Oil & Natural Gas Technology

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Quarterly Research Performance

(Period Ending 6/30/2019)

Characterizing Baselines and Change in Gas Hydrate Systems using EM Methods

Project Period (10/01/2016 – 09/30/2019)

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

Office of Fossil Energy

TABLE OF CONTENTS

EXECUTIVE SUMMARY

This review period was largely occupied responding to comments from a USGS internal review of a draft manuscript for submission to *Journal of Geophysical Research.* The manuscript is now submitted for publication. We continue to make conductivity runs with silt as the sediment fraction, rather than sand as previously.

We are nearly finished with inversions of data from the Gulf of Mexico CSEM survey. At GC955, a shallow hydrate bearing fractured shale unit is present as a broad shallow resistor. A deeper resistor is coincident with a hydrate bearing sand interval. We have started preparing material for a manuscript on this work.

ACCOMPLISHMENTS

Major goals of project

Methane hydrates require cool temperatures, high pressures, and methane in excess of solubility to form, conditions that are met in both marine and permafrost regions worldwide. Concentrated accumulations of structural hydrate may be the target for resource exploitation, and there have been several production tests of natural gas from hydrate, both on land, such as at the Mallik site in NW Canada or the Mt Elbert test well on the Alaska North Slope, and in the ocean, such as in the Nankai Trough and an ice platform off Prudhoe Bay.

Much naturally occurring hydrate exists at the edge of thermodynamic stability, and as such represents an environmental hazard that threatens release of a potent greenhouse gas as a consequence of warming. Also, one way to produce methane from hydrate is to destabilize the structure by depressurization.

Current geophysical surveying methods for identifying hydrates, such as seismic methods and well logging/coring, are limited. Quantifying the volume fraction of hydrate in sediments is possible with careful processing and inversion of seismic data, although the relationship between seismic velocity (or attenuation) and hydrate concentration is complicated and usually needs to be calibrated with well data. Electromagnetic (EM) methods, on the other hand, are sensitive to the concentration and geometric distribution of hydrate because regions containing hydrate are significantly more resistive when compared to water saturated zones. The current state of the art for imaging gas hydrate using EM methods is represented by the Vulcan system developed by Scripps Institution of Oceanography. This system uses multiple, 3-axis EM receivers towed at source-receiver ranges of up to 1,000 m behind an electric dipole transmitter. The whole array (transmitter and receivers) is "flown" 50–100 m above the seafloor in order to (a) reduce noise, (b) avoid seafloor infrastructure and other obstacles, and (c) allow all three components of electric field to be measured. The Vulcan system was used in 2014 and 2015 to successfully collect 1,000 km of high quality data over gas hydrate prospects in Japan, as well as two studies offshore San Diego, California.

For the next advance in this technology, under the current agreement we will collect extensive 3D Vulcan data sets over two or three sites in the Gulf of Mexico where drilling and coring of hydrate systems has been, or will be, carried out. We plan to study the Walker Ridge 313, Orca Basin, and Green Canyon 781 prospects, but as we did under previous NETL funding, we will consult with DoE and the drilling consortium before choosing final targets. With 2–3 days of data collection over each prospect, we will be able to collect at least 10 lines of data 10–20 km long. With a line spacing of 500–1,000 m, this will provide a dense data set of 100–200 line km covering 50–100 square km.

Under prior NETL funding we designed a specialty pressure cell plumbed for high-pressure gas access, in which we formed gas hydrate samples while simultaneously measuring impedance spectra. Such impedance measurements of methane hydrate are needed for modeling of gas hydrate systems, yet had never been established prior to our work. Under the current agreement, we plan to extend these laboratory experiments to further utilize the unique apparatus we have designed, and build on our previous results and baseline measurements. We will introduce additional parameters that mimic the effects of induced or environmental factors that may act to destabilize gas hydrate systems and contribute to the onset of partial dissociation to solid or liquid water.

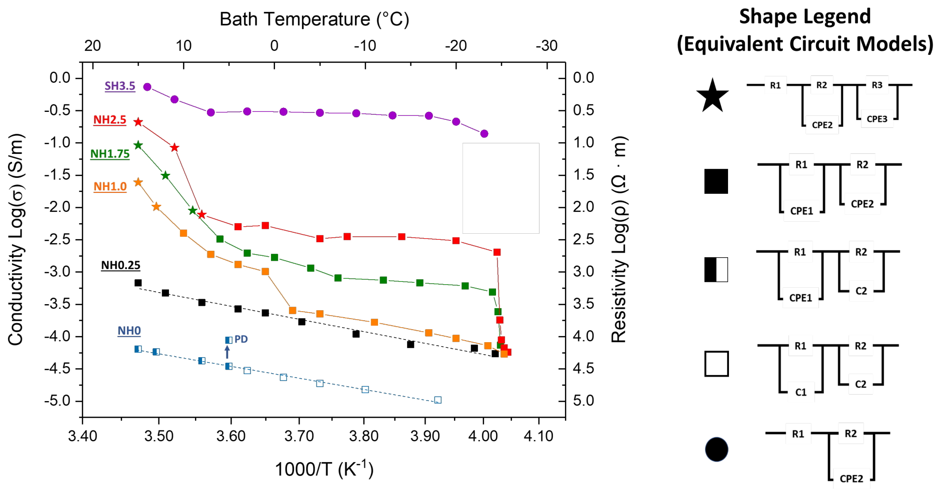

Figure 1. Conductivity log plot as a function of temperature for all methane hydrate samples. Each data point is fitted with an equivalent circuit model and markers are shown as different geometric symbols. Point PD shows the partially dissociated methane hydrate sample after generating pore water within it. The conduction pathways appear to change as a function of sample composition and corresponding conductivity values. Pure methane hydrate (NH0) has the lowest conductivity while methane hydrate synthesized from frozen seawater (SH3.5) has the highest conductivity for the entire temperature range measured. Conductivity of hydrate samples with added NaCl (NH0.25-NH2.5) plots in between these two extremes.

Work accomplished during the project period

Laboratory Conductivity Studies

The manuscript, *The effect of brine on the electrical properties of methane hydrate* by Lu R., Stern L.A., Du Frane W.L., Pinkston J.C., Roberts J.J., and Constable S., has been revised after USGS internal review and submitted to *Journal of Geophysical Research*. Figures 1 and 2 here have been abstracted from the manuscript to summarize the conclusions.

Figure 1 is a plot of log(electrical conductivity) versus reciprocal absolute temperature, which linearizes the exponential thermally activated Arrhenius equation. We see three conduction regimes: (1) at the lowest test temperatures below the solidus (-24°C) or at the lowest salinity (NH0.25), conduction is primarily by solid state diffusion of ionic defects in methane hydrate with no liquid. (2) Between the solidus and liquidus, where a connected saturated brine network forms for higher salinity samples and coexists with hydrohalite and ice, conduction depends greatly on the NaCl concentration but not significantly on temperature. (3) Above the liquidus, upon final melting of ice and hydrohalite, conduction is governed by the salinity (dissolved solute concentration) and volume of the brine network. In natural marine environments, gas hydrate bearing systems form above the liquidus and hence conductivity will be dominated by pore liquids (brine). Regardless, with the many kinetic factors to consider in these complicated mixed-phase systems, reaching thermodynamic and chemical equilibrium in the laboratory — by controlling time, temperature, and composition — is extremely important for obtaining accurate measurements that are relevant to the full range of conditions where gas hydrates can form in nature.

Figure 2 abstracts the conductivity–salt concentration relationships at four distinct temperatures. The exponential increase of electrical conductivity with salt concentration, particularly for the higher temperatures of +5°C and +15°C (Figure 2a-b), suggests that the addition of salt not only increases the salinity of the connected brine phase, but also increases the number of brine networks.

Last quarter we reported first results from our current work on using silt as a sediment fraction, for comparison with

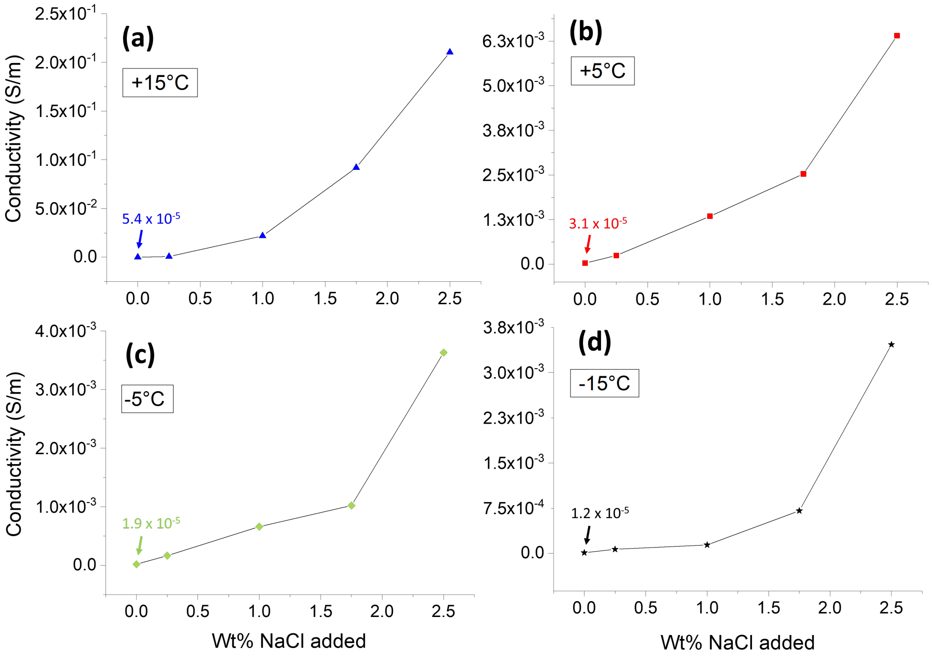

Figure 2. Conductivity plot as a function of bulk NaCl content for (a) +15°C, (b) +5°C, (c) -5°C, (d) -15°C. An exponential increase in conductivity is observed for methane hydrate samples with NaCl added.

previous studies using sand. Figure 3 shows cryogenic SEM images of our most recent run synthesizing samples from flash-frozen seawater and silt. Improvements in the SEM imaging allow us to see individual silt particles, and we have been able to verify that the silt is well distributed through the sample. We are currently working on the interpretation of electrical conductivity data from this and other samples.

Gulf of Mexico Field CSEM Data

The last two survey sites we collected data from during our Gulf of Mexico cruise were at Mad Dog (GC781) and GC955. The close proximity of these sites meant that it was more efficient to leave the array in the water and deep tow from Mad Dog to GC955. Between the two sites is the Green Knoll salt dome. Figure 4 shows the transect of resistivity inversions starting at Mad Dog, descending across the Sigsbee escarpment, rising over Green Knoll, and then across GC955. At Mad Dog, the graben structure is more conductive than the surrounding horsts. Increased resitivity is present at the base of the Sigsbee escarpment roughly coincident with the expected depth of the base of the hydrate stability zone. The salt dome shows very high resistivity, roughly 1000 Ωm, which is expected for salt. The salt body is overlain by a thin veneer of conductive sediments. At GC955, the shallow hydrate bearing fractured shale unit is present as a broad shallow resistor. The deeper resistor is coincident with a hydrate bearing sand interval.

Figure 5 shows the GC955 inversion line looking more conventionally from the south. Well logs from GC955 Joint Industry Project are in rough agreement with our results, with GC955 hole H showing significant increased resistivity interpreted to be hydrate, while hole Q, located upslope, shows no increased resistivity (Guerin et al., 2009). Without seismic structural constraints, the inversion is unable to differentiate the overlying hydrate fractured sediments with the underlying hydrate bearing sands that represent the bulk of the hydrate reservoir (Haines et al., 2017). Below the hydrate bearing interval is another resistor that is coincident with the depth of seismically inferred free gas bearing sediments (Boswell et al., 2012). Additionally, an area of increased resistivity is present between holes H and Q that is coincident with a mud volcano (Hutchinson et al., 2009). A Fence plot of all the Green Canyon 955 inversions in shown in Figure 6.

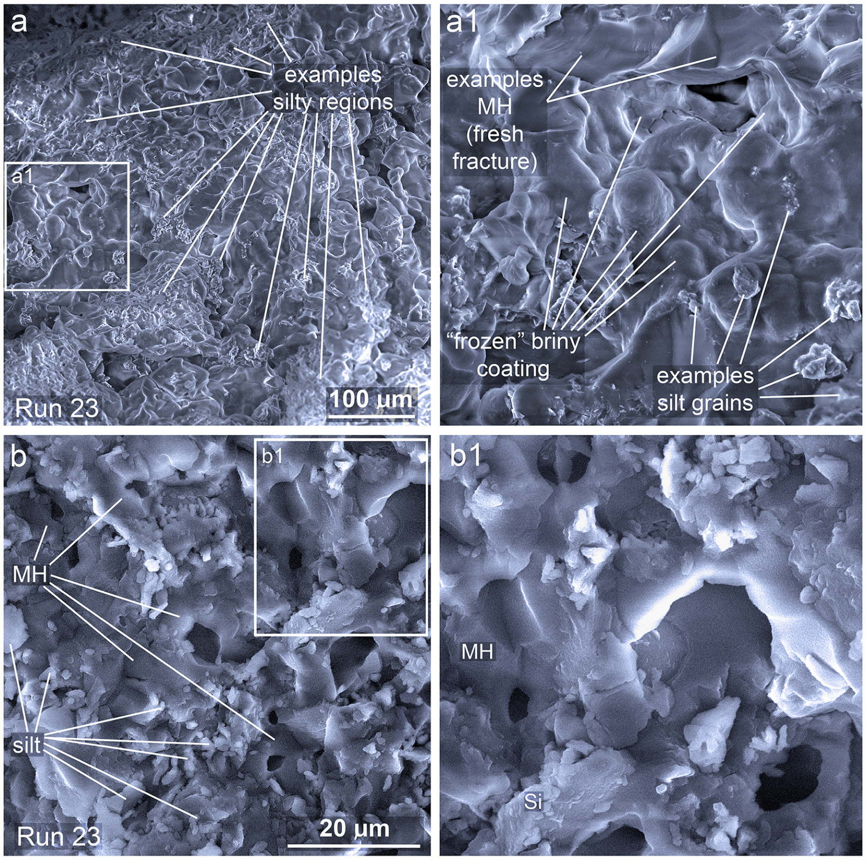

Figure 3. Cryo-SEM images of Run 23, methane hydrate formed from synthetic seawater with 50 vol% silt added, after quenching in liquid nitrogen. Individual particles or regions of silt are, in general, well-distributed throughout the hydrate, as seen at both lower-magnification (panel a) and higher-magnification (panel b) scales. Boxed insets are expanded in panels a1 and b1 respectively.

References cited.

Boswell, R., Collett, T.S., Frye, M., Shedd, W., McConnell, D.R., Shelander, D., 2012. Subsurface gas hydrates in the northern Gulf of Mexico. *Mar. Petrol. Geol.*, **34**, 4e30.

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Hutchinson, D., R. Boswell, T. Collett, J. Dai, B. Dugan, M, Frye, E. Jones, D. McConnell, K. Rose, C. Ruppel, W. Shedd, D. Shelander, and W. Wood, 2009. Proceedings of the drilling and scientific results of the Gulf of Mexico gas hydrate joint industry project leg II: Green Canyon 955 site selection. , , .

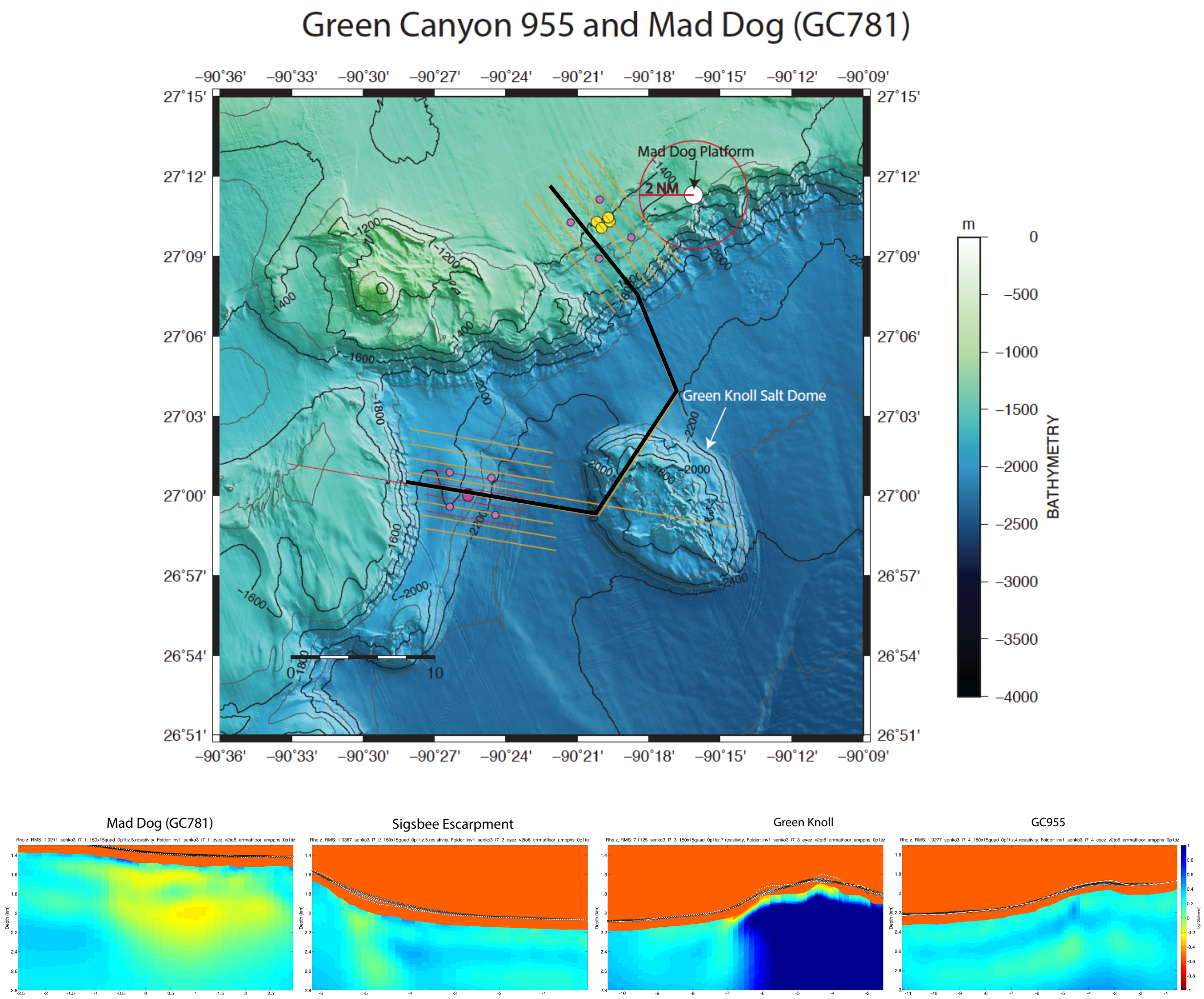

Figure 4. GC 955 and GC 781 tow lines (top). The inversions (bottom) are for the four segments of the black line, which was a single tow from GC781 to GC955.

Other activities

Training and professional development.

Peter Kannberg, then a PhD student at SIO, acted as co-chief scientist on the data collection cruise. He is currently working on this project as a postdoc.

Ryan Lu, a junior scientist at LLNL, continues work on the laboratory electrical conductivity studies and learning about hydrate synthesis and the operation of the conductivity cell.

SIO PhD students Dallas Sherman and Valeria Reyes-Ortega participated in the research cruise and learnt about the operation of the CSEM instruments. Sherman assisted with an industry-operated hydrate survey later in that year.

Peter Kowalczyk and Karen Weitemeyer, of Ocean Floor Geophysics, participated in the cruise as part of the industry cost-share component, and also gained some training in the operation of the equipment, which has been used for several proprietary surveys offshore Japan.

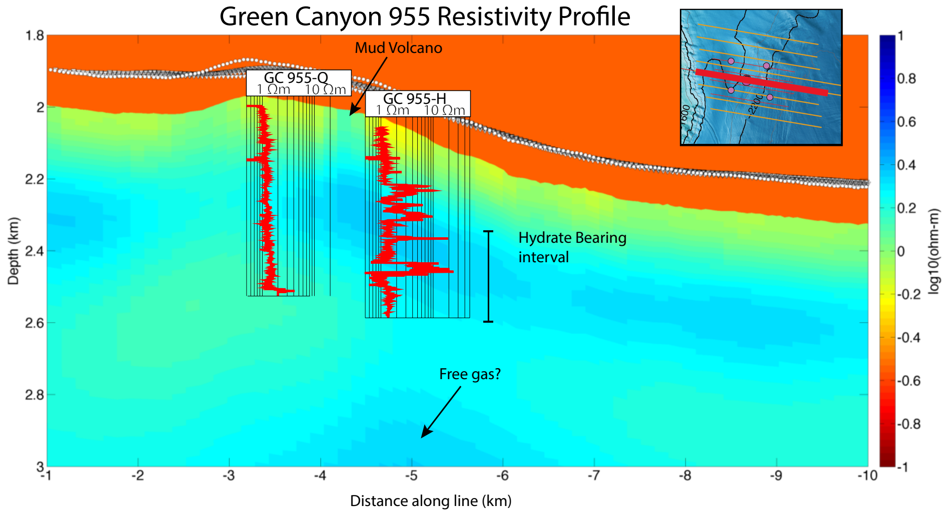

Figure 5. Inversion of the central line over Green Canyon 955, with overlain well logs.

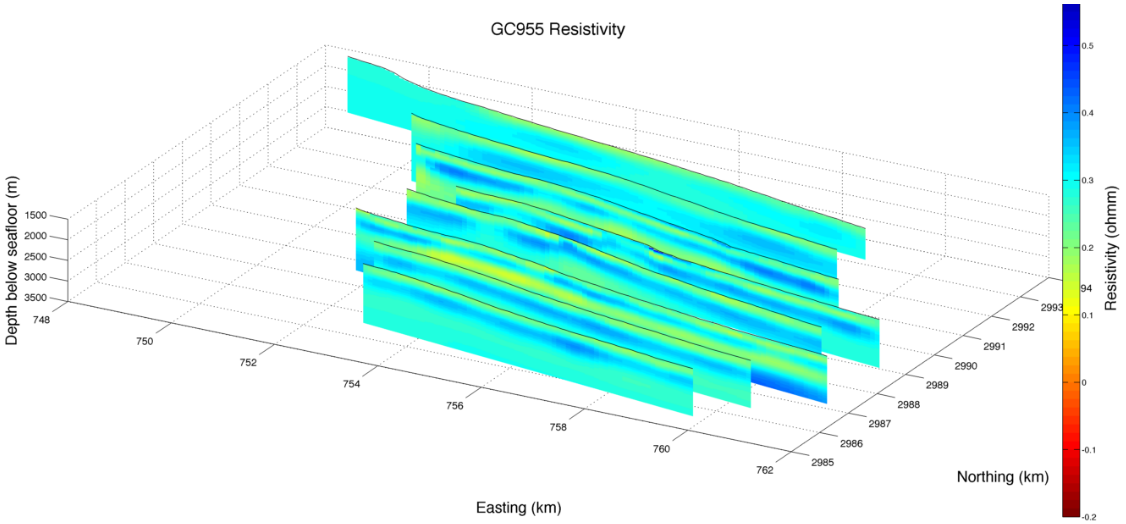

Figure 6. Fence plot of all the Green Canyon 955 inversions.

Plans for next project period.

During the next project period we will write up results from the GoM CSEM data for submission to *The Fire in the Ice*, as well as for a peer-reviewed publication. We will work up the hydrate-silt conductivity data with a view to submitting a manuscript to *Geophysical Research Letters*.

Table 1: Milestone status report.

Milestone Title	Planned Completion Date	Actual Completion Date	Verification Method	Comments on progress
First set of conductivity runs	08/1/2017	08/1/2017	Internal review	completed
Field data collection	12/1/2017	06/12/2017	200 line km collected	completed
Second conductivity runs	12/30/2017	12/30/2017	Internal review	completed
Final set of conductivity runs	8/1/2018	8/1/2018	Internal review	completed
Field data inverted	12/1/2018	7/1/2019	2D inversions done	completed
Publications(s) submitted	9/1/2019	7/11/2019	At least 1 pub. submitted	completed
Publications(s) accepted	12/30/2019		Publication accepted	

PRODUCTS

Project Management Plan. The revised Project Management Plan was accepted on 3 February 2017.

Project Web Page. http://marineemlab.ucsd.edu/Projects/GoMHydrate2017/index.html (check out the animated movie of the deep-two over Green Canyon at http://marineemlab.ucsd.edu/Projects/GoMHydrate2017/deeptowmovie.html)

Preliminary Cruise Report. http://marineemlab.ucsd.edu/Projects/GoMHydrate2017/CruiseReportReduced.pdf

Fire in the Ice article. Electrical Conductivity of Methane Hydrate with Pore Fluids: New Results from the Lab Ryan Lu, Laura A. Stern, Wyatt L. Du Frane, John C. Pinkston, and Steven Constable. Fire in the Ice, 18, 7–12.

AGU abstracts:

Kannberg, P., and S. Constable, 2017: Deep-towed CSEM survey of gas hydrates in the Gulf of Mexico. Contributed paper at the Fall AGU meeting, New Orleans.

Lu, R., L.A. Stern, W.L./ Du Frane, J.C. Pinkston, J.J. Roberts and S. Constable, 2018: Electrical characterization of methane hydrate with coexisting brine. Contributed paper at the Fall AGU meeting, Washington.

Kannberg, P., and S. Constable, 2018: Quantifying Methane Hydrate in the Gulf of Mexico Using Controlled Source Electromagnetic Methods. Contributed paper at the Fall AGU meeting, Washington.

Other abstracts:

Kannberg, P., and S. Constable, 2018, Detecting methane hydrate in the Gulf of Mexico using controlled source electromagnetic methods. Contributed poster at the Galveston Gordon Conference.

The following papers acknowledge this or past DoE funded research:

Sherman, D., and S.C. Constable, 2018. Permafrost extent on the Alaskan Beaufort Shelf from surface towed controlled-source electromagnetic surveys. *Journal of Geophysical Research: Solid Earth*, **123**, 1–13, /doi.org/ 10.1029/2018JB015859.

Weitemeyer, K., S. Constable, D. Shelander, and S. Haines, 2017. Mapping the resistivity structure of Walker Ridge 313 in the Gulf of Mexico using the marine CSEM method. *Marine and Petroleum Geology*, **88**, 1013–1031, /doi.org/10.1016/j.marpetgeo.2017.08.039.

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Du Frane, W., L.A. Stern, S. Constable, K.A. Weitemeyer, M.M. Smith, and J.J. Roberts, 2015. Electrical properties of methane hydrate + sediment mixtures. *Journal of Geophysical Research*, **120**, 4773–4787, doi:10.1002/2015JB011940.

Weitemeyer, K., and S. Constable, 2014. Navigating marine electromagnetic transmitters using dipole field geometry. *Geophysical Prospecting*, **62**, 573–593, doi: 10.1111/1365-2478.12092.

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Weitemeyer, K.A., S. Constable, S. and A.M. Trehu, 2011. A marine electromagnetic survey to detect gas hydrate at Hydrate Ridge, Oregon. *Geophysical Journal International* , **187**, 45-62.

Weitemeyer, K., G. Gao, S. Constable, and D. Alumbaugh, 2010. The practical application of 2D inversion to marine controlled-source electromagnetic sounding. *Geophysics*, **75**, F199–F211.

Weitemeyer, K., and S. Constable, 2010. Mapping shallow geology and gas hydrate with marine CSEM surveys. *First Break*, **28**, 97–102.

PARTICIPANTS AND OTHER COLLABORATING ORGANIZATIONS

Name: Steven Constable
Project Role: PI
Nearest person month worked: 1
Contribution to project: Management, scientific direction
Funding support: Institutional matching funds
Foreign collaboration: Yes
Country: Canada
Travelled: No

Name: Peter Kannberg
Project Role: PhD student/SIO
Nearest person month worked: 3
Contribution to project: Data processing and inversion.
Funding support: This project
Foreign collaboration: Yes
Country: Canada
Travelled: No

Name: Laura Stern
Project Role: Scientist/USGS
Nearest person month worked: 1
Contribution to project: Gas hydrate synthesis and conductivity measurements.
Funding support: USGS
Foreign collaboration: No

Name: Wyatt DuFrane
Project Role: Scientist/LLNL
Nearest person month worked: 1
Contribution to project: Postdoc supervision/conductivity measurements.
Funding support: This project
Foreign collaboration: No

Name: Ryan Lu
Project Role: Junior Scientist/LLNL
Nearest person month worked: 1
Contribution to project: Conductivity measurements.
Funding support: This project
Foreign collaboration: No

CHANGES/PROBLEMS

There are no changes or problems arising from this review period.

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