Oil & Natural Gas Technology

DOE Award No.: DE-FE0013998

Quarterly Research Performance Progress Report

(Period ending 06/30/2015)

Characterizing the Response of the Cascadia Margin Gas Hydrate Reservoir to Bottom Water Warming Along the Upper Continental Slope

Project Period: October 1, 2013 – September 30, 2016

Submitted by:
Evan Solomon

University of Washington
DUNS #: 605799469
4333 Brooklyn Ave NE
Box 359472
Seattle, WA 98195-0001
e-mail: esolomn@u.washington.edu
Phone number: (206) 221-6745

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

August 5, 2015

Office of Fossil Energy

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, Suite 225
Sugarland, 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:
1-800-553-7681

TABLE OF CONTENTS

EXECUTIVE SUMMARY

In October 2013, the University of Washington initiated a three-year study funded through DOE-NETL entitled: Characterizing the response of the Cascadia margin gas hydrate reservoir to bottom water warming along the upper continental slope. The objective of this project is to understand the response of the WA margin gas hydrate system to contemporary warming of bottom water along the upper continental slope. Through pre-cruise analysis and modeling of archive and recent geophysical and oceanographic data, we (1) inventoried bottom simulating reflectors along the WA margin and defined the upper limit of gas hydrate stability, (2) refined margin-wide estimates of heat flow and geothermal gradients, (3) characterized decadal scale temporal variations of bottom water temperatures at the upper continental slope, and (4) used numerical simulations to provide quantitative estimates of how the shallow boundary of gas hydrate stability responds to modern environmental change. The results of the pre-expedition analysis of historic bottom water temperatures and the simulations of the response of the upper limit of gas hydrate stability to intermediate water warming on the Washington margin have been published (Hautala et al., 2014), the work on characterizing regional heat flow has been presented at the AGU Fall Meeting (Salmi et al., 2014; 2015), and a synthesis of seep distribution along the Washington margin has been submitted for publication (Johnson et al., *in Review, G-Cubed;* Johnson et al., 2015) These pre-cruise results provided the context for a systematic geophysical and geochemical survey of methane seepage along the upper continental slope from 48° to 46°N during a 10-day field program on the *R/V Thompson* from October 10-19, 2014. This systematic inventory of methane emissions along this climate-sensitive margin corridor and comprehensive sediment and water column sampling program provided data and samples for Phase 3 of this project that focuses on determining methane sources (microbial, thermogenic, gas hydrate dissociation), sinks, and fluxes within the sediment and water column, and how they relate to contemporary intermediate water warming. To date, we have completed Phases 1 and 2 of the project; pre-expedition analyses and expedition execution. We started Phase 3/Budget Period 2 of the research program in April 2015.

During the 2014 research expedition, we discovered 9 active seep sites between ~470 and 520 m water depth and imaged 22 bubble plumes with heights commonly rising to ~300 m below sea level with some reaching to near the sea surface. Some of the seep sites appear to be controlled by local margin structure, mainly extensional faults and ridges. We collected 22 gravity cores and 20 CTD/hydrocasts from the 9 seeps. The sediment cores were sub-sampled at high-resolution for pore water geochemical analyses. In addition, we collected ~400 water samples to characterize the hydrocarbon concentrations and distribution within the water column at the 9 active seep sites surveyed at the upper limit of methane hydrate stability. We analyzed for pore water salinity, pH, and alkalinity shipboard, as well as bottom water C_1-C_4 concentrations. The shore-based geochemical program is in progress. To date, we have completed 60% of the Cl, SO_4, and O/H isotope ratio analyses, 50% of the δ^{13}C-DIC analyses, and have completed all the porosity analyses. In the next reporting period, we will start analysis of the pore water major and minor element concentrations, and water column hydrocarbon concentrations.

Hydrocarbons heavier than CH_4 were not detected in bottom water samples, suggesting any gas hydrate present is Structure I. Preliminary pore water data show decreasing salinity downcore at each site with measured values as low as 10 psu, and the sulfate-methane transition zone occurs between 50-80 cm below the sea floor. Pore water freshening can be the result of gas hydrate dissociation, meteoric water, and/or clay dehydration at depth, and determining the relative contribution of each fluid source is a primary objective of Phase 3 of the research program. Preliminary pore water solute, noble gas, and isotope ratios indicate freshening from at least one site is not the result of hydrate dissociation, but rather is due to clay dehydration at depths where temperatures exceed 60°C. Only a few of the sites have pore water profiles in steady state, suggesting a dynamic biogeochemical system at the upper continental slope along the entire WA margin. Further analyses and modeling are underway to constrain the nature and timing of these transient profiles and whether they are the result of recent methane hydrate dissociation. The preliminary geochemistry and modeling results will be presented at the fall American Geophysical Union meeting in San Francisco (Whorley et al., 2015).

During this quarter, we also submitted a manuscript to G-cubed that reviews existing compilations of seep sites and archive mid-water column sonar data to characterize the depth distribution of seeps on the Cascadia margin (Johnson et al., submitted). We identified methane emission sites extending from the deformation front to the shelf along the margin with plume density anomalies associated with both the continental shelf (<200 m) and the depth of the upper limit of methane hydrate stability range near 500 meters in the NE Pacific. Although other geological processes could be partially responsible for the plume distribution anomaly at the upper limit of methane hydrate stability, a component of this seepage may be related to dissociation of methane hydrates related to contemporary warming of bottom water along the Cascadia margin. This hypothesis is currently being tested during the Phase 3 geochemical program described above.

Two graduate students from Dr. Rick Colwell's microbiology laboratory at Oregon State University joined us on the October 2014 research expedition on the *R/V Thompson* and collected samples for microbial community characterization. The microbiology samples were collected immediately adjacent to pore water samples with the objective of developing a metabolic model of ANME-SRB consortia within methane-bearing sediments and to couple this to a geochemical reaction-transport model for these margins. This is a collaborative project between the Solomon and Colwell labs, and the microbial community characterization will be coupled with our measurements of sediment physical properties and pore water chemical profiles. The results of this project have the potential to increase understanding of ANME-SRB consortia, their surrounding microbial communities, and their role in carbon cycling within continental margins. In addition, they pave the way for future efforts at developing a metabolic model of ANME-SRB consortia and coupling it to geochemical models of the US Washington margin. The preliminary results of this work will be presented at the AGU fall meeting in San Francisco (Graw et al., 2015).

PROGRESS, RESULTS, AND DISCUSSION

Task 1.0 Project management and planning

Completed in previous reporting period - The project management plan was finalized and submitted on October 17, 2013.

Task 2.0 Compile relevant archive data

Completed in previous reporting period – We have compiled the relevant MCS profiles and swath bathymetry on the WA margin. All available high-resolution CTD, glider and ARGO float temperature profiles, extending to depths below 200 m, were extracted and compiled from the World Ocean Database 2013 (National Oceanographic Data Center) for the region 124.5°W to 127.5°W and 46.5°N to 48.5°N off the Washington margin. We have also compiled all of the acoustic backscatter data from archive and recent (EM122 and EM302 data) *R/V Langseth*, *R/V Thompson*, and *R/V Atlantis* expeditions at the Washington margin.

Task 3.0 Estimate sediment porosity and in situ thermal conductivities
Completed in a previous reporting period – We converted existing archive MCS data to Vp-vs-depth profiles and then used these data to estimate sediment porosities. From the estimated sediment porosities, we calculated thermal conductivities along the WA continental slope. We have completed a compilation of sediment core archives from legacy coring programs on WA margin for sediment lithology in order to provide guidance regarding the distribution and partitioning of the sediments into turbidites and pelagic sediments within a specific geographic area. These data are necessary to convert seismic velocities and structural components into a plausible model of thermal conductivity.

Task 4.0 Constrain hydrate distribution and geothermal gradients
Completed in a previous reporting period – We have evaluated Bottom Simulating Reflectors (BSRs) from the COAST MCS cruise to establish the distribution of gas hydrates and geothermal gradients along the WA margin in combination with heat flow measured during our recent WA margin heat and fluid flow survey (Johnson et al., 2013; Johnson et al., 2014). This work has been completed for the region surveyed during the COAST MCS expedition in 2012, which overlaps with our proposed track-line for our research expedition in October 2014. We evaluated BSRs from other legacy datasets along the WA margin, including both commercial (Western Geophysical) and USGS MCS expeditions in the area.

Task 5.0 Analyze recent temperature data and long-term bottom water record
Completed in a previous reporting period – As stated in the Executive Summary, after filtering, there are 2122 high-quality, open-ocean temperature profiles that were linearly interpolated to 10 m depth intervals ranging from 50 to 1000 m. Averaged over the entire region, the temperature at the upper limit of gas hydrate stability shows persistent warming over the last 40 years. The time series also clearly shows the influence of the Pacific Decadal Oscillation (PDO) at the upper limit of gas hydrate stability. Taking into account other independent variables such as latitude, water depth, and the monthly Pacific Decadal Oscillation (PDO) index, our calculations studying sensitivity to methodological choices yield a constant and significant warming trend off the WA margin from 1960 to present.

Task 6.0 Non-steady state thermal simulations and impact of bottom water warming on the upper limit of the gas hydrate stability field
Completed in a previous reporting period – In collaboration with Robert Harris at Oregon State University we used a 2-D finite-element conductive heat flow model to simulate the change in temperature distribution in the shallow sediments at the upper limit of gas hydrate stability resulting from the warming intermediate-depth water temperatures. The upper boundary of the thermal model is based on the historic temperature records on the WA margin, and the bottom

boundary condition is set by the heat flow estimated from regional BSR data, historic heat flow surveys, and borehole data. In situ thermal conductivity is estimated from MCS data using vertical seismic velocity profiles to estimate porosity, then porosity is converted to thermal conductivity (Task 3.0). Thermal diffusivities were also measured during a recent GeoPRISMS expedition off the coast of WA by Johnson and Solomon (Johnson et al., 2013, EOS: Homola et al., *Elementa*, 2015). The base of the gas hydrate stability zone is calculated integrating the Pitzer equations in Tishchenko et al. (2005). The model is stepped through time over the 45-year historic record of bottom water temperatures for the WA margin. Results show that the upslope limit of the gas hydrate stability zone on the WA margin is sensitive to the contemporary warming of intermediate waters and retreats downslope over the 40-year period along all three profiles simulated along the margin. This modeling effort guided the field program in Phase II of the research project. The results of the characterization of the long-term bottom warming trend and these model simulations are described in Hautala et al. (2014).

Task 7.0 Planning and Preparations for Research Expedition
Completed in a previous reporting period – During this reporting period, the PIs met weekly to discuss our sampling strategy, work flow, and cruise track. We completed planning and preparations for the October 2014 research expedition at the beginning of the quarter. The expedition occurred from 10-19 October 2014, and we successfully achieved the objectives of the cruise plan and were able to sample many more sites than originally planned.

Task 8.0 Research Expedition
Completed in a previous reporting period – We surveyed the upper continental slope of the WA margin from the Strait of Juan de Fuca to the Columbia River. During the expedition, we sampled nine independent seep sites at the upper limit of gas hydrate stability, deployed 39 gravity cores and two piston cores, deployed 20 CTD casts for full water column sampling, and sub-sampled >300 sediment whole-rounds for pore water geochemical analyses. We conducted 'localized' EM 302 surveys over each seep site to better refine targets for detailed coring and water column sampling. The survey at each site included EM302 and 3.5 kHz cross-track surveys, ADCP surveys to determine 'down-current' direction of emissions, CTD and Niskin bottle casts, and a suite of gravity cores for pore fluid chemistry. The cores were immediately sub-sampled shipboard in a cold room for both geochemistry and microbiology, and hydrocarbon samples collected along the core length will be analyzed via headspace methods on shore. Pore fluids were extracted in Ti squeezers under a hydraulic press and with Rhizon samplers. Salinity, alkalinity, and pH were immediately analyzed shipboard, and the remaining pore fluid samples were preserved for shore-based hydrocarbon, major and minor element, and stable isotope ratio analyses. Approximately 23 Niskin water samples were collected from each of the 20 during CTD/hydrocasts targeting the seep sites. Water samples were preserved for shore-based geochemical analyses.

Task 9.0 Processing of Geophysical Data
In progress – We are currently processing the remaining ship-board geophysical data, including ADCP, CTD, and 3.5 kHz profiles. Though we processed the multi-beam bathymetry and mid-water column data in real-time shipboard using Fledermaus and the FM-Midwater tool, additional post-expedition processing is in progress.

Tasks 10.0-12.0 Shore-based Geochemical Analyses and Modeling

In progress – Pore water and water column sub-samples were preserved for each type of analyses and are stored under the appropriate conditions at UW. We are currently conducting the Cl, SO_4, C_1-C_4 hydrocarbon, oxygen and hydrogen isotope ratio, and δ^{13}C-DIC analyses, and they should be near completion by the next reporting period. The remaining concentration and isotope ratio analyses of both pore water and water column samples will be the primary focus of the research program over the next several months

CONCLUSIONS

The first six tasks comprise Phase 1 of the research project aimed at providing the context for a systematic geophysical and geochemical survey of methane seepage along the upper continental slope of the WA margin. These six tasks have been completed. We completed the preparations for the research expedition (Task 7), and successfully conducted the field program from 10-19 October 2014 completing Phase II of this project. We have now moved on to Phase III/Budget Period 2, as of April 2015, focused on post-expedition analyses, interpretation, publication, and reporting.

MILESTONE STATUS

Milestone #1 – Determination of the gas hydrate distribution and geothermal gradients along the WA continental slope based on COAST MCS data
Completed June 2014, however additional work continues on legacy datasets north of the COAST survey area.

Milestone #2 – Finalize planning for cruise tracks/stations, identification of shipboard scientific party, and preparations for on-board data/sample acquisition and processing.
Completed September 2014.

Milestone #3 – 2014 field program on the R/V Thompson
Completed October 2014.

Milestone #4 – The first series of reports and publications reporting the results of the research program
Partially completed, August 2015 – Three abstracts were submitted to the 2015 AGU Fall Meeting, and one manuscript was submitted for publication in G-cubed.

COST STATUS

During the sixth quarter, a total of $36,864 was spent to support the post-expedition analytical program (the cost breakdown by month is below).

April 2015 = $11,495
May 2015 = $12,146
June 2015 = $13,223

PROBLEMS OR DELAYS

None.

PRODUCTS

Completion of this quarterly report

Johnson, H.P., Miller, U.K., Salmi, M.S., Solomon, E.A., *in review.* Analysis of bubble plume distributions to evaluate methane hydrate decomposition on the upper continental slope, submitted to *Geophys. Geochem. Geosyst.*

Whorley, T.L.*, Solomon, E.A., Torres, M.E., Johnson, H.P., Berg, R.D., Philip, B.T., 2015. Evaluating active methane hydrate dissociation along the Washington margin in response to bottom water warming, submitted to AGU Fall Meeting.

Salmi, M.S.*, Harris, R.N., Johnson, H.P., Solomon, E.A., 2015. High resolution thermal model of the Washington margin of the Cascadia subduction zone, submitted to AGU Fall Meeting.

Graw, M.F.*, Solomon, E.A., Treude, T., Pohlman, J., Colwell, F.S., 2015. Towards biogeochemical modeling of anaerobic oxidation of methane: Characterization of microbial communities in methane-bearing North American continental margin sediments, submitted to AGU Fall Meeting.

Johnson, H.P., Miller**, U.K. , Salmi M.S. , Solomon, E.A., 2015. Analysis of bubble plume distributions to evaluate methane hydrate decomposition on the Cascadia margin, submitted to AGU Fall Meeting.

* denotes graduate student presenters at AGU meeting
** denotes undergraduate student presenter at AGU meeting