Oil & Natural Gas Technology

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Quarterly Research Performance

(Period Ending 12/31/2017)

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

During this reporting period we processed up navigation data from the research cruise carried out earlier in the year. During the marine controlled-source EM data collection over 4 prospects in the Gulf of Mexico, we navigated the EM transmitter and receiver array using a long base-line (LBL) acoustic ranging system. We estimate that this system provides about 10 m accuracy for the array positioning, which will become very important during inversion of the data.

We carried out electrical conductivity measurements and cryogenic electron microscopy on samples of gas hydrate with added salt, with starting concentrations of 1 and 2.5 weight percent salt. The salt forms brine on the surface of the gas hydrate grains, which creates a connected electrical conduction path and increases the conductivity significantly over that of pure methane hydrate. However, at sufficiently low temperatures the brine freezes to form halite or hydrohalite. The electrical conductivity gives a clear indication of the point at which this percolation threshold is breached, which is -4°C for 1% salt and -24.5°C for 2.5% salt. Below these temperatures the conductivity approaches that of pure hydrate.

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

Electrical conductivity measurements.

For this quarter, we focused on only two-component systems involving just brine and methane hydrate to get a more fundamental understanding of the behavior of this simpler system before embarking on more complicated ones. The temperature cycling method has allowed us to fully react pure ice into methane hydrate. However, the addition of salt in mixtures with the starting seed ice caused some small amount of sample to remain as a brine regardless of the number of temperature cycles that were performed. For these two-component synthesis experiments, we mixed NaCl salt (<75μm) in concentrations of 0-2.5 wt% and seed ice (180μm-250μm) inside of a chest freezer maintained < -60°C. Fine grain salts were used to allow a more uniform distribution along the grain-boundaries of the slightly courser seed ice. The sample was transferred into the cooled vessel ($\approx$25°C), which was then promptly transferred into a cooled d-limonene bath within a chest freezer ($\approx$25°C). The bath sits above a temperature-controlled ring heater. The vessels were then pressurized with methane gas at a starting value of 2700 psi. The bath is then temperature cycled between -20°C and +15°C for 10 or more cycles.

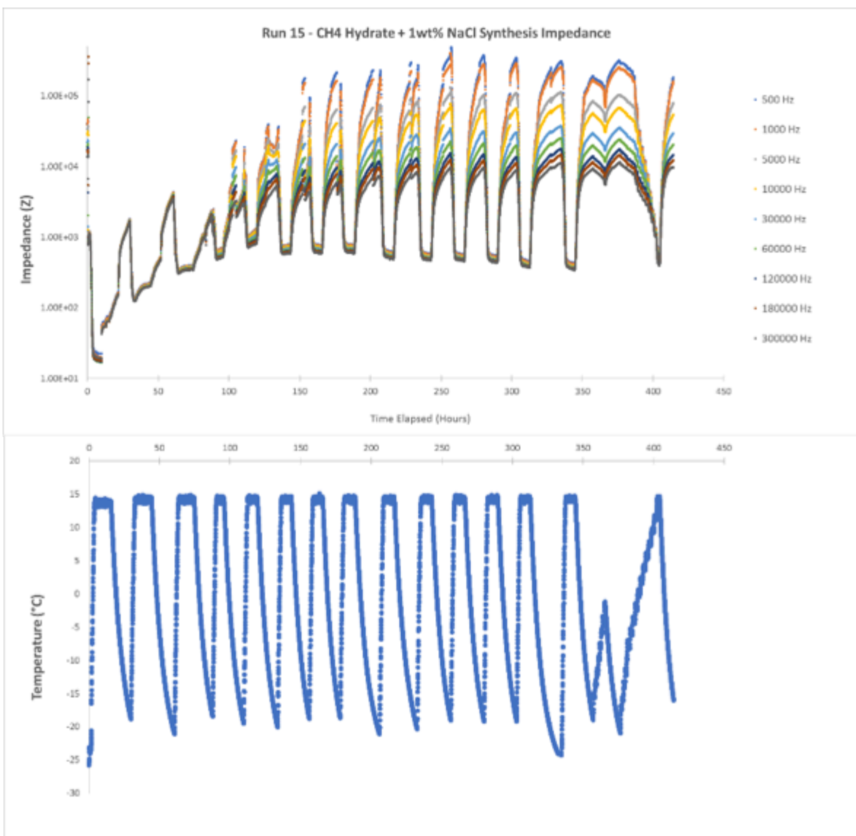

Figure 1. Run 15 (1wt% NaCl) entire synthesis cycle comparing impedance versus time elapsed.

For Run #15, we used 1wt% NaCl salt in seed ice. Figure 1 below shows the impedance as a function of time during the entire synthesis process. This synthesis curve reveals that the electrical conduction mechanism for the first three synthesis cycle is primarily through interconnected brine in the sample regardless of temperature. By the fourth temperature cycle, sample impedance decreases, particularly at the lowest temperatures within the measured range. After 7-8 cycles the sample no longer exhibited significant change in its impedance properties on subsequent cycles (See Figure 1), likely indicating that there was no longer significant gas hydrate formation occurring in the sample past this point. A step-dwell heating method was employed for heating in the 15th and final cycle to allow the sample to re-equilibrate to each increment in bath temperature and precisely determine the temperature dependence of the impedance spectra. The lower magnitude impedance and narrow spread in values as a function of frequency is an indication of good electronic conduction, which indicates that the brine was well connected throughout in the early stages of the synthesis process, and only at elevated temperatures after several cycles.

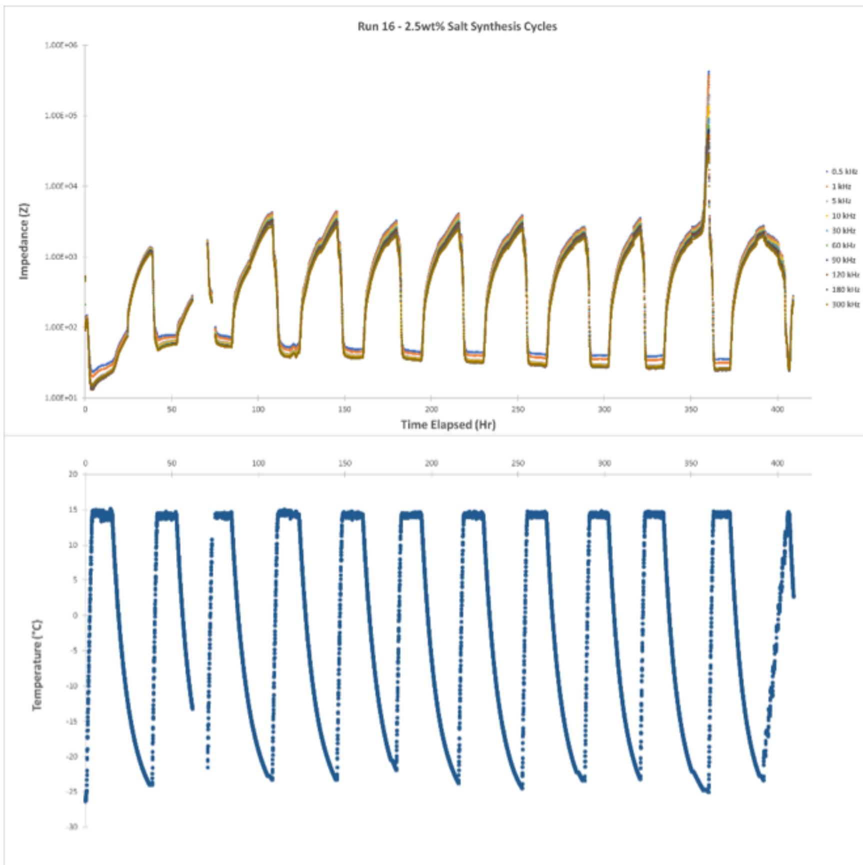

Figure 2. Run 16 (2.5wt% NaCl) entire synthesis cycle comparing impedance versus time elapsed.

For Run #16, we mixed 2.5wt% NaCl salt in the seed ice. Figure 2 below shows the impedance as a function of time throughout the entire synthesis process. This sample stopped exhibiting significant change to its impedance properties after 4-5 temperature cycles, and underwent a total of 12 cycles. There was little variation in the impedance as a function of frequency for the entire run, indicating that the brine was well connected for temperatures of between -24.5°C to +15°C. On the 10th cycle, we allowed additional cooling time to allow the bath temperature to get to -25.0°C. When the bath temperature reached -24.7°C, the impedance begins to sharply increased (Figure 3). We suspected that there was still liquid brine in the hydrate system even at a bath temperature of -24.5°C. The tiny amount of remaining brine was well distributed enough to create a conductive pathway with impedance around 10^3 Ω. At temperatures cooler than -24.5°C, the remaining bit of brine finally freezes and forms hydrohalite which hinders the current flow, hence the impedance sharply rises to 10^6 Ω. When inferring electrical conductivity from the impedance spectra, we observed more than a 14-fold increase in the conductivity of the sample with 2.5 wt% NaCl (Run #16) over the sample with 1 wt% NaCl (Run #15) at 15°C, and a 4300-fold increase over the sample with 0 wt% NaCl (Run #11). This suggests even 1wt% of NaCl added to the hydrate system significantly influences the electrical characteristics. Currently, we have an ongoing experiment on a sample with 0.25 wt% NaCl (Run #17).

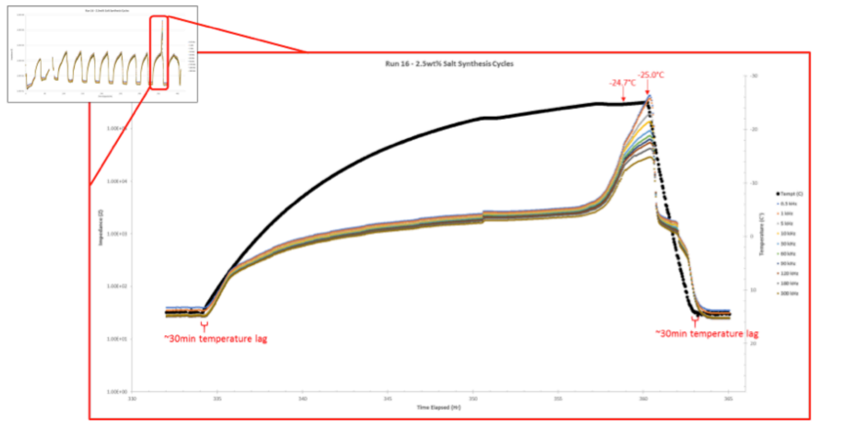

Figure 3. Run 16 (2.5wt% NaCl) magnified into the 10th synthesis cycle.

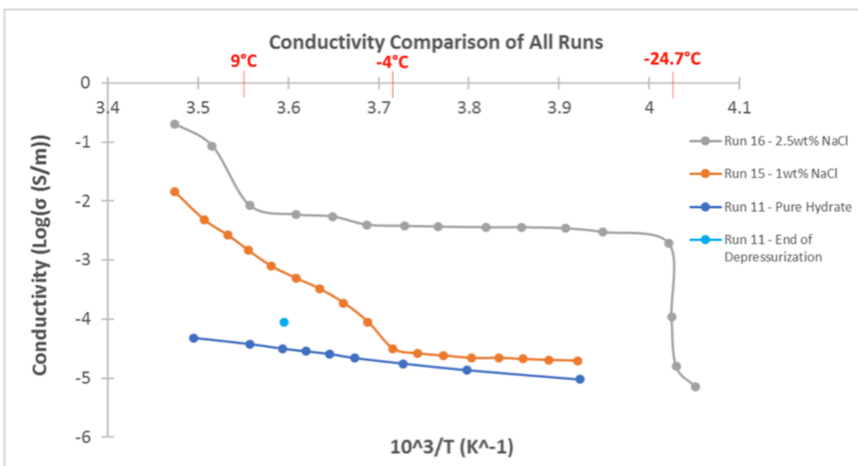

Figure 4. Log of conductivity versus temperature for different Runs.

The temperature required to freeze the brine such that it was no longer well connected was heavily influenced by the NaCl concentration. In the case of 1 wt% NaCl (Run #15) the brine became poorly connected at bath temperatures of -4°C, but for 2.5wt% NaCl (Run #16) bath temperature had to decrease to -25°C to cross this percolation threshold for the remnant brine. For Run #16 there was an apparent increase in conductivity at temperatures above +9°C and we are still investigating the cause for this.

Cryogenic Scanning Electron Microscopy of Methane Hydrate/Brine Samples

Samples with 1 and 2.5 wt% NaCl (Runs 15 and 16) were evaluated by cryogenic scanning electron microscopy (SEM). The SEM lab manager left the USGS, but a hiring search is currently underway. The NaCl-bearing samples exhibit some interesting phenomena. Examination along freshly fractured surfaces indicates that the brine developed during the synthesis and formed thin rims around many of the methane hydrate grains, and to further extent at grain junctions. This was apparent in both runs 15 and 16, although in both samples also contained regions with only

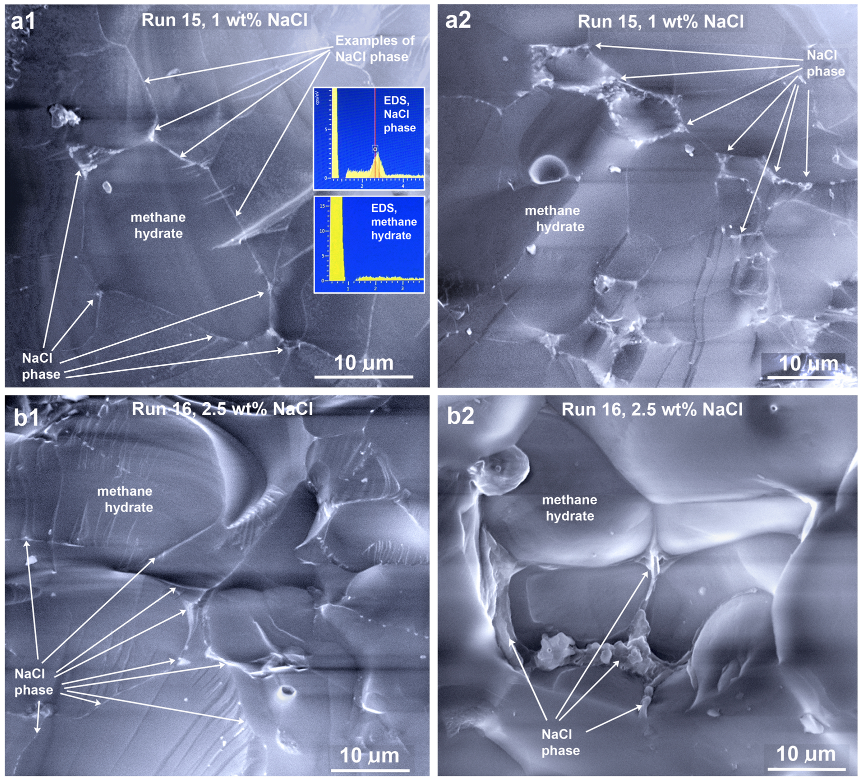

Figure 5. Cryogenic SEM and EDS analytical results on samples with 1 wt% NaCl (Run #15) and 2.5 wt% NaCl (Run #16).

hydrate-on-hydrate grain boundaries and no NaCl briny rims. Overall, the NaCl is reasonably well distributed through both samples without having segregation or accumulation at the base of the sample.

In most places frozen brine could be identified with energy dispersive x-ray spectroscopy (EDS) due to the detection of a small Cl peak and sometimes a Na peak (as shown in panel Figure 5 a1). Sometimes there was the appearance of small, thin, elongate crystals that are either a salt precipitate (either halite or hydrohalite) or part of the original salt in SEM images. It is highly likely this is a precipitate rather than leftover, undissolved salt based on distribution and morphology. In the case of Run 16 with 2.5 wt% NaCl, there appeared to be a little more salt precipitate in the cavities (as evident in Figure 5 b2). To be clear, these sample underwent no dissociation whatsoever and everything in these images is either methane hydrate or frozen NaCl phase (either brine or precipitate). In exposed cavities, there were virtually no faceted crystal faces on methane hydrate grains typical to samples with no salt added (i.e. Run #11). The NaCl appears to inhibit growth of large and fully-formed methane hydrate crystals. These images demonstrate proof-of-concept as far as adding small amounts of sieved NaCl to the seed ice in advance of reacting to methane hydrate, and developing a reasonably well distributed brine coating along grains in most regions of samples.

CSEM data collection.

During the last quarter we finished data collection in the Gulf of Mexico, and carried out preliminary data processing in order to evaluate data quality. This quarter we embarked on the detailed data reduction needed to start inverting the data for conductivity structure. In particular, we processed up the data from the long base line (LBL) acoustic navigation system that we deployed during data collection.

Normally ultra-short base line (USBL) acoustics are the tool of choice for underwater navigation, but these systems are really only reliable if they are permanently installed on the vessel and well maintained and calibrated. Experience with bolt-on solutions for ships of opportunity have generally been disappointing. Importantly, USBL systems will

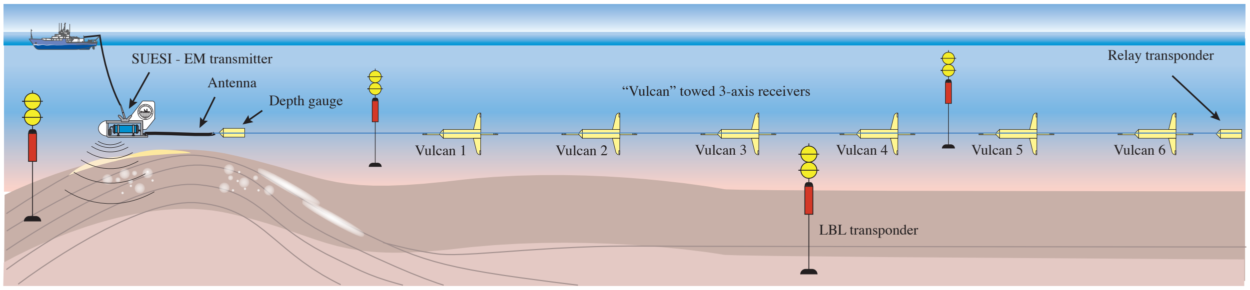

Figure 6. Long baseline (LBL) acoustic navigation system used for the navigation of the Vulcan CSEM system.

not work with the several kilometer layback that our 1,600 m EM array has. Our alternative was to deploy a LBL transponder net, moored 10 m above the seafloor and surveyed in by driving a pattern around the transponders with the vessel while collecting acoustic ranges. Figure 6 shows a picture of the scheme as deployed.

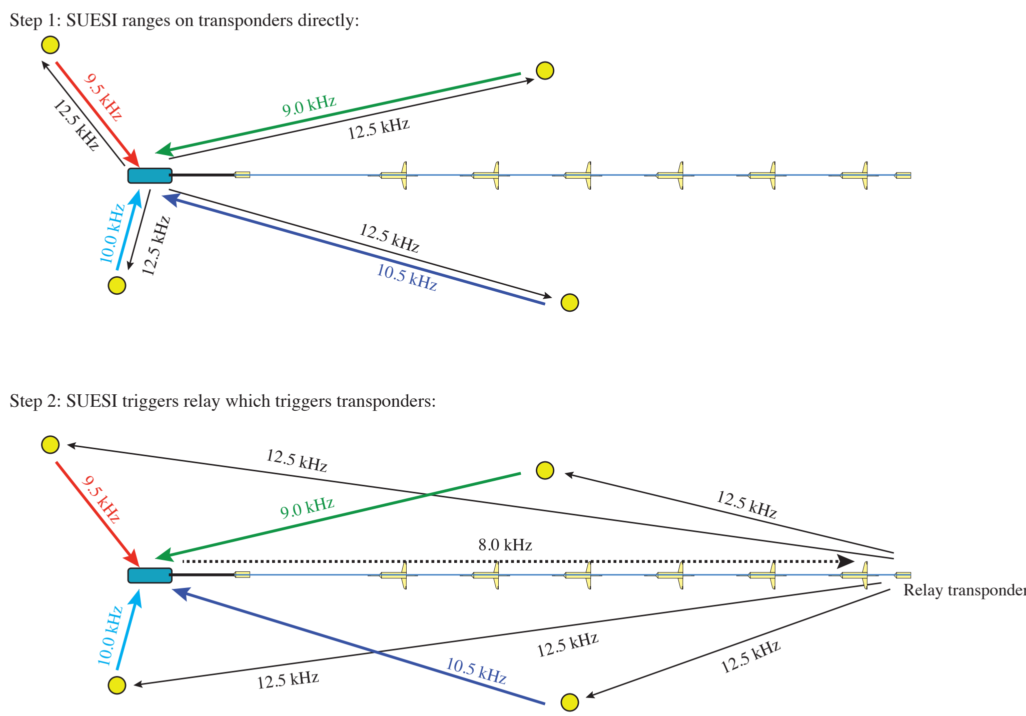

Figure 7. Every second ping ranges directly on the transponder net (Step 1), and every other ping triggers the relay transponder which in turn triggers the transponder net (Step 2).

Figure 7 shows how the method works. The navigation transponders all listen at 12.5 kHz and reply on four different frequencies between 9.0 and 10.5 kHz. Our deep-towed EM transmitter (SUESI) is equipped with a 4-channel Benthos ranging system, which first sends out a 12.5 kHz ping to trigger all the transponders that are in range (up to about 8 km, depending on bathymetry etc.). The (up to 4) replies are all timed, and the information is telemetered to the ship via the tow cable. The times are converted to ranges using water velocity (also measured by SUESI), and, along with depth recorded by a pressure sensor on SUESI, allows SUESI's location to be triangulated.

A relay transponder at the end of the 1650 m array of EM receivers listens at 8.0 kHz and replies at 12.5 kHz. SUESI triggers the relay transponder with a second, 8.0 kHz, ping, the relay transponder's reply triggers the navigation transponders. Since the length of the array is fixed (and known), and the distances between SUESI and the transponder net have just been measured, we can subtract both of these times/distances from the round-trip travel times to allow the relay transponder to be triangulated using the transponder net. The relay transponder also has a depth recorder.

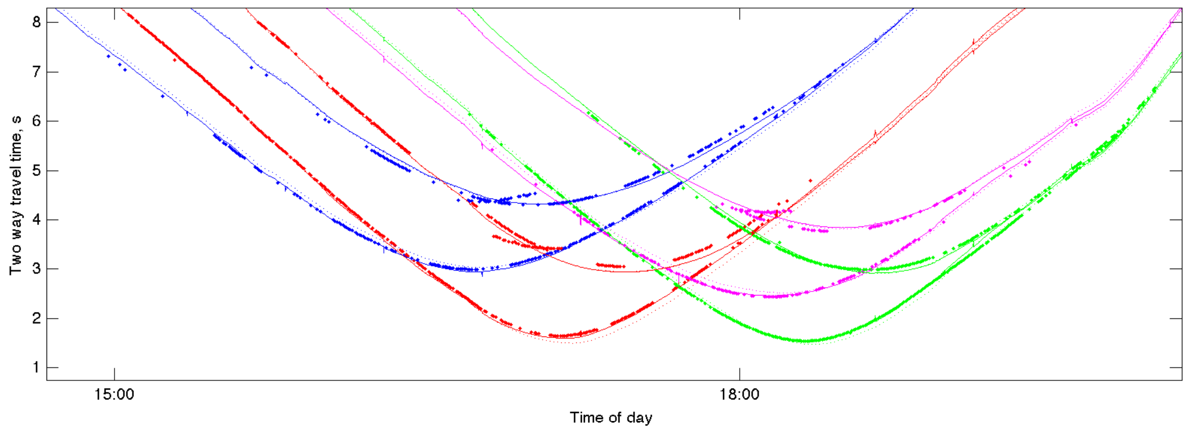

Figure 8. LBL data from the four transponders (coded by color) during one tow line of the Vulcan system. The first arrivals are the direct ranges on the transponder net, and the second arrivals are the relays. Dotted line is the starting model using layback from the vessel, and solid lines are the forward solutions using the acoustic positions.

Because acoustic ranges come and go, depending on multi-pathing, bathymetry, noise conditions, range, etc., rather than solve for positions during every ping cycle we compute a starting model based on ship positions and layback computed from SUESI depth and wire out records, and then used the acoustic records to correct for errors in layback and crossline set. Figure 8 shows an example of data and forward computations for one tow line (out of 30). Corrections to the layback estimate are generally less than 100 m, except for Green Canyon 955, which appears to be subjected to strong bottom currents.

Other activities

We presented a poster at the 2017 Fall AGU Meeting, and Peter Kannberg has applied to, and been accepted by, the next Gordon Research Conference in Galveston, February 25–March 2, 2018.

Training and professional development.

Peter Kannberg, PhD student at SIO, acted as co-chief scientist on the data collection cruise. He plans to submit his thesis by the end of summer and will continue work on this project as a postdoc.

Ryan Lu, a postdoc 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 the 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.

Plans for next project period.

During the next project period we will continue to collect laboratory data at Menlo Park, and continue with the data processing and inversion of the CSEM field 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		Internal review	completed
Final set of conductivity runs	9/1/2018		Internal review	
Field data inverted	12/1/2018		2D inversions done	
Publications(s) submitted	9/1/2019		At least 1 pub. submitted	
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

The following papers acknowledge this or past DoE funded research:

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.

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

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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:	Planning field program. Experimental design.
Funding support:	This project
Foreign collaboration:	Yes
Country:	Canada
Travelled:	No

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

Name:	Ryan Lu
Project Role:	Posdoc/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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