Oil & Natural Gas Technology

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Quarterly Research Performance

(Period Ending 9/30/2019)

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

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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.

Work accomplished during the project period

Laboratory Conductivity Studies

The final methane hydrate conductivity experiment (Run 24), methane hydrate formed from flash-frozen seawater + 50% silt + CH4 gas, was completed and has been analyzed by cryo-SEM and EDS (Figure 1). This completes all of the experiments that we originally proposed for multi-component systems of methane hydrate + sediments (sand or silt) ± fluids (pure water or brine).

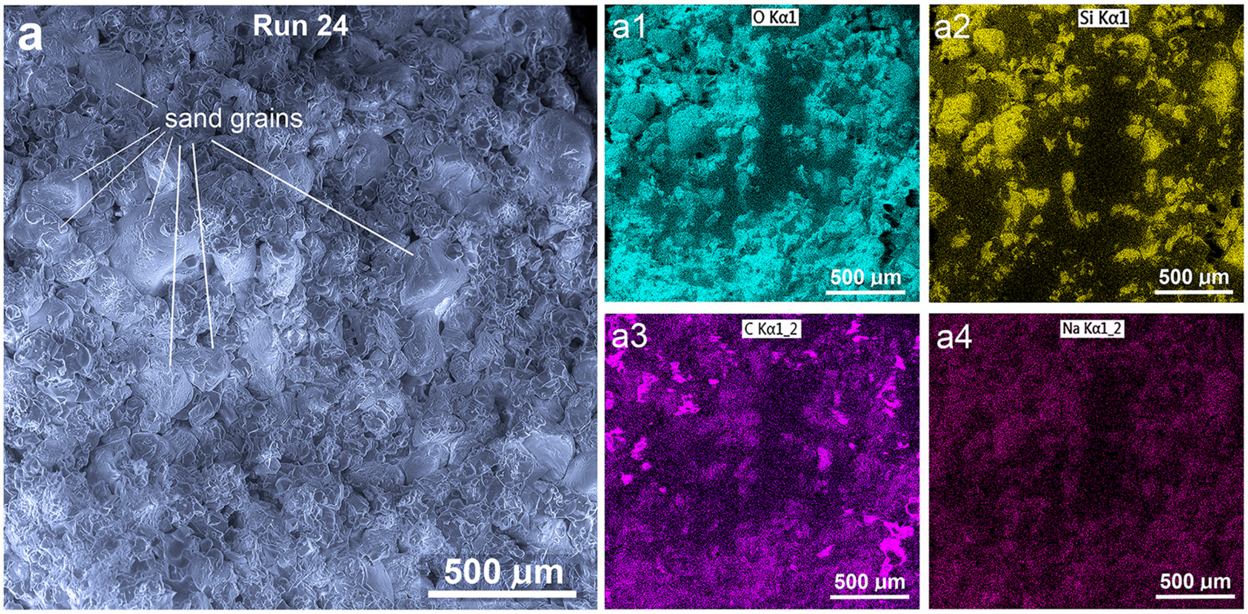

Figure 1. Cryo-SEM image and EDS compilations of Run 24, methane hydrate formed from synthetic seawater + CH4 gas + 50 vol% quartz sand. The SEM image shown in (a) is matched with EDS elemental maps of O (a1), Si (a2), C (a3), and Na (a4). A map of Cl was also collected but is not shown here; as expected, it appears virtually identical to Na (a4). While not quantitative, the EDS maps clearly illustrate the general distribution of components in the SEM image; oxygen (a1) corresponds to both methane hydrate and quartz sand, which can then be further differentiated by comparing the C versus Si maps (a3 vs a2). The overall good distribution of frozen brine and/or salt phases is indicated by the Na map (a4).

We completed one additional experiment (Run 25) addressing the unresolved question of whether the composition of the guest molecule itself in a sI clathrate hydrate structure affects sI hydrate conductivity, which in turn speaks to the fundamental conduction mechanism in gas hydrate. Results show that guest-molecule composition can indeed contribute a modest and measurable effect.

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 accepted by *Journal of Geophysical Research*. The article is available at

https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2019JB018364

We submitted a 2019 Fall AGU abstract titled "Electrical properties of multi-component methane hydrate systems, a potential tool for constraining volumetric distribution of fluids in high-saturation formations". The abstact can be viewed at https://agu.confex.com/agu/fm19/meetingapp.cgi/Paper/606871

and the text is provide here for reference:

> Controlled source electromagnetic surveys (CSEM) is a promising geophysical method for remotely detecting naturally formed gas hydrate in marine settings, with sensitivity to concentration and distribution of hydrate/fluid saturations within seafloor sediment. However, overall electrical conductivity of these systems is a complicated product of multiple components. Pure methane hydrate has relatively low electrical conductivity, on the order of 10-4 to 10-5? S/m, although sand can increase this by an order of magnitude due to the presence of impurities. Even higher concentrations of salt can stabilize a secondary hydro-salt phase at low temperature (T) that melts incongruently into highly conductive brine. Here we present the electrical properties of various sediments (sand, silt, or glass beads) in semi-porous mixtures with methane hydrate formed from either high-purity H2O ice or flash-frozen seawater in a pressurized CH4 gas environment. Hydrate synthesis was achieved through multiple T cycles (-24 to +15C) with in situ monitoring of electrical impedance. Samples were then quenched for cryogenic scanning electron microscopy and energy dispersive spectroscopy (cryo-SEM/EDS). Frozen brine was distinguished from gas hydrate or sediment by texture, as well as its Na and Cl contents. Equivalent circuit modeling was used to isolate sample conductivity from systemic effects such as electrode polarization, to monitor changes to the impedance structure, and proved to be sensitive to the various phase boundaries traversed during T cycling. High salinity samples formed from flash-frozen seawater saw a marked increase in electrical conductivity and diminished electrode polarization at higher frequency. In these cases, cryo-SEM/EDS verified that brine was present at sufficient volumes to cross the percolation threshold. Electrical conductivity of samples with well-connected brine was largely controlled by solute content, whereas conductivity of lower salinity samples was lower with greater T dependence. These results suggest that CSEM in regions with high gas hydrate saturations, like those found offshore of Japan, may exhibit high contrast boundaries associated with this percolation threshold that could be used to constrain the fluid volume ratio and the overall salinity of these formations.

Gulf of Mexico Field CSEM Data

Resistivity models were inverted for 8 profiles across WR 313 (See map: Figure 2). These are anisotropic inversions, where the vertical resistivity can vary from the horizontal resistivity. Increased resistivity is interpreted to be due to the presence of either hydrate or salt. Six of the eight lines shown here have accompanying depth-migrated seismic profiles (S. Haines, personal communication), and can be used to differentiate salt from hydrate in the resistivity models.

Salt tectonics at WR 313 profoundly affects the structure of modeled resistivity inversions. Salt bodies flank the basin on all sides, and are apparent in the inversions as regions of high resistivity surrounded by a conductive halo (Figure 3). This halo is interpreted to be the result of the combination of increased pore fluid salinity and temperature adjacent to the salt bodies. Additionally, the rising salt bodies control the local thrust faulting in the basin. When the resistivity models are overlain on seismic sections, increased resistivity is found in the unnamed unit that is bounded by the aqua and yellow sands (Figure 4). Within this unit, resistivity is further enhanced adjacent to faults. These faults appear to be forming a structural petroleum trap, with hydrate concentrating in these areas.

Anisotropic inversions are necessary to produce geologically realistic models. Isotropic inversions introduce horizontally alternating conductive and resistive artifacts that result from trying to fit anisotropic data to an isotropic model. On the northwestern side of line 5 at 7 kilometers (Figure 4) the vertical resistivity shown in the model is highest where the bedding is most horizontal. Vertical resistivity decreases as the dip of the beds increases. However, horizontal resistivity is enhanced where the beds dip steeply. This suggests that the resistors being modeled are conformal to bedding planes. In this setting, the combination of increased resistivity and bedding conformal anisotropy suggest the presence of alternating beds of hydrate-bearing and brine-saturated sediments that are individually below the resolution of the CSEM method.

We also see increased resistivity at depths where we expect to find the base of the hydrate stability field. These are

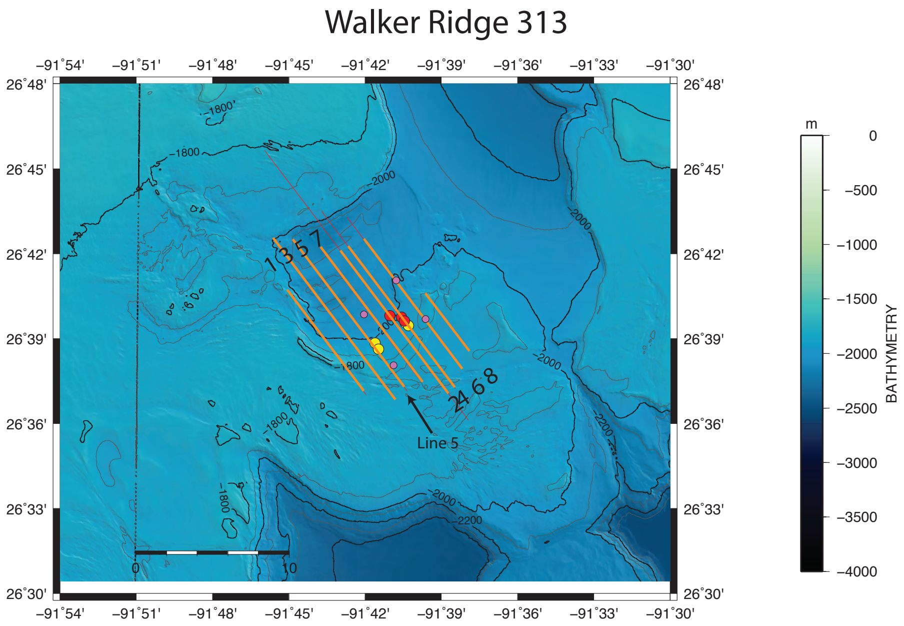

Figure 2. Map of CSEM tow lines collected over WR 313.

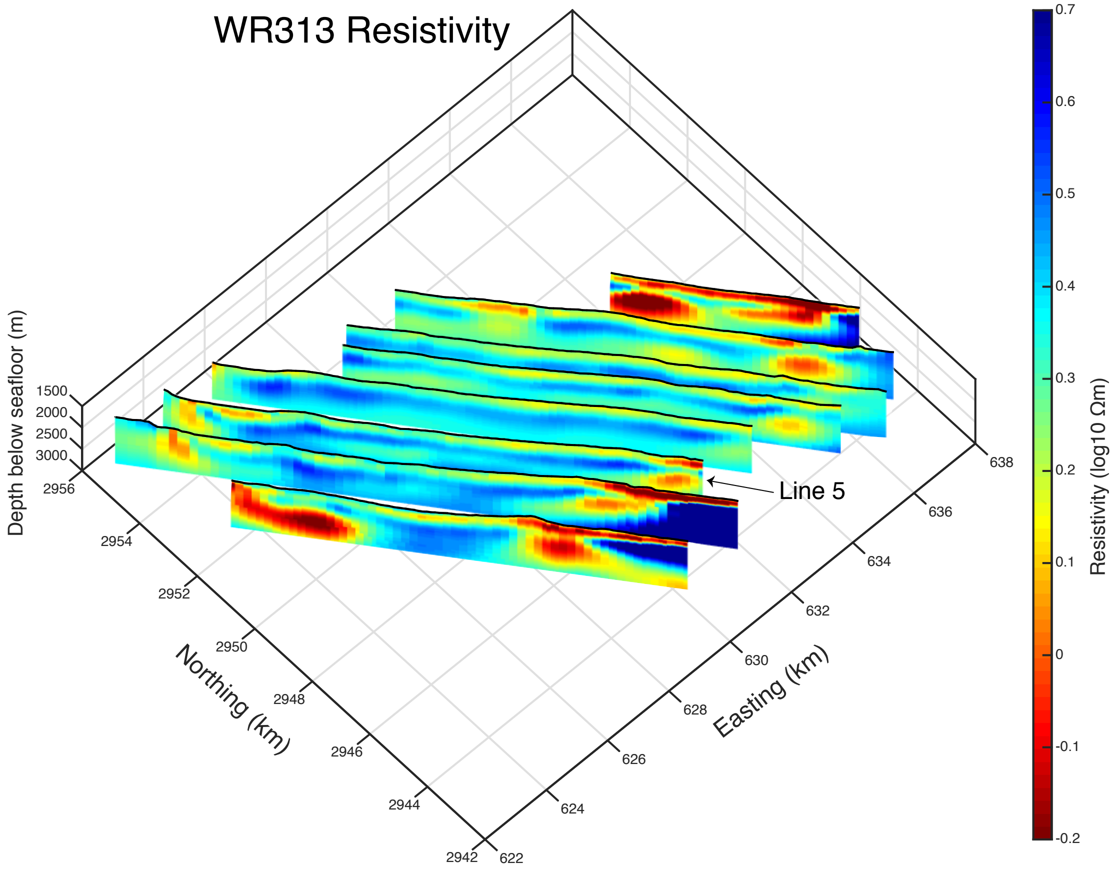

Figure 3. Fence plot of vertical resistivity from anisotropic inversions of the WR 313 CSEM tows.

found between kilometer 2–4 in Figure 4. These are collocated with sand beds thought to be hydrate-bearing which were the target of the logging operations during the Gulf of Mexico Gas Hydrate Joint Industry Project Leg II (JIP). The resistivity modeled here is roughly the same value that was modeled in the unconstrained synthetic inversions based on logging resistivities from that JIP. Future inversions will focus on constraining the models using the depth migrated seismic profiles.

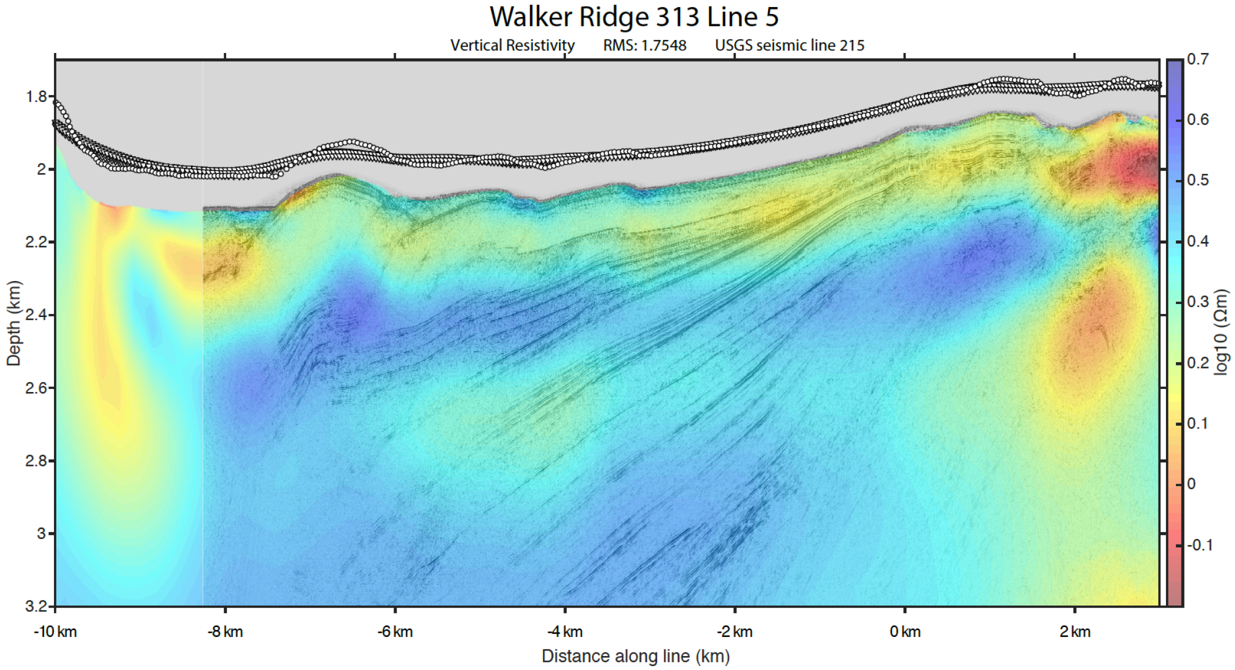

Figure 4. Line 5 WR 313 inversion overlain on seismic reflectivity (courtesy of S. Haines).

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.

Plans for next project period.

This concludes this project, so there is no future project period and no carry-over funds. All project goals and milestones have been met. However, we anticipate that sometime in the future 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, and submit a manuscript to *Geophysical Research Letters* on the silt conductivity data.

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	9/25/2019	Publication accepted	completed

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:

Lu, R., L.A. Stern, W.L. Du Frane, J.C. Pinkston, J.J. Roberts, and S. Constable, 2019. The effect of brine on the electrical properties of methane hydrate. *Journal of Geophysical Research*, doi/10.1029/2019JB018364 .

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.

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Constable, S., P. K. Kannberg, and K. Weitemeyer, 2016. Vulcan: A deeptowed CSEM receiver. *Geochemistry, Geophysics, Geosystems*, **17**, doi:10.1002/ 2015GC006174.

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.

Du Frane, W.L., L.A. Stern, K.A. Weitemeyer, S. Constable, J.C. Pinkston, J.J. Roberts, 2011. Electrical properties of polycrystalline methane hydrate. *Geophysical Research Letters*, **38**, doi:10.1029/2011GL047243.

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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