Oil & Natural Gas Technology

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Quarterly Research Performance

(Period Ending 3/31/2019)

Characterizing Baselines and Change in Gas Hydrate Systems using EM Methods

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

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EXECUTIVE SUMMARY

During this review period we continued to collect electrical conductivity measurements and cryogenic electron microscopy on samples of gas hydrate, and have sumitted a draft of a paper for submission to *JGR* for USGS internal review.

We continue to carry out inversions of data from the Gulf of Mexico CSEM survey, which show resistors in the area targeted by GOM∧2 drilling. We also see resistors associated with a slump feature on the western side of the Orca Basin survey area, as well as a conductive plume above a nearby salt body.

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

During this quarter two experimental runs (Run 21 and 22) have been completed and one (Run 23) is currently in progress. Run 21 and 22 both attempted to investigate the effects of silt on the electrical properties of methane hydrate. We have previously investigated the effect of coarse silica particles, sand (>100μm) in the Du Frane et al., (2015) study and hope to now learn more about the effect of finer silica particles (<40μm). Run 23 involves the synthesis of a methane hydrate and silt mixture from flash-frozen seawater (similar to Run 20 described in previous reports.) This experimental run aims to study the effect of using seawater salts on the electrical properties of methane hydrate mixtures (50vol% silt) to mimic hydrates compositions observed in nature.

Table 1. Activation energy, Ea, for the various runs shown in Figure 1.

Run #	Mixture type	Ea (kJ/mol)
22	50vol% Silt	37.8
21	10vol% Silt	31.3
17	0.25wt% NaCl	36.6
11	Pure Hydrate	33.5
5	10vol% Sand	37.8
4	45vol% Sand	5.9

Run 21 and 22 were both synthesized through the same temperature cycle range (+15 to -25°C) as previous runs. However, due to the low salt impurity content in silt, no formation of hydrohalite at <-24°C was observed in these samples. Comparison to Run 17 involving 0.25wt% NaCl shows that even at 50vol% silt, the level of impurities is still presumably less than 0.25wt% salts (Figure 1). When compared to sand, silt has a much smaller effect on the activation energy (derived from the slope values of the linear-fit dotted lines) as shown in Table 1. This is possibly due to their finer particle size which allows them to sit in methane hydrate grain junctions without significantly disturbing the solid-state hydrate conduction pathway.

Microscopy images of Run 21 involving 10vol% was also collected and shown in Figure 2. (See caption for more detail)

Run 22 involving 50vol% silt was partially dissociated after synthesis and step-dwelled to monitor the effect of pore water accumulation within the sample (not shown here), in order to compare with pure methane hydrate (Run 11) undergoing partial dissociation. We are holding off in forming conclusions about the effects of water formation until we complete the currently-underway Run 23.

The manuscript, *Electrical properties of methane hydrate mixtures with brine* by Lu R., Stern L.A., Du Frane W.L., Pinkston J.C., Roberts J.J., and Constable S., has been submitted for USGS internal review prior to submission to *Journal of Geophysical Research*. The abstract of this pre-print is presented below.

Abstract of manuscript:

Gas hydrates possess significantly higher electrical resistivity than water and even ice, such that electromagnetic (EM) methods can be employed to help identify natural gas hydrate formations in marine and permafrost environments. Controlled laboratory studies offer a means to isolate and quantify the effects of changing individual components within gas-hydrate-bearing systems, in turn offering insight into the behavior of natural systems. Here we investigate the electrical properties of polycrystalline methane hydrate in the presence of brine. Initially, pure methane hydrate was synthesized from H_2O ice and CH_4 gas while undergoing electrical impedance measurement, then partially dissociated to assess the effects of pore water accumulation and to better understand natural systems near the edge of methane hydrate stability. Methane hydrate + brine mixtures were then synthesized using either pure NaCl (0.25 – 2.5wt%) or seawater (3.5wt% salts) as a reactant. Impedance was measured in situ while temperature cycled between

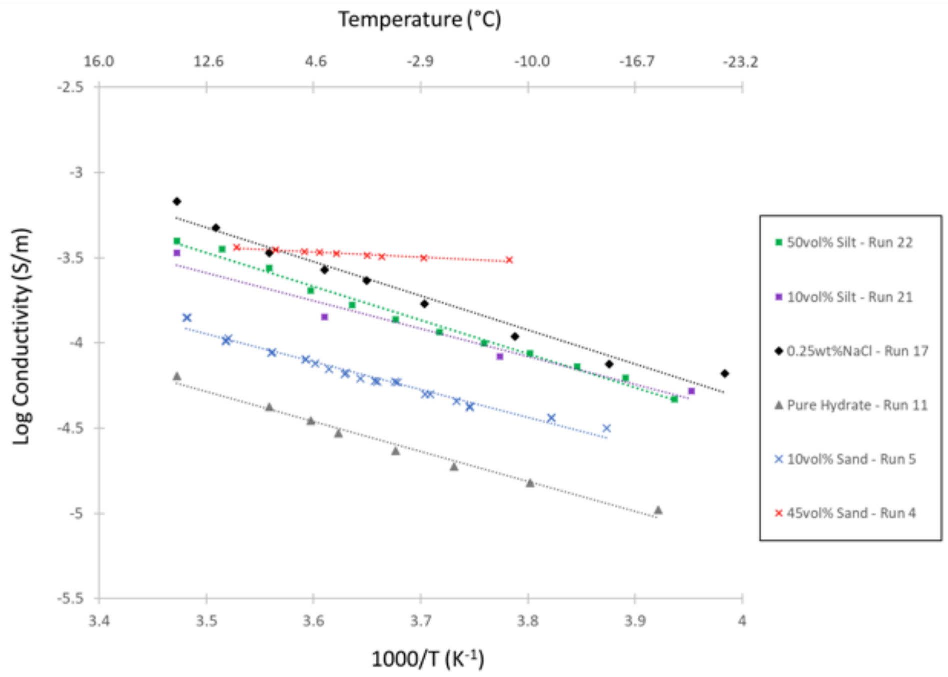

Figure 1. Conductivity versus temperature plot of methane hydrate mixtures with sand, silt, and NaCl for comparison.

+15°C and -25°C. Conductivity (inverse of resistivity) was calculated from the impedance spectroscopy results and several possible conduction mechanisms were determined using equivalent circuit modeling. Samples with low NaCl concentration show a doping effect and a log-linear conductivity response as a function of temperature. For higher salt content samples, conductivity increases exponentially and the log-linear relationship no longer holds true across the temperature range measured; instead, we observe evidence of phase changes within the samples according to NaCl-H_2O-CH_4 phase equilibria. Final samples were quenched in liquid nitrogen and imaged by cryogenic scanning electron microscopy (cryo-SEM) to assess grain-scale characteristics and phase distribution.

Gulf of Mexico Field CSEM Data

During this review period we continue to invert the Gulf of Mexico CSEM data. Here we report the results of a higher resolution inversion targeting the slump feature in Orca Basin (WR 100). There is some evidence that this feature is associated with upslope destabilization of gas hydrate. It appears that we are imaging conductive fault features on the edges of the scarp (Figure 3) and resistive hydrate near the seafloor in the middle of the slump feature.

A recently published seismic line (Sawyer et al., 2019) perpendicular to our cross-slump inversions shows that there is a salt body that shoals along the northern portion of our CSEM lines. The increased geothermal gradient associated with the uplifting salt body appears to be shoaling resistors interpreted to be hydrate on the northern lines, while resistors on the southernmost line are at a depth expected based on the regional geothermal gradient.

Increased hydrate concentrations within the slump suggests a correlative link between hydrate and slope failure in the Orca Basin. Historically, hydrate mediated slope failure is expected to occur at the base of the hydrate stability field (HSF), where free gas causes overpressure, leading to slope failure along the plane of the base of HSF (Maslin et al., 2004). However there is limited evidence that such a mechanism is a widespread occurrence. Recent studies show that over-pressurizing sediments within the HSF is a modeled and observed mechanism for hydrate driven slope failure (Elger et al., 2018) (Figure 4). Such mechanisms manifest as a vertical pipe structure of hydrate or free gas that extends above the base of HSF and terminates at an impermeable barrier, increasing pore pressures laterally along the

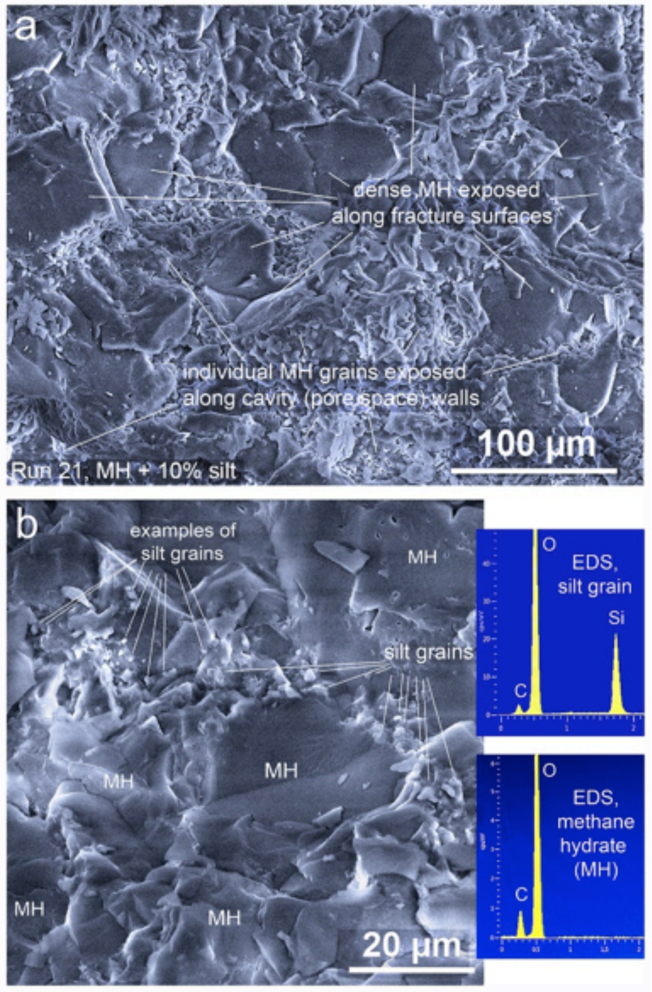

Figure 2. Cryo-SEM images of Run 21, methane hydrate + 10vol% silt. Panel **a** illustrates the general uniformity of the sample, with dense regions of methane hydrate surrounding open cavities. At this scale, silt is not visible. Panel **b** shows silt grains (≈1-2 micron diameter) surrounding methane hydrate grains or clusters. Although silt is near the limit of resolution of our cryo-SEM abilities, advances in EDS capabilities this quarter now allow us to verify their identification, as well as verifying the carbon peak in methane hydrate (blue boxes at right).

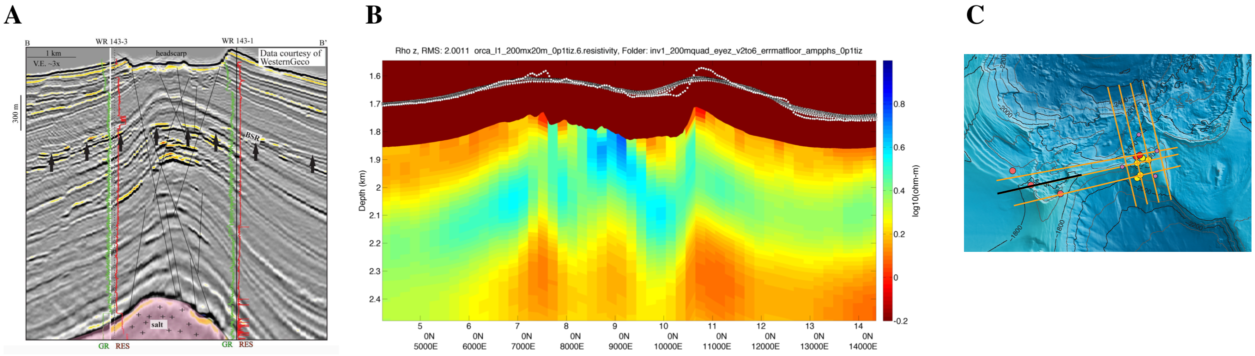

Figure 3. Seismic reflectivity from Sawyer et al. (2019) (**A**), resistivity inversion (**B**), and location map (black line on **C**) of the slump feature in Orca Basin.

base of the trap. One of our inversions across the Orca Basin slump (Figure 3) shows a dipping resistor that spreads laterally at the seafloor. This resistor could be the remains of a pipe structure that follows a high-permeability fault. This structure would have over-pressurized the surrounding sediments, causing slope failure along the upper limit of the pipe structure, leaving behind an increased concentration of hydrate near the seafloor. A slope failure mechanism such as this would be retrogressive, which is what is occurring at Orca Basin slump (Elger et al., 2018; Sawyer et al., 2019).

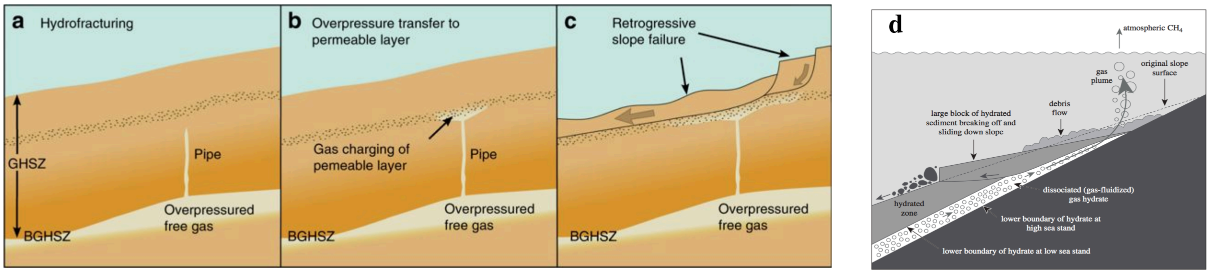

Figure 4. Scenarios for hydrate-induced slope failure. **a–c**, over-pressured sediments with the HSF and vertical gas migration (Elger et al., 2018), and **d** over-pressure caused by free gas at the base of the HSF (Maslin et al., 2004).

In related work, we recently submitted a manuscript to *Geology* entitled *Characterization and quantification of gas hydrates in the California Borderlands*, by P.K. Kannberg and S. Constable. The abstract of this pre-print is given below:

Abstract of manuscript:

Characterizing hydrate deposits is difficult using traditional seismic methods, but electromagnetic methods are directly sensitive to electrically resistive gas hydrates. Using a 1 km long deep towed marine electromagnetic system, six survey lines were towed coincident with legacy seismic reflection data in the Santa Cruz Basin in the Outer California Borderlands. While the strongest seismic indicators place hydrate in the central basin, resistors inferred to be hydrate are located predominantly on the flanks of the basin, coincident with gas migration pathways such as faults and steeply dipping strata. Two features consistent with the resistivity profile from previously imaged seafloor methane seeps were also found. Resistivity is related to hydrate saturation through ArchieÕs law, and total hydrate volume of the Santa Cruz Basin is estimated to be 45 billion m^3.

Cited references:

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.

Elger, J., Berndt, C., Rücke, L., Krastel, S., Gross, F., and Geissler, W.H., 2018. Submarine slope failures due to pipe structure formation. *Nature Communications*, **9(1)**, 715, https://doi.org/10.1038/s41467-018-03176-1 .

Marlin, M. A., Owen, M., Day, S. and Long, D., 2004. Linking continental slope failure to climate change:testing the clathrate gun hypothesis. *Geology*, **32**, 53-56 (doi:10.1130/G20114.1).

Sawyer, D. E., Mason, R. A., Cook, A. E., and Portnov, A., 2019. Submarine Landslides Induce Massive Waves in Subsea Brine Pools. *Nature - Scientific Reports*, **128, 9, 1**, 2045-2322. https://doi.org/10.1038/s41598-018-36781-7.

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.

During the next project period we will continue to invert the GoM CSEM data, and submit the *JGR* paper on the laboratory conductivity work.

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		2D inversions done	ongoing
Publications(s) submitted	9/1/2019		At least 1 pub. submitted	USGS internal review
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.

Sherman, D., P. Kannberg, and S. Constable, 2017. Surface towed electromagnetic system for mapping of subsea Arctic permafrost. *Earth and Planetary Science Letters*, **460**, 97–104.

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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