann et al., 2006a, b). At these high-flux sites, AOM rates have been estimated to be on the order of several millimoles per square meter per day. A third core (core Lunde 886MC) was retrieved from a soft-sediment site characterized by the extensive occurrence of tubeworms and bacterial mats (Fig. 2) at the adjacent active Lunde Pockmark. Sulfate concentrations in this core showed only a moderate decrease with sediment depth and traces of methane were detected in the upper 20 cm of the core (Fig. 4c). These data are consistent with observations of low sulfide concentrations and TA. Together, our results indicate a substantially lower methane flux and efficient methane retention through AOM in sediments at this coring site, similar to previous findings from seep sites characterized by macrofauna-inducing bioventilation (e.g., Niemann et al., 2006a, b; Levin et al., 2016). Although core Lunde 886MC is located in a diffusive system, the convex shape of the sulfate concentration profile along with increasing methane concentration at the bottom suggest non-steady-state conditions. The convex shape of the sulfate profile can be related to an ongoing increase in methane flux (Fischer et al., 2013; Hong et al., 2017b). It may also be related to the intrusion of seawater into the shallower sediments, which can be induced by bioventilation, and/or ascending methane bubbles from the sub-seafloor (Haeckel et al., 2007; Hong et al., 2016). Our visual investigations of the seafloor revealed the presence of tubeworms but there are a few bivalves; therefore bioventilation would be moderate. Methane concentration in the upper sediment section was very low, and we did not observe methane bubbles emanating from the seafloor at the coring site. We thus assume that moderate bio-irrigation and a recent increase in the diffusive methane flux at the coring site (Lunde 886MC) can explain the non-steady-state sulfate and methane profiles in the Lunde pockmark core.

3.2 Methanotrophic community development

To further investigate the role of the detected mini-fracture in core Lomvi 893MC on the biogeochemistry and microbial community, we investigated archaeal and bacterial lipid biomarkers and their associated stable carbon isotope signatures that are diagnostic for AOM communities (Niemann and Elvert, 2008, and references therein). ANMEs typically produce a suite of glycerol ether lipids comprising isoprenoidal alkyl moieties that may also occur as free hydrocarbons in environmental samples. We found the isoprenoidal dialkyl glycerol diethers archaeol and *sn2*-hydroxyarchaeol in all three cores (Fig. 4a–c). Furthermore, the ^{13}C-depleted signatures of these compounds provide evidence that their source organisms mediate sulfate-dependent AOM. Indeed, ANME biomass is characterized by a strongly ^{13}C-depleted isotope composition because the metabolized methane is typically ^{13}C-depleted, and AOM is associated with a strong kinetic isotope effect (Whiticar, 1999). The sulfate-reducing

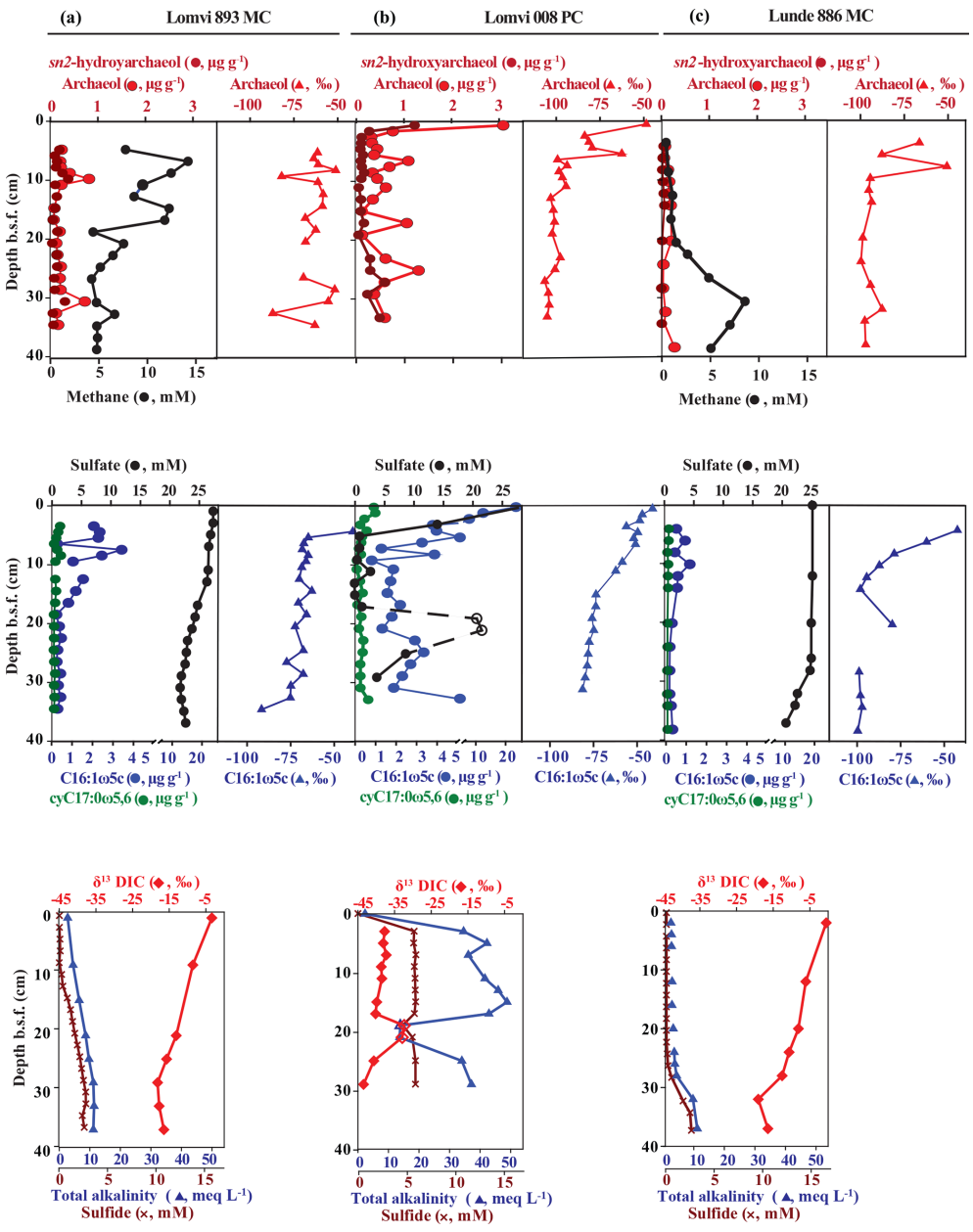

Figure 4. Biogeochemical profiles of archaeal (*sn2*-hydroxyarchaeol, archaeol) and bacterial lipid biomarkers (fatty acids C16 : 1ω5c, cyC17 : 0ω5, 6), methane, and pore water constituents (sulfate, sulfide, DIC, and total alkalinity) in the three cores: Lomvi 893MC **(a)**, Lomvi 008PC **(b)** and Lunde 886MC **(c)**.

partner bacteria involved in AOM produce characteristic fatty acids (C16 : 1ω5c, and cyC17 : 0ω5, 6) which we observed at relatively high concentrations (Fig. 4a–c). As these bacteria incorporate ^{13}C-depleted DIC produced by the anaerobic methanotrophs (Wegener et al., 2008), their stable carbon isotope signature was also depleted in ^{13}C. The biomarker data are consistent with an active AOM microbial population at all Vestnesa Ridge sites.

Our data also show, however, clear differences in the abundance of AOM-derived lipids at the three investigated coring sites (Fig. 4a–c). To highlight these differences, we calculated average concentrations and the isotopic depletion of archaeol and fatty acid C16 : 1ω5c (i.e., typical ANME and associated SRB lipids) relative to source methane ($\Delta\delta^{13}$C values) and compared these values to a non-seeping reference site south of Svalbard (Yao et al., 2017) and a known high methane flux site at Hydrate Ridge (Elvert et al., 2005) (Fig. 5). We chose Hydrate Ridge as the high flux comparison site because the only other observation of a mini-fracture was documented from that location (Briggs et al., 2011). We

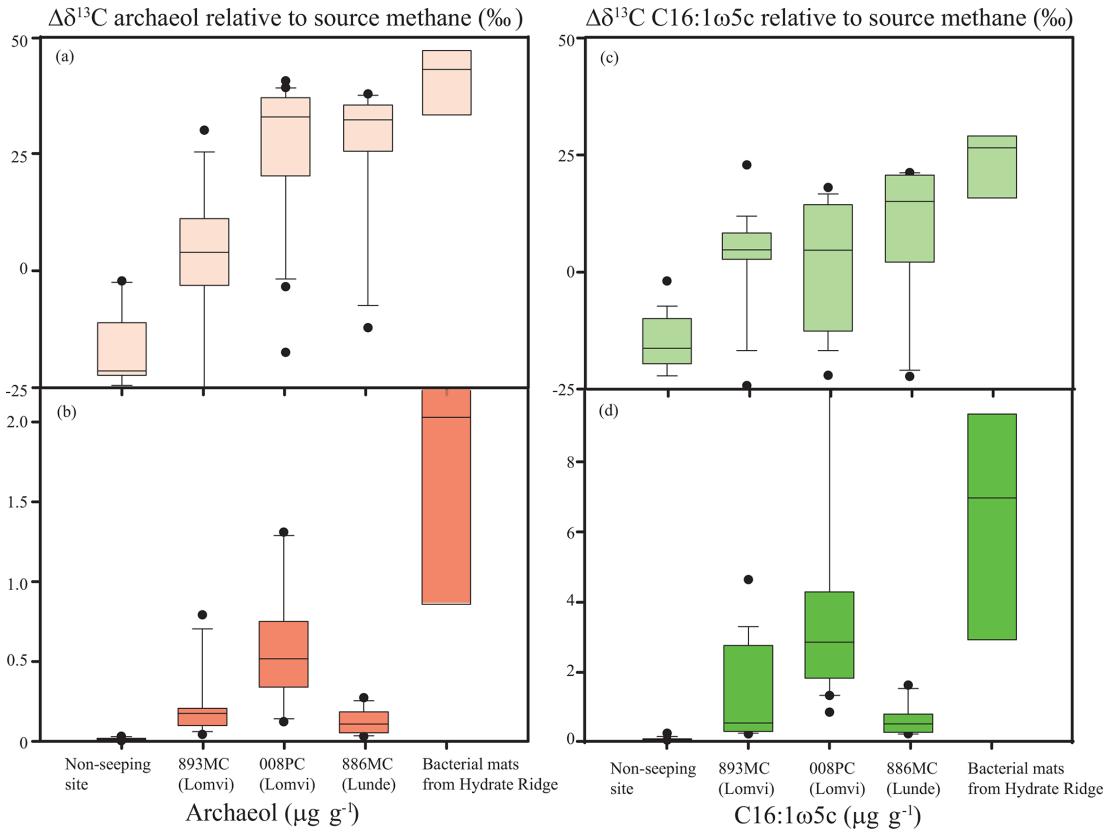

Figure 5. Average lipid biomarker concentrations and isotopic differences to source methane of the archaeal lipid archaeol ($\Delta\delta^{13}$C) **(a, b)** and the bacterial fatty acid C16 : 1ω5c **(c, d)**. Cores Lomvi 893MC (averaged from 0–35 cm), Lomvi 008PC (averaged from 0–33 cm), and Lunde 886MC (averaged from 0–38 cm) are compared to a high flux site at Hydrate Ridge (Elvert et al., 2005) and a core from a non-seeping site south of Svalbard (1522GC, 76.107° N, 15.957° E, averaged from 0–350 cm; Yao et al., 2017).

found the lowest concentrations of the diagnostic lipids at the non-seeping reference site, followed by the core Lunde 886MC, the core Lomvi 893MC, the core Lomvi 008PC, and finally the Hydrate Ridge core. The substantially higher concentration of AOM-derived lipids at the Lomvi (particular in core Lomvi 008PC) compared to the Lunde site (core Lunde 886MC) is consistent with the geochemical signals of AOM (e.g., sulfate, sulfide, δ^{13}C of DIC) in the respective cores. The differences in concentrations of diagnostic lipids suggest a high standing stock of AOM communities in core Lomvi 008PC, and a much lower one in the other two cores. AOM communities grow very slowly, with doubling times of several months (Nauhaus et al., 2007; Zhang et al., 2011; Timmers et al., 2015). A sudden increase in methane flux and methane concentrations in the sulfate-rich sediments, which comprise only a small initial standing stock of AOM microorganisms, may eventually lead to elevated AOM activity, but with a significant lag time of several months to years. Our biomarker data suggest that the methanotrophic community at coring site Lomvi 893MC was not well developed, indicating that the increase in methane concentrations at that site occurred rather recently, probably less than a few years prior to our sampling campaign. We found a more mature AOM community at the site Lomvi 008PC. Similarly, the previous findings of biofilms associated with the mini-fracture at Hydrate Ridge (Briggs et al., 2011) indicate a more mature AOM community at this site. This suggests that the methane flux was higher at these sites for a longer period of time, allowing for the establishment of the slow-growing AOM community.

Because of the spatial dynamics of venting at the Lomvi pockmark in Vestnesa Ridge (Bohrmann et al., 2017; Hong et al., 2017a, b; Panieri et al., 2017), it is likely that the biomarker results reflect the cumulative history of microbial AOM activity, rather than solely the most recent situation. Nonetheless, we observed a general decrease in δ^{13}C of both bacterial and archaeal lipids in horizons of present-day sulfate depletion, indicating a higher contribution of AOM-derived compounds to the lipid pool. Such a decrease in δ^{13}C was apparent at $\sim$ 10 cm b.s.f. in Lomvi 893MC where sulfide started to accumulate, at $\sim$ 5 cm b.s.f. in core Lomvi 008PC where sulfate was depleted, and at 10–15 cm b.s.f. in Lunde 886MC where methane began to increase downcore (Fig. 4). At these depths, the ratios of *sn2*-hydroxyarchaeol

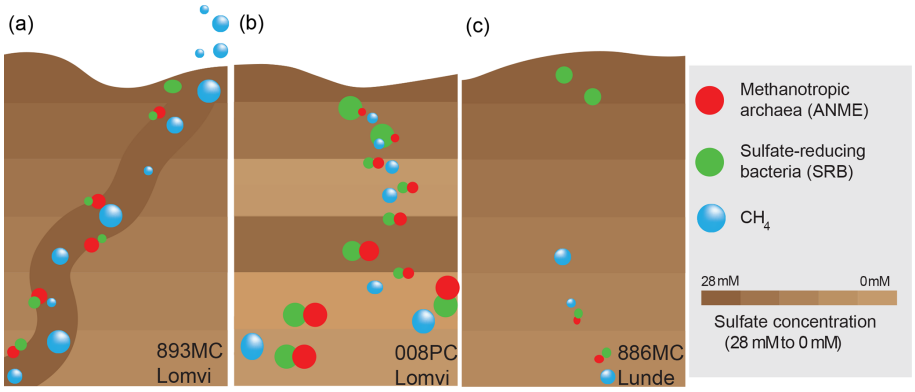

Figure 6. Schematic illustration of different methane transport modes in the study area (big bubble and circle sizes highlight high methane concentrations and the approximate size of the standing stocks of AOM communities, respectively). Low amounts of methane in a diffusion-dominated setting sustain a weakly defined AOM microbial community **(c)**. Mini-fracturing enhances the methane availability and fosters AOM community growth **(a)**. The AOM community is fully developed after advective methane transport has continued for a longer period of time **(b)**.

to archaeol were 0.98 (core Lomvi 893MC), 0.37 (core Lomvi 008PC), and 0.26 (core Lunde 886MC), indicating that ANME-1 is likely to be a key AOM organism at all the investigated coring sites (Niemann and Elvert, 2008). The known SRB types associated with ANME-1 and ANME-2 belong to the *Deltaproteobacteria, Desulfosarcina/Desulfococcus* clade Seep-SRB1, which typically display distinct ratios of the fatty acids C16 : 1ω5c relative to isoC15 : 0. In systems dominated by Seep-SRB1 associated with ANME-1 this value is commonly < 2, while it is $\gg 2$ in systems where Seep-SRB-1 is associated with ANME-2 (Niemann and Elvert, 2008). At all coring locations, this biomarker ratio was > 2 (3.2, core Lomvi 893MC; 5.4, core Lomvi 008PC; 7.9, core Lunde 886MC), which is indicative of an SRB eco-type associated with ANME-2 rather than ANME-1. At this point, we can only speculate about these contradicting lipid patterns, and additional DNA-based tools would be needed to further identify the key AOM microbes at the investigated sites.

The ^{13}C values of lipids from AOM communities are mainly influenced by isotope fractionation during AOM and the δ^{13}C value of the carbon sourced from methane (Summons et al., 1994; Riou et al., 2010), though other environmental parameters such as substrate availability and temperature are also known to influence lipid δ^{13}C signals. δ^{13}C CH_4 values are typically low and the additional isotope fractionation during AOM results in AOM-derived lipid, with δ^{13}C values $\ll -50$ ‰. Our reference site showed δ^{13}C values of archaeal and bacterial lipids that were not conspicuously depleted. This indicates a low or negligible standing stock of AOM microbes at this site. Here, archaeal and bacterial lipids likely originated from processes other than AOM (e.g., organic matter degradation by heterotrophs). At site Lomvi 893MC, the δ^{13}C values of archaeal and bacterial lipids were not as negative as at the other three sites. The differences in the δ^{13}C signature of archaeol with respect to the source methane (δ^{13}C $CH_4 = -57.8$ ‰ in core Lomvi 893MC and -62.9 ‰ in core Lunde 886MC; Panieri et al., 2017), were slightly lower in core Lomvi 893MC than in core Lunde 886MC (Fig. 5a). This may reflect an overprint by lipids that are not related to AOM, which supports our assumption that the mini-fracture in core Lomvi 893MC and the associated AOM community developed rather recently. We do not know the source methane δ^{13}C value for core Lomvi 008PC, but, assuming a uniform source methane value of -55 ‰ for the whole Lomvi pockmark area, the highest $\Delta\delta^{13}$C values were observed at Lomvi 008PC (Fig. 5). Together with the biomarker evidence for a significant AOM community and the rapid depletion of sulfate in this core, this indicates that AOM biomass (and probably AOM activity) is more dominant at the Lomvi 008PC coring site than at the other two investigated sites. Although the AOM community seemed lower at Lunde 886MC, the $\Delta\delta^{13}$C values were similar to the ones observed at Lomvi 008PC. This suggests that here, despite the lower methane flux, AOM communities also dominated the overall microbial community.

4 Summary and conclusion

At the Lomvi pockmark, we found evidence for advective methane transport, with an indication for different onsets of gas seepage at the different coring sites, while at the coring site at the Lunde pockmark, methane transport is dominated by diffusion (Fig. 6). Together with the porewater geochemical constraints, the distribution of ^{13}C-depleted lipid biomarkers underscores that the pockmark methane biogeochemistry is differentially affected by the advective vs. diffusive transport regimes. Our data show that high standing stocks of AOM communities thrive in surface sediments where methane concentrations are high, while in sediments

where methane availability is limited, only a comparably low AOM biomass developed. The co-occurrence of a well-developed AOM standing stock and high CH_4 concentrations, however, cannot be considered a universal rule. Despite high methane concentrations in sediments featuring a mini-fracture, sediments contained a comparably low standing stock of AOM communities, and geochemical signals for AOM activity were rather subtle. Methane transport through mini-fractures is advective and fractures thus represent important conduits for methane, facilitating the development of an active AOM community. Yet a high biomass of the slow-growing AOM communities require that advective transport has proceeded for an extended period of time after the onset of sediment fracturing (i.e., the development of AOM communities temporally lags behind). Our data suggest that the mini-fracture detected here opened rather recently, whereas methane transport at the other coring sites probably started much earlier. Mini-fractures are rarely recognized because they are below the resolution of seismic imaging tools and their detection is mostly incidental. Our study clearly highlights their relevance for benthic methane dynamics and adds to the very limited knowledge on the potential contribution of fracture networks to benthic carbon cycling.

Data availability. All the data in the paper can be found in the Supplement.

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/bg-16-2221-2019-supplement.

Author contributions. HY and GP collected biomarker samples. WLH, MET, and SS contributed to porewater sampling and analyses. HN and MFL supported lipid biomarker analyses. HY wrote the majority of the paper. GP and HN supervised the research. All authors contributed to the discussion of data and the writing of the paper at different stages.

Competing interests. The authors declare that they have no conflict of interest.

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