Oil & Natural Gas Technology

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Quarterly Research Performance

(Period Ending 6/31/2018)

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

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EXECUTIVE SUMMARY

We continue to collect electrical conductivity measurements and cryogenic electron microscopy on samples of gas hydrate. During this project period we compared the results of synthesizing hydrate + brine from a mix of pure ice and NaCl, with flash-frozen seawater. The conductivity as a function of temperature for the seawater sample is consistent with the earlier ice plus salt results, giving us confidence that these results are applicable to the real world (in some sense). However, cryogenic scanning electron microscopy shows that the hydrate crystal structure and brine distribution is somewhat different in the sea-water samples than the H2O+NaCl samples.

We also refined our modeling of complex impedance versus frequency for the laboratory samples. Previously, we have been choosing data at minimum phase angle as a proxy for grain interior conduction (as apposed to electrode conduction or grain surface conduction). Using impedance modeling software, we fit equivalent circuit models to all the hydrate+NaCl data. Results suggest that as temperature and salt content increase, brine becomes a conductivity pathway in addition to current flow through the hydrate.

We started to look at the process of converting resistivity images derived from marine CSEM data to estimates of total hydrate volumes, using a previously acquired data set from the Santa Cruz Basin as a test bed. This methodology will be applied to the Gulf of Mexico results as we continue to invert the GoM data sets.

We have submitted a *Fire in the Ice* article, two AGU abstracts, and are in the process of writing up a paper for *JGR*.

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.

Since last quarter, we have conducted a methane hydrate synthesis experiment from frozen seawater instead of pure ice while performing in-situ impedance measurements. The seawater was a certified reference standard from High Purity Standards. The seawater was quenched with liquid nitrogen, blended into a powder, and sieved to less than 250 μm. Our goal with this experiment was to simulate the environment of which methane hydrate forms in nature (seawater, methane gas, high pressures, and low temperatures). The seawater-hydrate undergoes >7 synthesis cycles similar to our previous runs for NaCl-bearing hydrate samples (Figure 1). The last synthesis cycle involved a step-dwell segment which was used to calculate Arrhenius conductivity.

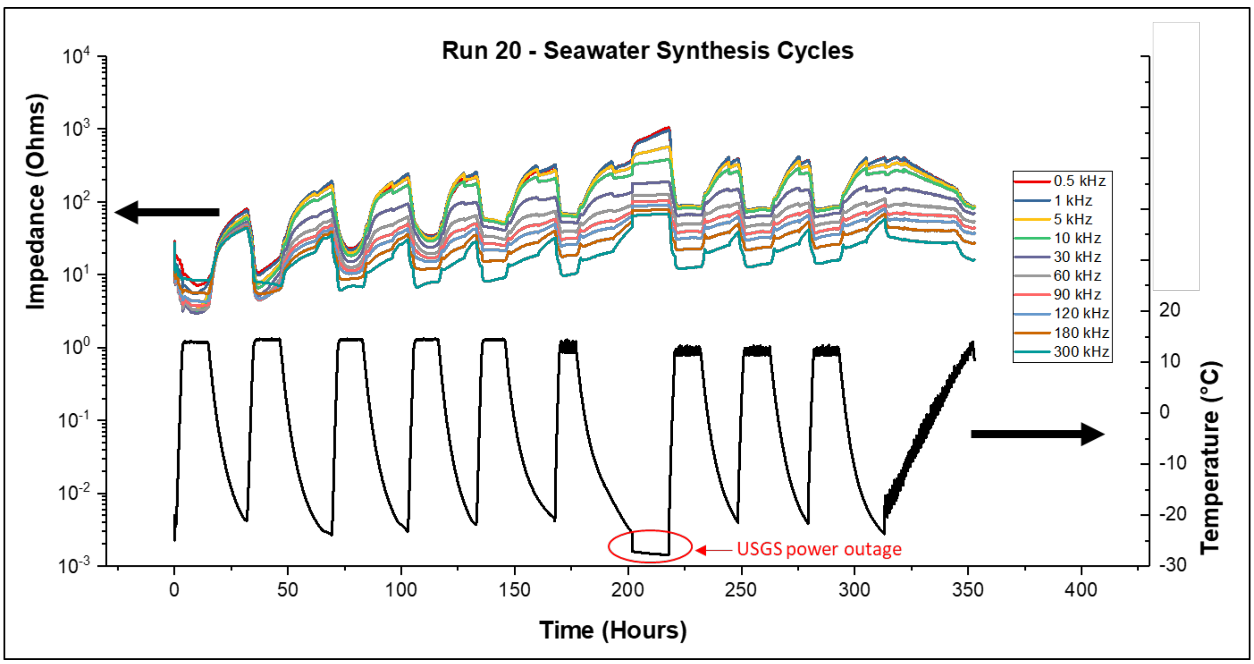

Figure 1. Seawater + hydrate synthesis cycles with in-situ impedance measurements

From the Nyquist (cole-cole) plot, the impedance at the minimum phase angle was selected and converted to conductivity values for a range of temperatures (+14 to -18 °C). When the Arrhenius conductivity is plotted alongside the NaCl-bearing hydrate samples, the seawater-hydrate sample behaved like a normal resistor-capacitor circuit with typical semi-circular arcs (Figure 2). In the Arrhenius conductivity log-scale plot, the seawater-hydrate sample was observed to have the highest conductivity when the sample temperature is less than 10 °C and this is expected since this sample had the highest salt content (Figure 2b).

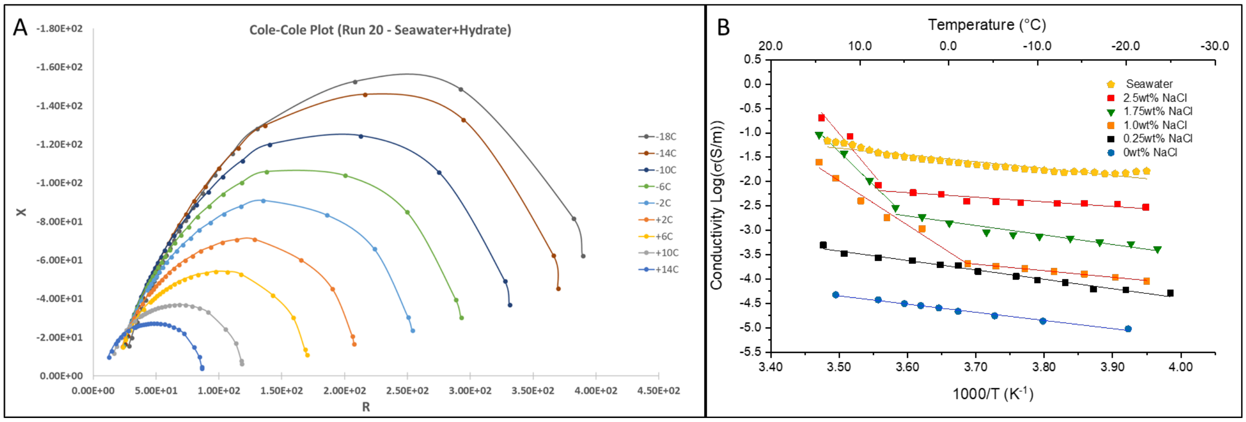

Figure 2. (a) Nyquist (cole-cole) plot of Run 20 – methane hydrate synthesized from seawater. (b) Arrhenius conductivity plot comparing all experimental runs including the seawater + hydrate sample.

Because the brine in the hydrate can change in morphology as a function of NaCl content and temperature, our group attempted to model the conduction mechanisms of these highly complicated hydrate systems. Using impedance modeling software, four different equivalent circuit models were determined for our selected sample conditions (Figure 3).

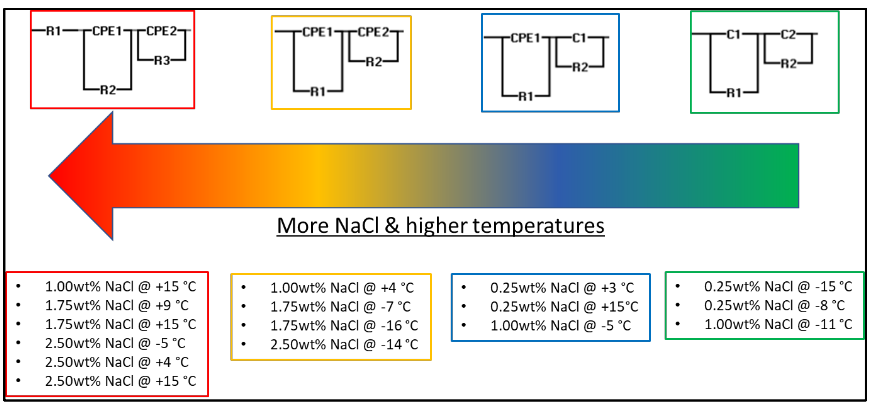

Figure 3. Equivalent circuit models for methane hydrates at different NaCl content and temperatures. "R" represents a resistor element. "C" represents a capacitor element. "CPE" represents a constant phase element.

We learned that at higher NaCl contents and higher temperatures, the capacitor element in the typical methane hydrate circuit model (green box) gradually gets converted into a constant phase element. This finding suggests the brine networks in the hydrate are morphing inhomogenously which caused a non-uniform current distribution throughout the sample. Eventually both capacitor elements become constant phase elements and gains a new resistor element in series (red box). This suggests brine becomes an additional pathway for current flow instead of through pure hydrate, which is not surprising, but these methods will help us quantify these effects.

Microscopy characterization

Cryogenic SEM imaging of final, quenched samples continues to provide us with important insights into their evolution during synthesis and the final distribution of components within them (Figure 4). In this quarter we imaged our two most recent runs, one being methane hydrate with 1.0 wt% NaCl (a re-run of a previous 1.0% sample to corroborate previous results), and the second being the methane hydrate sample formed from flash-frozen synthetic seawater described above. Consistent with previous results, fresh fracture surfaces through sample material reveal open cavities where methane hydrate crystals grow freely into original pore space, as well as clean fractures through dense hydrate material that expose the distribution and connectivity of the frozen brine phase. In the 1.0 wt% NaCl sample, the methane hydrate crystals growing into open pores show a two-or-more stage growth process with a secondary fine-grain layering of methane hydrate formed along the surface of larger grains beneath (Figure 4a). This is consistent with impedance measurements during synthesis that indicate the hydrate-forming reaction progresses over several thermal cycles for NaCl-bearing samples, unlike pure methane hydrate that can often reach full reaction during 1 cycle and that do not exhibit crystals with secondary growth textures. A clean fracture through the 1.0% NaCl sample (Figure 4b) then reveals some of the thin borders of frozen brine, sometimes interconnected, and again fully consistent with other NaCl-bearing samples.

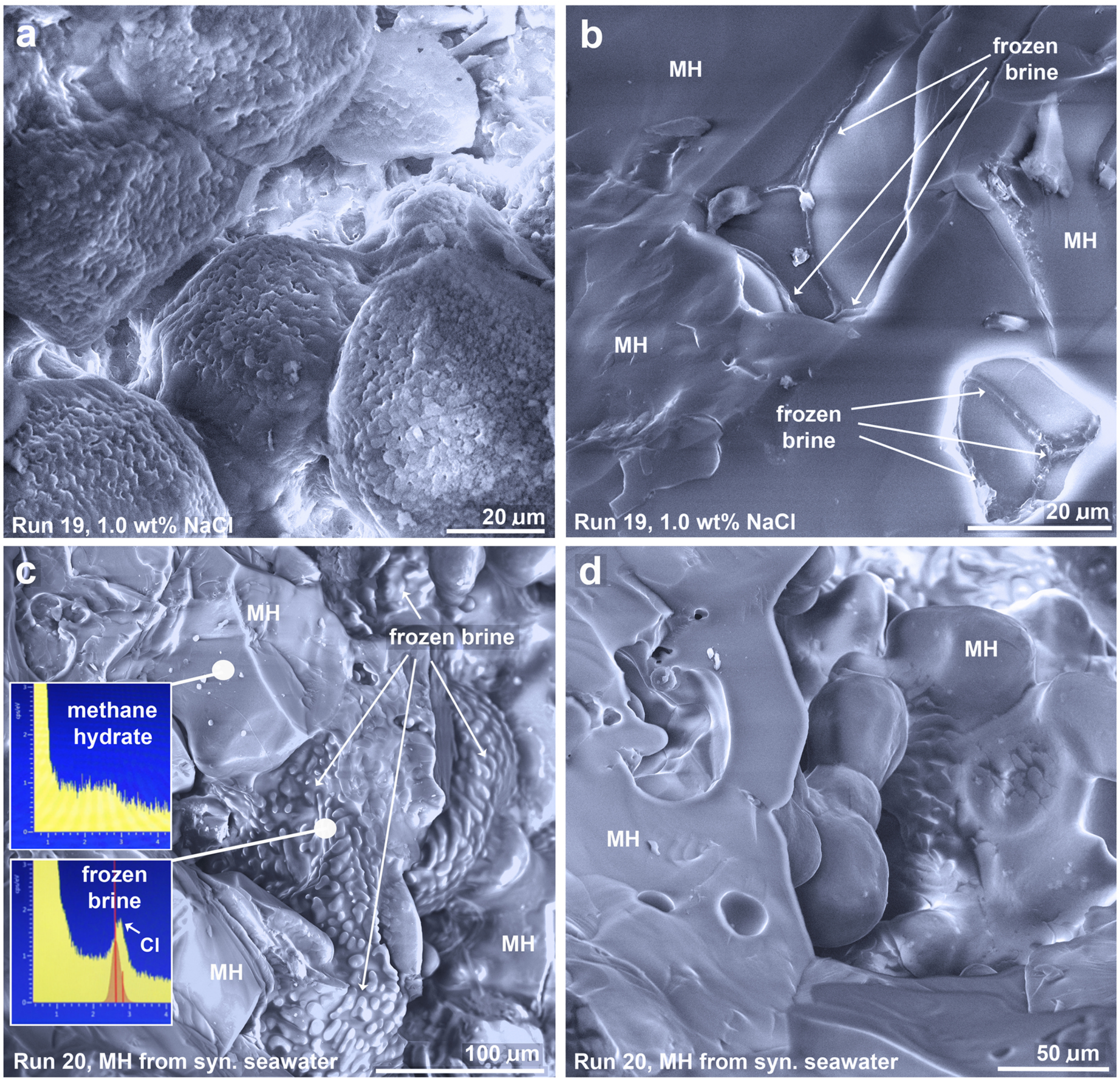

Figure 4. Cryo-SEM images of Run 19, methane hydrate + 1.0 wt% NaCl (panels a and b), and Run 20, methane hydrate formed from flash-frozen seawater (panels c and d). Labels within panels point out examples of each component, methane hydrate (MH) or frozen brine. EDS spectroscopy was used to verify phase identification, with 2 spectra shown in panel c as examples.

Imaging of Run 20 (Figure 4c,d), methane hydrate formed from frozen seawater, reveals sample textures different from the previous NaCl-bearing samples. This sample exhibits considerably more frozen brine than previous runs that appears here as small pods that line the interiors of pores or channels within the surrounding methane hydrate. These pods are most likely the final brine in the sample to freeze, and show a distinct Cl peak in their EDS spectra that helps us differentiate brine from methane hydrate (Figure 4c). Another difference between this sample, made from seed ice comprised of frozen seawater rather than pure, triple-distilled water, is the extremely rounded or blunt development of crystal faces (Figure 4d) that show none of the distinct faceting or isometric habit development that is commonly exhibited in pure methane hydrate samples grown by the seed ice method. We have not yet isolated what is causing this difference in crystal habit development (i.e. is it driven by the impurities or by the associated brine, or both?) but note that we have observed this trend in all salt-bearing runs to date.

CSEM data interpretion.

Last quarter we made very good progress in starting to invert the marine CSEM data collected in July 2017. We use the adaptive finite element 2D code, MARE2DEM, developed by Kerry Key, to invert individual lines of data.

This quarter we started to look at the process of converting such resistivity inversions into maps of hydrate saturation, using a study of the Santa Cruz Basin which is closer to completion. The data collection for this work was funded by the BOEM in 2014. This change of emphasis was convenient for us, as this work is part of Peter Kannberg's PhD thesis, which he is defending on the 3rd of August. Peter needed to submit his thesis at the end of the quarter.

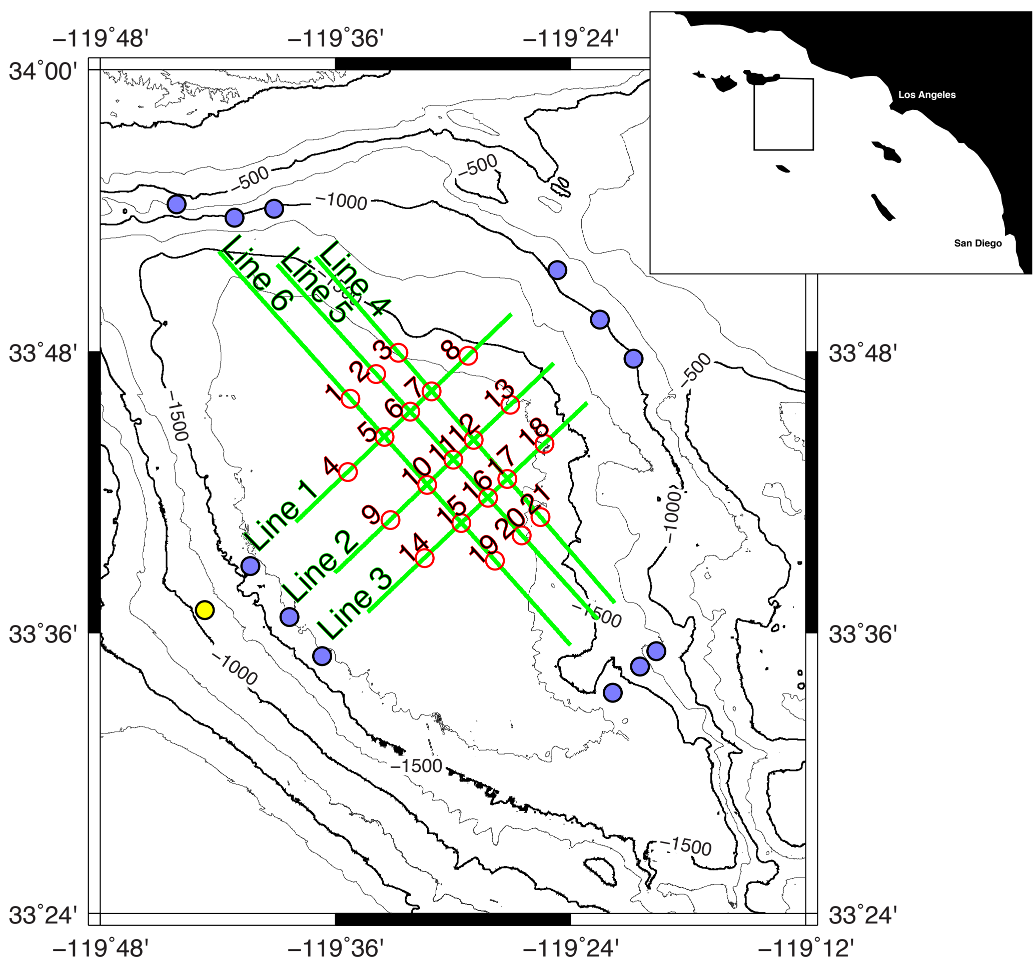

Figure 5. Location of the Santa Cruz Basin, offshore southern California, showing the Vulcan tow lines (green), locations of seafloor receivers (red circles), and the run-in and run-out points for the tow lines (blue disks).

Figure 5 shows the location map of the area and the layout of the data collection. Six crossing lines covered most of the basin and some of the flanks.

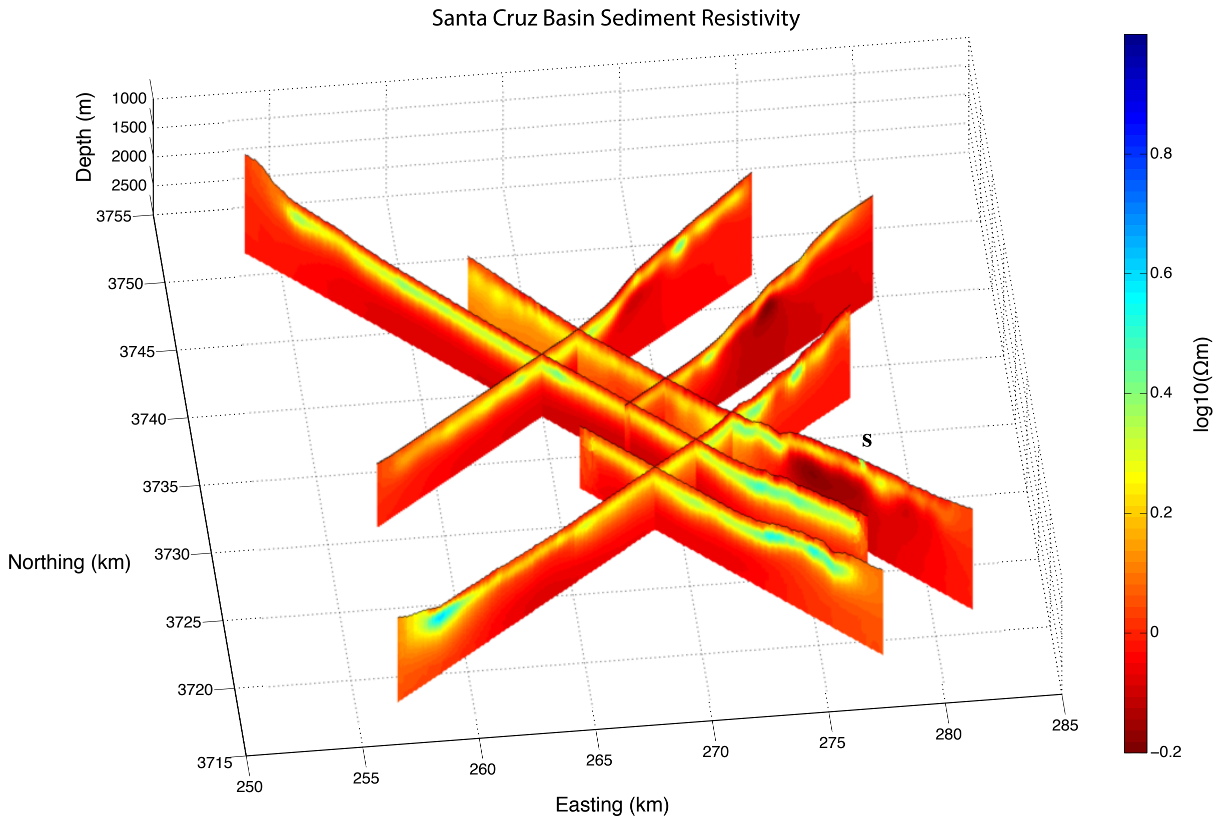

Figure 6. Fence plot of 2D inversions of individual lines. Blue/green is resistive relative to conductive (red) sediments. **s** marks the position of a seep-like feature on line 4.

Figure 6 shows the resistivity inversions displayed as a fence plot, which shows that the line-crossing ties are good and that most of the more resistive features sit on the flanks of the basin, even though a BSR can be traced across most of the basin sediments. Near the SE end of line 4, the northeastern most NW–SE line, we see a narrow resistor extending to the surface with a very similar morphology to a resistor imaged under the Del Mar Seep by Constable *et al.* (2016), and so we think this feature represents a previously undiscovered seep structure.

Figure 7 shows a similar fence plot of hydrate saturation, computed from the resistivity data shown in Figure 6. We assumed a sediment porosity of 50% and used Archie's law with parameters calibrated by well logs. Again, it can be seen that the most significant hydrate concentrations are on the flanks of the basin, where we suspect that faulting can assist the migration of gas into the shallow section. Total gas in place estimated using this method is ≈15 trillion cubic feet (or 424 billion cubic meters), about one third of estimates using conventional methods based on seismic and other data.

Marine sediments are expected to compact with depth, which will decrease porosity and thus increase resistivity, and so it is an interesting to consider what impact this might have on our interpretations. The California Borderlands have a relatively high heat flow; we measured 90°/km in the San Nicolas Basin just south of the study area. Thus there will be an increase in pore water conductivity with temperature and depth that tends to oppose the increase in resistivity due to loss of pore space. We modeled these competing effects for the Santa Cruz Basin, and the results are shown in

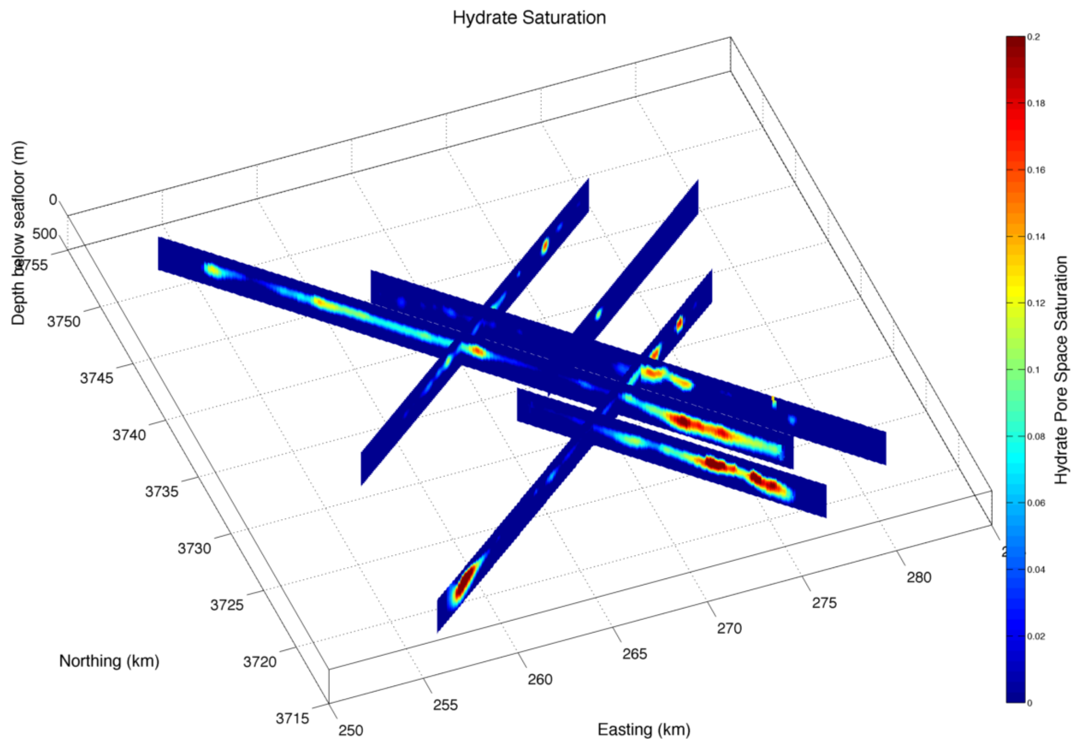

Figure 8. Fence plot of hydrate saturation, computed from resistivity shown in Figure 6.

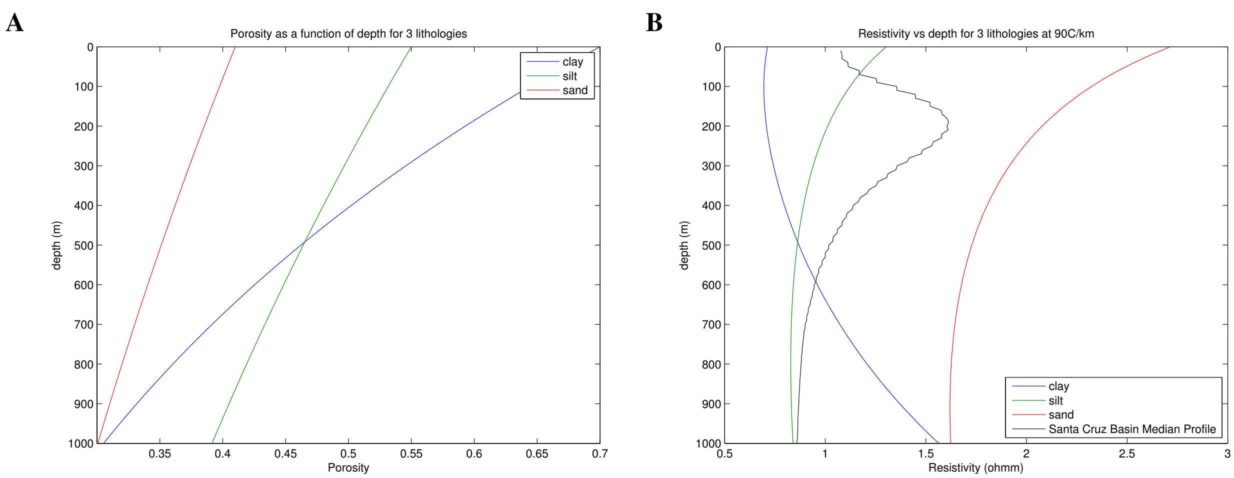

Figure 7. **A**. Porosity predicted as a function of depth and compaction for three different lithologies. **A**. Resistivity as a function of depth computed from predicted porosity and water temperature predicted by a 90°C/km geothermal gradient. The median resistivity profile from the center of the Santa Cruz basin follows the silt model, except for slightly higher resistivities in the gas hydrate stability zone.

Figure 8. The inverted median resistivity profile from the center of the Santa Cruz basin follows a porosity model for silt, except for slightly higher resistivities in the gas hydrate stability zone.

Other activities

We have submitted an article to *Fire in the Ice* describing some of the laboratory conductivity studies, and have submitted two AGU abstracts to the Fall Meeting, one on the laboratory work and one on the CSEM data collection.

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 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 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 return to inverting the GoM CSEM data, and submit a *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	
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

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

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.

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

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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:	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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