Oil & Natural Gas Technology

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Progress Report (Period Ending 09/30/2017)

Project Title

Assessing the response of methane hydrates to environmental change at the Svalbard continental margin
Project Period (11/1/2013 to 10/31/2018)

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EXECUTIVE SUMMARY

In November 2013, Oregon State University initiated the project entitled: **Assessing the response of methane hydrates to environmental change at the Svalbard continental margin**. In this project, we will take advantage of a unique opportunity to collect samples from the Svalbard continental margin. The overall objective of this research is to constrain the biogeochemical response of the gas hydrate system on the Svalbard margin to environmental change. Because of a delay in the planned expedition, we reconfigured the program based on discussions with NETL program managers and submitted a revised SOPO. In the new plan, we collected samples in six expeditions: RV Helmer Hanssen, Oct., 2014; RV Helmer Hanssen, May, 2015; RV Heincke, July-August 2015 and August-Sept, 2015; RV Helmer Hanssen, June 2016, and MeBo drilling expedition in August-September, 2016.

PROGRESS, RESULTS, AND DISCUSSION

1. Water column results. Water column analyses are completed and resulted in one publication in the journal "Scientific Reports" (www.nature.com/scientificreports) doi:10.1038/srep42997. And in an article in the FITI magazine (attached). These results were presented at two international conferences: Gordon Research Conference (Galveston, March 2016) and ICGH (Denver, June 2017).

- Geochemistry: Data from a series of cores recovered at on the fan of Storfjordrenna, west Barents Sea documents recovery of gas hydrate at ~ 0.82 mbsf indicate that the increase in methane flux inferred sulfate profile, may be linked to an enhanced gas hydrate dissociation in this area. Ongoing studies are aimed at testing this postulate, with the aim to bridge the gap between hydroacoustic flare detection in the water column and the mapping of hydrate reservoir at depth, and provide additional clues to unravel the complex interactions among ice, ocean, microbiology and climate and their sensitivity to both natural and anthropogenic change in Arctic regions. First results were published in the journal Nature Communications on 7th June 2017(http://www.nature.com/ncomms) doi: 10.1038/NCOMMS15745; and presented in two international conferences: Gordon Conference on Natural Gas Hydrates March, 2016; and Gas In Marine Sediments conference to be held in Tromsoe, September 2016.

2. Data integration/synthesis for the Vestnesa seeps. Based on collaborations with Norwegian colleagues, a synthesis of the data collected during various cruises to the Vestnesa Ridge, were integrated in a manuscript published in Marine Geology (Panieri et al., 2017. This synthesis include results from the CAGE15-5 expedition in which I participated, and which was highlighted in a FITI article in 2015.

3. MSM57 expedition (29 July-07 September, 2016). Analyses of samples from drilling expedition using the MeBo seafloor drill are underway. Preliminary data from drilling offshore Prinz Karl Forland were presented at the ICGH, with a manuscript planned for this fall. Hydrocarbon data from Vestensa Ridge, including isotope analyses of methane and dissolved inorganic carbon, will be presented at the upcoming GeoBremen2017, in Sep-

tember of this year. A manuscript with those data is in preparation. Analyses of pore fluids is ongoing, and preliminary data is indicative of various fluid sources/pathways feeding the hydrate system off Vestensa; a poster summarizing these preliminary observations was presented at Additional studies that incorporate a larger suite of analyses are underway, preliminary results were presented at the recent Goldschmidt Conference, Paris Aug 2017 (abstract attached), and a manuscript is in preparation. We conducted a series of XRF scans of three gravity cores collected on the Svyatogor Ridge during the MSM57 expedition, with the idea of presenting these data at the upcoming AGU meeting in New Orleans.

4. Microbiology incubations: A timeseries of incubations spanning several months was carried out on sediments collected from two regions overlying methane hydrates and one methane-free reference from CAGE cruise 16-5 (June-July 2016). Preliminary results are summarized in the Appendix, and are the topic of a dissertation for doctoral candidate Scott Klasek. These results will be presented at the upcoming Ocean Sciences meeting, Portland 2018.

5. Problems or delays

We requested and got approval for a one year no cost extension, which will allow us to complete some to the analyses/papers that are still underway. We originally had some delays because of problems with the research vessel R/V Merian. Even though this was unfortunate, this delay provided many alternate opportunities to collaborate with both German and Norwegian researchers to collect samples using a variety of tools/approaches. I believe this collaboration and multidisciplinary approach has been extremely beneficial, as evidenced by papers already published in high visibility journals. We are however, still generating (microbiology and geochemical) data from the most recent expeditions. As an example, to address the microbiological objectives, we had to change from a field sampling approach to cultivating microbes under in situ conditions to test the role that different levels of methane has on the microbial communities. These experiments are using samples collected using an ROV expedition last summer 2016, are underway and the samples still need to be analyzed for their microbial community structure. Sediment and pore water samples collected by the MeBo drilling expedition are still being analyzed and the data interpretation will be challenging due to the complexity of the system. Additional analyses such as high resolution XRF scans of the cores (now in Bremen) and some isotopic systematics in the fluids have been included in the overall data base to best constrain fluid migration and diagenetic processes.

Products

- Two papers published on numerical model aspects of the project. Full citations: Peszynska, M., Medina, F.P., Hong, W.L. and Torres, M.E., 2015. Reduced Numerical Model for Methane Hydrate Formation under Conditions of Variable Salinity. Time-Stepping Variants and Sensitivity. Computation, 4(1), p.1.

Peszynska, M., Hong, W.L. Torres, M.E., and Kim, J-H., 2015. Methane Hydrate Formation in Ulleung Basin Under Conditions of Variable Salinity: Reduced Model and Experiments. Transport Porous Media DOI 10.1007/s11242-016-0706-y

- A paper published in Nature-Scientific Reports.
  Mau, S., Römer, M., Torres, M.E., Bussmann, I., Pape, T., Damm, E., Geprägs, P., Wintersteller, P., Hsu, C.W., Loher, M. and Bohrmann, G., 2017. Widespread methane seepage along the continental margin off Svalbard-from Bjørnøya to Kongsfjorden. Scientific Reports, 7.

- A paper published in Nature Communications.
  Hong, W. L., Torres, M. E., Carroll, J., Crémière, A., Panieri, G., Yao, H., & Serov, P. (2017). Seepage from an arctic shallow marine gas hydrate reservoir is insensitive to momentary ocean warming. Nature communications, 8, 15745.10.1038/NCOMMS15745.

- A paper published in Marine Geology: Fluid flow in Vestnesa Ridge pockmarks: evidence for temporal and spatial variability of methane discharge into the Arctic by Giuliana Panieri, Stefan Bünz, Daniel J. Fornari, Javier Escartin, Pavel Serov, Joel J. Johnson, Pär Jansson, WeiLi Hong, Simone Sauer, Marta E. Torres, Rafael Garcia, Nuno Gracias.

- Abstracts submitted to International Conference on Gas Hydrates, Denver June 2017; three abstracts submitted to the GeoBremen17 meeting; two presentations at the Bubbles17 school, Tromso, Norway; an abstract submitted to the Goldschmidt Conference, Paris, Aug 2017; an abstract submitted to the Ocean Sciences meeting, Portland Feb. 2018.

Fracture-induced fluid migration in an Arctic deep water pockmark: Porewater geochemistry from the MEBO drilling (MSM57) in Vestnesa Ridge (Svalbard)

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During the 2016 MEBO drilling expedition, several sites were drilled in a deep water pockmark (Lunde) from Vestnesa Ridge to investigate gas hydrate dynamics in this region. One of the drilled sites targeted a fracture zone within the pockmark, imaged in sesimic records. Lithium and strontium concentrations in pore fluids indicate active fluid flow between 600 and 1000 cmbsf, which corresponds to the depth where the fracture zone was intercepted by drilling. Within this depth interval, we recovered gas hydrate at saturations ranging from 10 to 35% of the pore space. Massive carbonate was recovered from two horizons above and below the zone with anomalous pore fluid data. We present both the concentrations of major/minor porewater species and the isotopic signatures of several key constituents ($\delta^{13}C$-DIC, $\delta^{18}O$, δD, $\delta^{11}B$, and $^{87}Sr/^{86}Sr$) to establish the source of fluid and further establish the role of fractures in controlling deep fluid migration in this pockmark. We discuss the role of fluid migration in accumulation of gas hydrate and development of carbonate cements. This work is supported by the Research Council of Norway through its Centres of Excellence funding scheme (project number 223259) and NORCRUST as well as US Department of Energy (grant DE-FE0013531.). We acknowledge the assistance from the captains and crews onboard RV Maria S. Merian.

Characterization of microbial communities in Arctic seafloor gas hydrate mounds experiencing methane flux increases on centurial to millenial timescales

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To compare responses of microbial communities in high-pressure methane enrichments to *in situ* microbial communities undergoing recent methane enrichment, native sediment samples that had been collected on the same CAGE 16-5 cruise were analyzed. DNA was extracted from 43 samples collected from cores at gas-hydrate-rich seafloor mounds off Storfjordrenna, Svalbard. 16S gene fragments were amplified, sequenced, and taxonomically analyzed to obtain microbial community profiles (Figure 1).

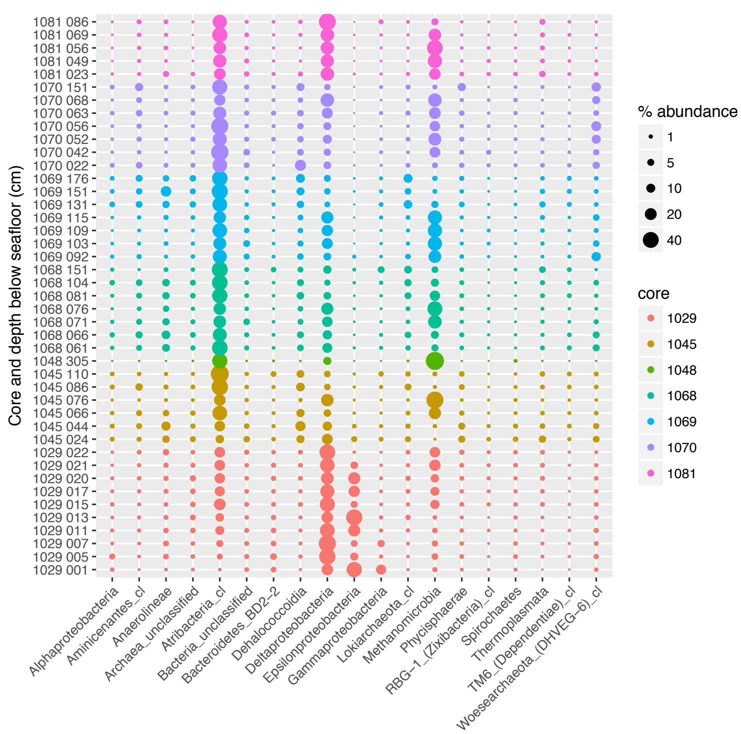

Figure 1. Percent abundances of Archaeal or Bacterial classes whose abundances totaled >90% of all sequence reads in all samples.

Porewater sulfate profiles revealed certain cores to be undergoing increases in subseafloor methane flux, while others showed a linear decline in sulfate with depth that suggested a system at steady-state. Communities from cores at steady-state with respect to methane and sulfate dynamics were different from those undergoing recent methane increases (AMOVA, p-value <0.0001).

Three geochemical zones were assigned to samples based on whether sulfate was available as an electron acceptor, and if so, whether or not the sulfate profile indicated a recent methane flux at that depth based on diffusion modeling. Microbial communities inhabiting non-steady-state regions of the sulfate profile above the sulfate-methane transition zone were different from those below it (AMOVA p-value=0.0018). Other pairwise comparisons between zones were not statistically significant. Microbial communities are plotted below by geochemical zone in Figure 2.

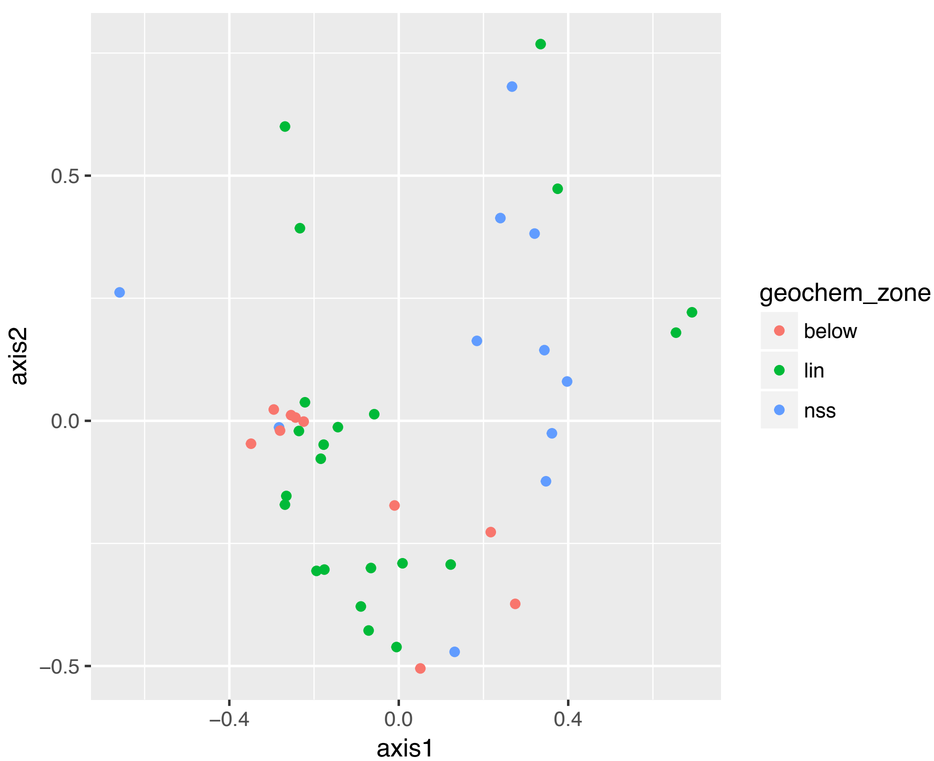

Figure 2. Nonmetric multidimensional scaling ordination of microbial communities sorted by the geochemical zone they inhabited (below= below sulfate-methane transition zone, lin=linear region of the sulfate profile, and nss=non-steady state region of the sulfate profile). Each point represents a microbial community. Points that are closer together indicate community similarity. R^2=0.86, stress=0.18.

Diffusion-based modeling will reveal estimates of when methane supply has increased at each sample depth. This will allow us to examine how the duration of methane supply structures microbial communities *in situ*. Concentrations of 16S and mcrA genes belonging to anaerobic methanotrophs are expected to increase with methane exposure time.

Methane Release Along Continental Margins: Natural Process or Anthropogenically Driven?

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Introduction

Gas hydrate stability along continental margins worldwide may be susceptible to changes in ocean temperatures associated with global climate change. Gas hydrate dissociation in this scenario could lead to widespread anthropogenically-driven release of methane. In support of this hypothesis, Westbrook and co-authors suggested that numerous gas plumes emanating from the seafloor offshore Prins Karls Forland (PKF; Figures 1A and 1B) are sourced from dissociating hydrates that have been destabilized by an increase in intermediate water temperature over the past 30 years. Hydroacoustic records, showing gas discharge

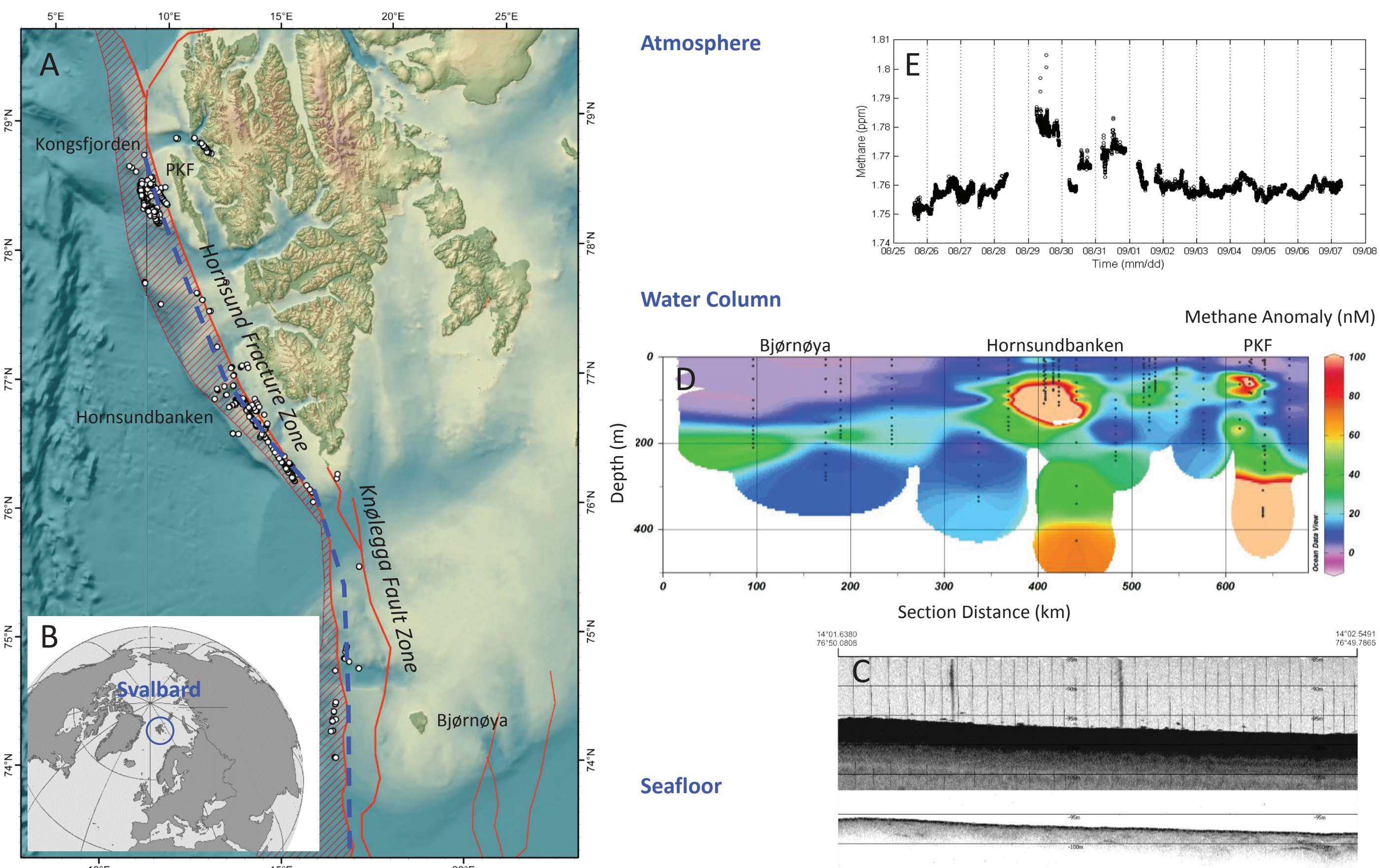

Figure 1. ***A*** *Flare locations observed during HE387, HE449, and HE450 illustrated as white dots and main structural features including the Hornsund Fracture Zone. PKF stands for Prins Karls Forland.* ***B*** *Overview map.* ***C*** *Example of a sub-bottom profile showing flares on top of hard ground where most of the flares occurred.* ***D*** *South – North transects of dissolved methane concentrations along the shelf; position of the transect is shown as a blue line in A. Above the contour plot, the approximate location along the transect is indicated. Methane anomaly was derived by subtracting the atmospheric methane equilibrium (2.6-3.5 nM).* ***E*** *Methane concentrations of air measured during cruise HE450 using a GGA (Los Gatos Research). Air was continuously pumped trough a tubing at ~10 m above sea-surface to the GGA. Elevated concentrations were measured crossing Hornsundbanken (08/29) and near Kongsfjorden (08/31). Figure A and D are simplified versions of the figures in Mau et al. 2017.*

on the North American Atlantic continental slope and along the Cascadia margin, have also been tied to gas hydrate destabilization at the landward edge of the gas hydrate stability zone. These postulated gas hydrate destabilization events have been proposed by Johnson and co-authors to have far-reaching consequences, including oxygen consumption, pH changes harmful to benthic biota, tsunami-generating slope failures, and climate feedbacks that enhance global warming.

We evaluated the validity of this hypothesis for the Svalbard continental shelf by examining: (1) the timing and duration of continental margin gas seepage there; and (2) the quantity of methane originating from gas hydrate dissociation at this location. Our evaluation argues against the hypothesis that the Svalbard seeps are sourced by anthropogenically-driven dissociation of gas hydrates.

Timing of Continental Margin Seepage

We argue that the presence of methane-derived authigenic carbonate deposits along Svalbard and elsewhere is evidence that methane discharge is a natural process that has been ongoing for much longer time periods than anthropogenically-driven global climate change. On the Cascadia margin, for example, carbonate deposits indicate that methane seepage dates back to the Eocene. Abundant carbonate crusts found at methane discharge sites off Prins Karls Forland provide evidence that seepage off Svalbard has been ongoing for at least 3000 years. These observations point to long-lived methane seepage at these sites, challenging the idea that methane release at these locations is driven by recent, anthropogenic change.

Methane Release Along the Svalbard Continental Margin

In addition to establishing the timing of the onset of seepage, it is important to constrain the quantity of methane released at the upper end of the hydrate stability zone, relative to its natural discharge levels. A water column survey in 2015, aimed at mapping methane release in the global warming-sensitive Arctic region offshore Svalbard, documents that Prins Karls Forland gas emissions are part of a much broader seepage system, which extends from 74° to 79° N.

Along this seepage trend, more than a thousand gas discharge sites were imaged in hydroacoustic data. Extensive gas seepage from this system generates a dissolved methane plume, designated as the Svalbard plume, which is hundreds of kilometers in length and transports ~8.4 Gg (gigagrams) methane. This methane load is on the upper end of what has been observed in dissolved methane plumes originating from natural seepage systems elsewhere. For example, the down-current portion of the methane plume originating from the well-known Coal Oil Point seep field in California transports ~50 Mg (megagrams); methane seepage loads at Hydrate Ridge (off the coast of Oregon) and the Batumi seep area (eastern Black Sea) amount to approximately 37 and 11 Mg, respectively. The annual methane release from mud diapirs offshore Costa Rica is estimated to be only 0.2-8 kg (kilograms).

Methane release feeding the Svalbard plume follows the trace of the Hornsund Fracture Zone (HFZ; Figure 1A). The majority of the gas emission sites feeding this plume are located on bathymetric highs characterized by acoustically highly-reflective hard grounds (Figure 1C). This suggests that fine-grained postglacial deposits in the troughs seal structural pathways or at least limit methane-rich fluid migration to the seafloor. The long trend of methane emission sites feeding the Svalbard plume intersects the critical boundary of gas hydrate stability offshore Prins Karls Forland. However, methane release along the Hornsund Fracture Zone is not limited to 400 m water depth, but is observed in water depths from 33 to 429 m. The highest methane concentrations were found near locations of intense seepage at 90 m water depth on Horsundbanken, and at 80 m and 350 m off Prins Karls Forland (Figures 1A and 1D).

Consistent with reports recently summarized by Ruppel and Kessler, that methane released along the edge of gas hydrate stability does not contribute to global atmospheric inventories, data from the Svalbard plume also suggest significant methane consumption by microbes. Measured methane oxidation rates within the Svalbard plume range from 0.01 to 2.19 nM d^{-1} (nanomolar per day) and are in agreement with previous measurements offshore Prins Karls Forland. Microbial activity in this area thus consumes 0.02 to 7.7% of the dissolved methane input.

It is worth noting that gas emission zones feeding the Svalbard plume shallower than ~120 m extend from the seafloor to the sea surface. Highest dissolved methane concentrations were measured above the shallow seeps off Prins Karls Forland, Hornsundbanken, and Soerkappbanken, with values reaching 878 nM (nanomolar) above atmospheric equilibrium (Figure 1D). High supersaturation values during summer surveys lead to highs in sea-air fluxes of up to 2.0 nmol m^{-2} s^{-1} (nanomoles per square meter per second). The increase in wind speeds during the winter months may increase this flux, as has been demonstrated for natural seeps in the central North Sea. Furthermore, direct gas bubble transport will likely enhance the fluxes based on dissolved methane, because seeps are located in water less than 120 m deep.

It remains unclear whether atmospheric methane anomalies measured in the 2015 surveys (Figure 1E) represent direct input from the shallow mapped seeps, from seeps closer to land, or from methane discharge on the island itself. Nonetheless, supersaturation values measured in the upper 10 m of stations closer to the shelf indicate a contribution to the atmosphere from the shallow portion of the Svalbard plume. Whereas it has been shown that methane release along continental slopes does not contribute to the atmosphere, it is important to evaluate the potential sea-air flux from natural seeps along continental shelves.

Conclusions

Large methane plumes such as the Svalbard plume appear to be long-lived, natural phenomena. Advances in hydroacoustic detection tools have significantly increased our knowledge of bubble emission sites, and they

SUGGESTED READING

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

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have shown that gas emissions sourcing the Svalbard plume, and other plumes along continental margins worldwide, are located at and above the gas hydrate stability zone. It is thus likely that few, if any, of these methane discharge events along continental slopes are directly tied to anthropogenic climate change and global warming. Seepage at these locations is instead part of long-term continental margin processes that respond to hydrogeologic mechanisms, and not necessarily to gas hydrate stability constraints. Of additional significance, methane discharge from the part of the continental shelf that lies *above* the limit of gas hydrate stability may constitute a substantial source of methane release to the atmosphere, and this source needs to be better characterized.

It is undeniable that the atmospheric increase in CO_2 is a serious problem, with wide-ranging effects including global warming, ocean acidification, and sea-level rise. However, based on our evaluation of Svalbard seepage timing and plume size, we argue that methane release offshore Svalbard is not a direct consequence of gas hydrate destabilization triggered by human-induced ocean warming. Instead, it appears to be part of a long-lived, natural process. As the Arctic is extremely susceptible to ocean warming, it is likely that our conclusions for the Svalbard area are also applicable to lower latitude regions.

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