Oil & Natural Gas Technology

DOE Award No.: DE-FE0013531

Quarterly Research Performance

Progress Report (Period Ending 06/30/2018)

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)

Submitted by:
Marta E. Torres

Oregon State University
DUNS #: 053599908
104 CEOAS Admin. Bldg.
Corvallis, OR 97331-5503
Email: mtorres@coas.oregonstate.edu
Phone number : (541) 737-2902

Prepared for:
United States Department of Energy
National Energy Technology Laboratory

Submission Date

U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

Office of Fossil Energy

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.

The very productive outcome of this collaboration is evidenced on seven papers published in highly ranked journals, with 2 more in preparation; two articles in the Fire in the Ice magazine; and more than 15 presentations at science conferences and meetings.

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).

2. Geochemistry: Geochemical analyses of cores generates lots of data to constrain fluid flow and gas hydrate formation in the margin. A first paper detailing results from the gas hydrate mounds region was published in the journal Nature Communications on 2017(http://www.nature.com/ncomms) doi: 10.1038/NCOMMS15745. These results were presented in three international conferences: Gordon Conference on Natural Gas Hydrates March, 2016; and Gas In Marine Sediments conference to be held in Tromsoe, September 2016, and at Goldschmidt Conference, Paris Aug 2017. In addition, a new manuscript has been published in Geophysical Research Letters (manuscript 2018GL077309R). that documents decoupled methane transport by gaseous and aqueous phases in Storfjordrenna (offshore Svalbard) and propose a three-stage evolution model for active seepage in the region where gas hydrates are present in the shallow subsurface.

3. 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.

4. MSM57 expedition (29 July-07 September, 2016). Sample and data analyses from drilling expedition using the MeBo seafloor drill continue. Results from samples offshore Prinz Karl Forland were presented at the ICGH in 2017, an a manuscript is now published in Nature Communications. Sediment cores drilled off Prinz Karls Foreland contain freshwater from dissociating hydrates. However, our modeling indicates that the observed pore water freshening began around 8 ka BP when the rate of isostatic uplift outpaced eustatic sea-level rise. The resultant local shallowing and lowering of hydrostatic pressure forced gas hydrate dissociation and dissolved chloride depletions consistent with our geochemical analysis. Hence, we propose that hydrate dissociation was triggered

by postglacial isostatic rebound rather than anthropogenic warming. Gas hydrate acts as a dynamic seal that regulates methane release from deep geological reservoirs. Hydrocarbon data recovered by drilling on Vestensa Ridge, was presented at the upcoming GeoBremen2017. Since we have generated more data on the isotopic composition of carbon in aqueous and gas phases in support of a manuscript in progress. This paper is planned for submission in Fall of 2018. We show that the study sites are characterized by different fluid fluxes, with lowest fluxes at our reference station (VR-2), intermediate at a non-seep site within the pockmark (VR-1) and highest at two sites (VR-3 and VR-4) drilled at sites of active seepage. At the reference VR-2 site, the deepest gas sample (62 mbsf) has a major component of migrated thermogenic hydrocarbons, as evidenced by the methane to higher hydrocarbon ratio in the gas phase (C_1/C_{2+}) relative to formation temperatures, and further demonstrated by carbon and hydrogen isotope data. With decreasing depth the fraction of microbial methane increases, with a prevalence of microbial hydrocarbons in sediments shallower than ca. 50 mbsf. Microbial methanogenesis also dominates the hydrocarbon component at a non-seep site within the pockmark (VR-1). Collectively, our data from sites VR-1 and VR-2 substantiates active in situ methanogenesis at sediment temperatures <4°C. However, despite abundant organic matter in the shallow sediments (mean TOC 0.8%), microbial formation at non-seep sites does not produce sufficient methane for gas hydrate precipitation. The hydrocarbons that sustain shallow gas hydrates at sites of active seepage are transported in the gas phase through a fault imaged in the seismic record. The gas migrates from depths >800 mbsf, as estimated using the thermal gradient derived from temperature data collected down to 60 mbsf. These hydrocarbons possibly originate from deeply-buried Miocene source rocks and are channeled upward thought a deep-rooted fault that intersect the drilled sites at 6–8 mbsf. Gas hydrates predominantly precipitate from these thermogenic hydrocarbons and the hydrate-bound hydrocarbons are representative for the gas chemical properties of the deeply buried source.The isotopic composition of the organic carbon at the seep sites, point to a contribution of de-novo organic carbon depleted in ^{13}C, which likely originates from chemoautothrophy at sites of methane release. Depletions in ^{13}C of the DIC at the SMI are documented at all sites, with a $\delta^{13}C$-DIC of -37 ± 2 ‰ V-PDB, independent of site-specific fluid flux magnitude and transport mechanisms, indicating active AOM at all sites investigated. Trends in stable carbon isotope compositions of methane and of DIC with depth showed that methane-bound carbon is transformed into DIC through the microbial filter at all sites. At low flux sites the microbial filter removes >XX% of the available methane; whereas at high flux sites only a small fraction of methane is consumed by microbes such that the isotopic composition measured in the bulk methane pool is not altered from the values at the source. Whereas the majority of methane bypasses the microbial filter rapidly at the high flux sites and escapes into the water column, the isotopic change in DIC measured at VR-3 and VR-4 shows that a fraction of the advecting gas is dissolved in the pore water and made available to microbes, which consume it at rates higher than at seep sites

5. Microbiology analyses A manuscripts are now in progress summarizing the results of the microbiology component of the study, and will constitute a chapter of the doctoral dissertation of Scott Klasek. A paper entitled Methane-driven microbial community succession in Arctic seafloor gas hydrate mounds (authored by Scott Klasek[1], WeiLi Hong[2], Marta Torres[3], Stella Ross[4], Katelyn Hostetler[5], Karin Andreassen[6], Alexey Portnov[7], Frederick Colwell) address the questions of How do microbial communities in marine sediments change as methane migrates through the sediment column? And How does the abundance and dominance of anaerobic methanotrophs and sulfate-reducing bacteria correlate with their time of exposure to methane? Cores from Arctic seafloor gas hydrate mounds showed sulfate profiles indicative of recent methane intrusion from deeper sediment layers. Microbiology analyses of these samples show that: Anaerobic methanotrophs and sulfate-reducing bacteria dominate communities near and slightly above the sulfate-methane transition zone, and decrease in relative abundance months to years after burial below the SMT. Highest *mcrA* gene abundances are seen in cores experiencing recent increases in methane flux, pointing to a boom-and-

bust dynamics of ANME growth. Below-SMT communities are similar regardless of methane flux dynamics, suggesting these regions select for similar community structures within several months to years.

6. Microbiology incubations. These are also completed and a manuscript by S. Klasek is in progress, as another chapter of his doctoral dissertation. Manuscript title Methane drives activity before structure in microbial communities inhabiting marine sediment sulfate-methane interfaces. Marine sediments collected from a seafloor gas hydrate-bearing mound offshore Svalbard (Arctic Ocean) were incubated for varying times at *in situ* temperature (4˚C) and pressure (4.0 MPa) under different methane concentrations to investigate how methane structures microbial communities and whether rates of sulfate-dependent anaerobic methane oxidation (AOM) are linked with community changes. Sulfate reduction rates increased, and dissolved inorganic carbon isotopes became lighter during later stages of longer (4-8 month) incubations with added methane, indicating that AOM was established. This effect was only seen in sediments collected from methane-rich areas, suggesting that longer times or higher methane concentrations are needed to stimulate AOM in methane-naïve sediments. However, concentrations of the methane-fixing *mcrA* gene did not notably increase in these enrichments. Methane-naïve sediment communities changed more drastically than sediments from methane-rich areas, though these changes were not methane-dependent. They may instead reflect that over months-long timescales, AOM activity precedes large-scale microbial community changes, particularly the growth of anaerobic methanotrophs, in marine sediments.

7. Biomarker studies. In addition to the above results, a short paper reporting results of biomarker analyses in sediments from Vestnesa Ridge was recently submitted to Biogeosciences. The manuscript is titled Fracture-controlled fluid transport supports microbial methane-oxidizing communities at the Vestnesa Ridge (authors: Haoyi Yao, Wei-Li Hong, Giuliana Panieri, Simone Sauer, Marta E. Torres, Moritz F. Lehmann, Friederike Gründger and Helge Niemann). The paper reports on a rare observation of a mini-fracture in near-surface sediments (30 cm below the seafloor) visualized by using 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 biomarkers signatures revealed clearly differences in the geochemical and biogeochemical regimes of this core compared with two additional ones recovered from pockmarks in Vestnesa Ridge, which we attribute to differential methane transport mechanisms. In the sediments 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 another core recovered from the same pockmark about 78 m away from the fractured core, we observed sulfate depletion in the top centimetres of the sediment and much higher signals for 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 side of the fractured core, while the indications for a well-established AOM community suggest on-going gas migration for a longer period of time at the second coring side at the Lomvi pockmark. A third core recovered from Lunde pockmark was dominated by diffusive transport with moderate/low geochemical and biogeochemical signals for AOM. Our study suggests that mini-fractures facilitate important pathways for advective fluid and gas transport in surface sediment, thereby generating hotspots of AOM.

1. **PROBLEMS OR DELAYS**
   No delays or problems during this quarter

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 with water column results.
  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 on the gas hydrate mounds.
  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 synthesis paper on Vestnesa Ridge published in Marine Geology:
  Panieri G, Bünz S, Fornari DJ, Escartin J, Serov P, Jansson P, Torres ME, Johnson JE, Hong W, Sauer S, Garcia R. An integrated view of the methane system in the pockmarks at Vestnesa Ridge, 79° N. Marine Geology. 2017 Aug 1;390:282-300.

- A paper published in Nature Communications on PKF hydrate dissociation by isostatic rebound:
  Wallmann K, Riedel M, Hong WL, Patton H, Hubbard A, Pape T, Hsu CW, Schmidt C, Johnson JE, Torres ME, Andreassen K. Gas hydrate dissociation off Svalbard induced by isostatic rebound rather than global warming. Nature Communications. 2018 Jan 8;9(1):83.

- A paper published in Geophysical Research Letters by W.-L. Hong, M.E. Torres, A. Portnov. M. Waage, B. Haley, and A. Lepland, Variations in gas and water pulses at an Arctic seep: fluid sources and methane transport. Geophysical Research Letters. 2018 May 16;45(9):4153-62.

National Energy Technology Laboratory

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880

13131 Dairy Ashford Road, Suite 225
Sugar Land, TX 77478

1450 Queen Avenue SW
Albany, OR 97321-2198

Arctic Energy Office
420 L Street, Suite 305
Anchorage, AK 99501

Visit the NETL website at:
www.netl.doe.gov

Customer Service Line:
1-800-553-7681

NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY