Oil & Natural Gas Technology

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Quarterly Report

July 2010 to September 2010

Gas Hydrate Characterization in the GoM using Marine EM Methods

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EXECUTIVE SUMMARY

Methane hydrate was successfully produced twice in the conductivity cell at Menlo Park by Laura Stern and Robert Pinkerton. Scanning electron microscopy images were generated following run 1 and are presented in this report. During the second hydrate synthesis electrical conductivity measurements were made by Wyatt DuFrane (Jef Roberts' new postdoctoral scholar) during and after hydrate formation. Two abstracts were submitted to the 7th international conference on gas hydrates (ICGH 2011), one pertaining to the laboratory studies and another to the controlled source electromagnetic field data. The OCCAM total field navigation appears to be working, but finer tuning is required before the entire data sets can be reprocessed with this new code. Preliminary results of the CSEM field data were presented at the 20th Electromagnetic Induction Workshop in Giza, Egypt (September 18-25, 2010) and were well received, so much so that OpenEM requested a copy of the poster to be presented at their booth during the SEG meeting in Denver. We were called upon to comment on a JIP project to collect OBS/high-resolution seismic data at one of two sites, GC 955 or WR 313. We also had a meeting at SIO with Kelly Rose and Mariam Kastner to discuss the EM data and future JIP coring efforts at WR 313 and GC 955. The Vulcan results from MC 118 have led to a couple of collaborations both in the private and public sector. The first collaboration with industry has been to further develop the Vulcan technology, representing a form of technology transfer generated from this DOE project. The second collaboration is with Carolyn Ruppel of the USGS to take another modified vulcan system and deploy it in the arctic Beaufort sea to map permafrost. We had the opportunity to work with Peter Kannberg, a masters student of Anne Tréhu at Oregon State University, to work up an EM data set we collected at the pinnacle of Hydrate Ridge in 2009; he has submitted an abstract to AGU about this work. Proofs have been returned for a *Geophysics* submission on inversion of the Hydrate Ridge data, and revisions are in progress for a *Geophysical Journal International* submission on the geological interpretation of the Hydrate Ridge data.

PROGRESS, RESULTS, AND DISCUSSION

Phase 1.

Task 1.0: Project Management Plan. Completed November 5, 2008.

Task 2.0: Technology Status Assessment. This is embodied in the original proposal.

Task 3.0: Collect Marine CSEM Field Data. Completed October 26, 2008.

Task 4.0: Preliminary Field Data Interpretation. Completed October 2009.

Task 5.0: Design and Build Conductivity Cell. Completed July 2010, results presented in Year 2, Quarterly Report 3.

Task 6.0: Make Hydrate and Hydrate/Sediment Conductivity Measurement.

Hydrate was formed in situ in the cell two times during this quarter. The cell is a stainless steel HIPTM pressure vessel which provides access for gas plumbing and internally-positioned Ag-foil electrodes or thermocouples. The cell forms (or accepts) a 5 cm diameter, 1.25 cm thick sample that is electrically insulated by a Teflon sleeve. Samples of gas hydrate and/or hydrate-sediment aggregates are synthesized from granular ice and gas mixtures by methods described previously in Stern et al. (1996, 2000). For the first hydrate synthesis the starting ice grains were packed tighter than normal to reduce porosity, and the sample ended up taking longer to fully synthesize than normal, a couple of weeks. A thermocouple was in the sample so we could gauge when hydrate formed.

The first sample of pure methane hydrate was created without electrodes so that a thermocouple could be

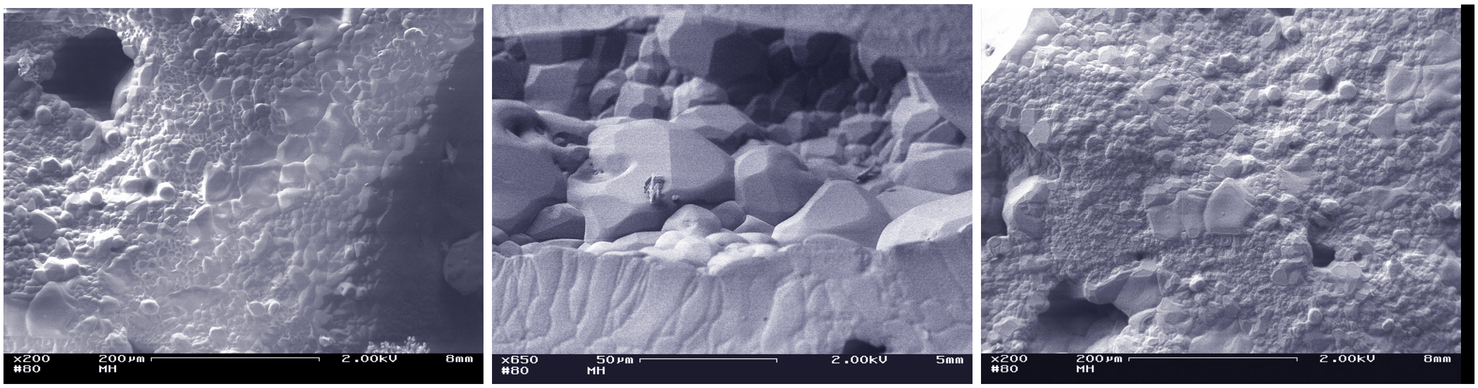

Figure 1: Cryogenic scanning electron microscopy images of pure methane hydrate formed in the electrical resistivity cell. The resulting polycrystalline material has 20-70 μm average grain size and 20% intergranular porosity (middle).

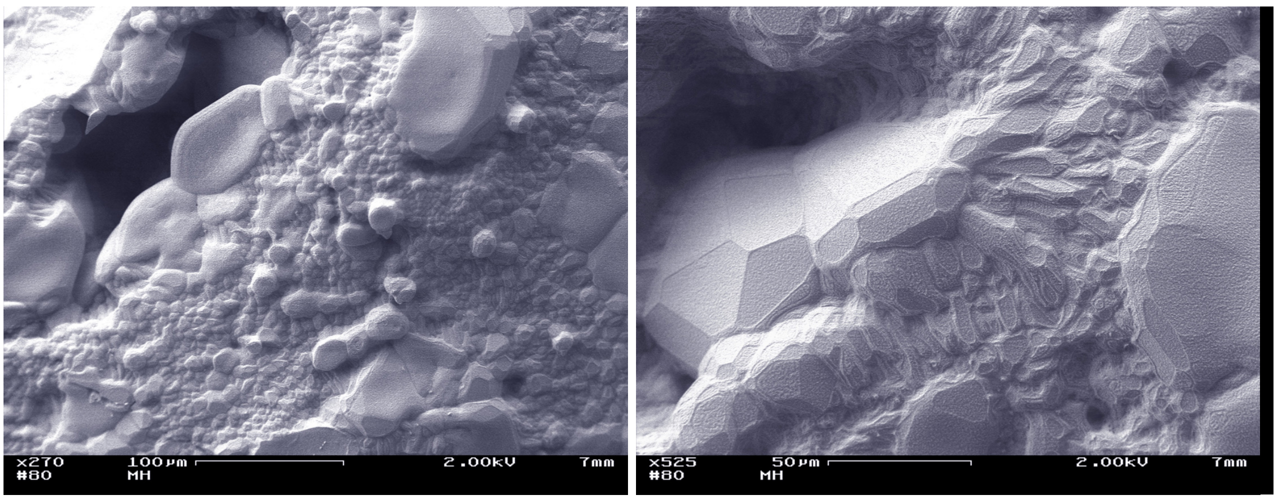

Figure 2: Higher magnification of Figure 1. Grains are still very easy to distinguish.

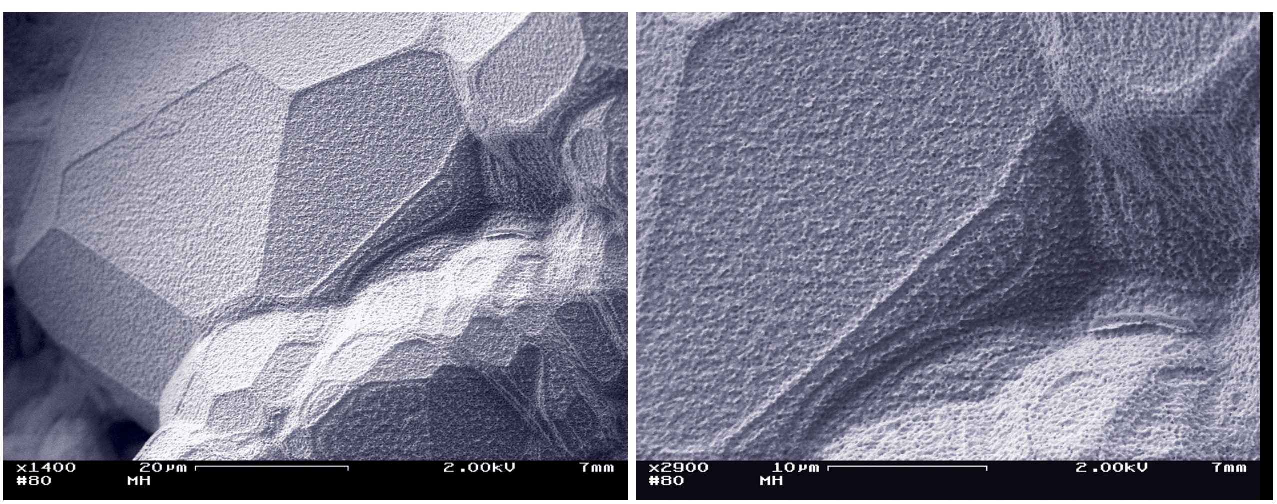

Figure 3: Two close-ups that show a nano-porous appearance.

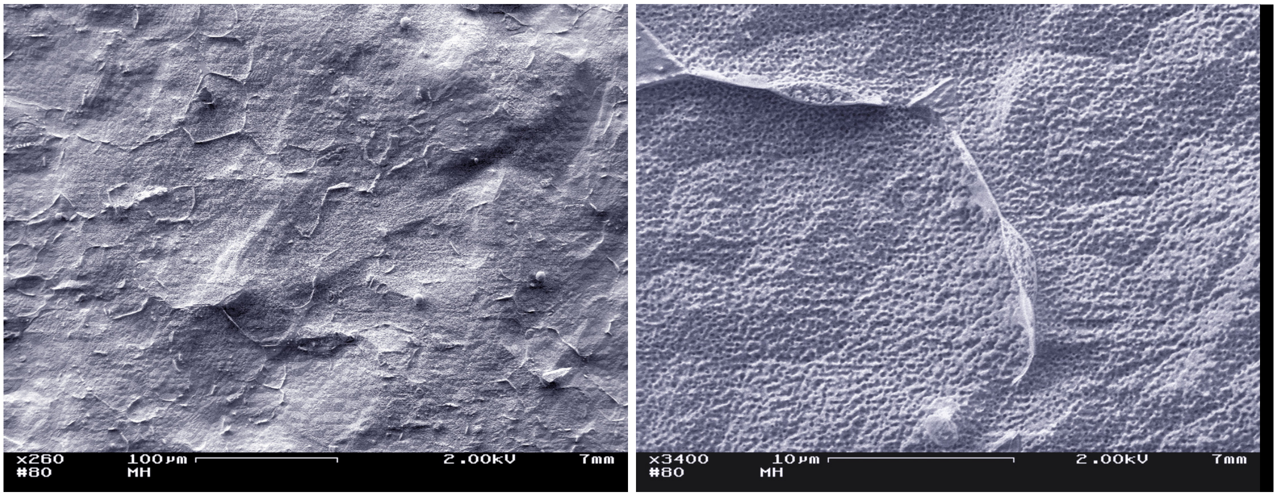

Figure 4: Grain boundaries in a dense section of hydrate. Original and smaller sub-grains are developing into coarser grains (left). A close up is shown on the right.

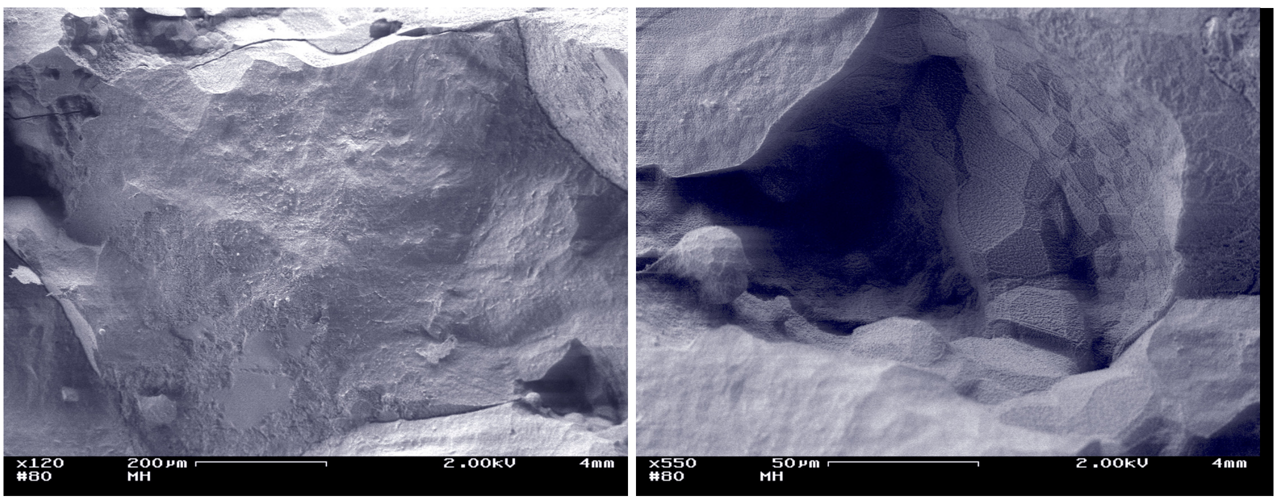

Figure 5: Low-magnification overview showing overall density of the sample (left). Detail of lower right cavity (right).

installed to calibrate the growth of hydrate in the new cell. The results appear excellent (Figures 1-5). Grains are coarser than usually produced, probably because the sample cycled to high temperature so many times. It is also less porous than usual (i.e. there is less pore space between the grains.) The overall sample porosity is about 20%, instead of the usual 30%.

Figures 1 to 7 are cryogenic scanning electron microscopy (SEM) images for this first sample of hydrate in the new cell. The grains typically range from 15 to 60 microns, which is similar to what Laura Stern has seen in gas hydrate from nature. Many grains here look smaller due to the small portion of the grain that is exposed. Some of the photos in Figures 1 to 7 show fresh fracture surfaces through grains, while others expose cavities where you can see well formed crystals. The grain size is consistent throughout.

Individual grains are fully dense as can be seen in the first several photos. Sublimation and surface deterioration gives the hydrate a nano-or meso- porous appearance. Numerous photos are shown here that help illustrate that process. The spongy appearance is merely an artifact of the high-vacuum conditions in the SEM chamber, and is not a property of the original material.

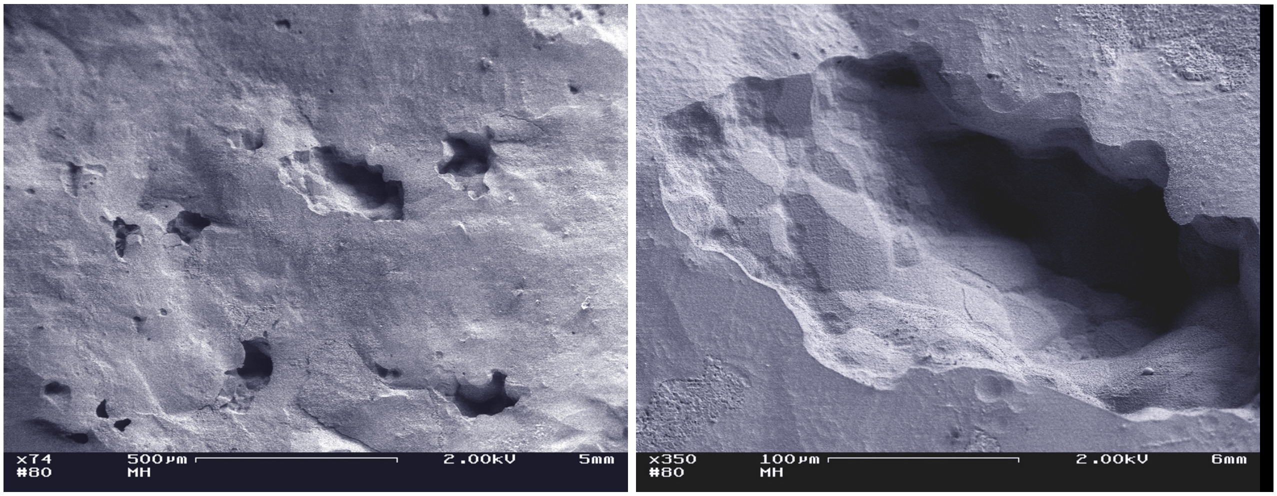

Figure 6: Another low-magnification overview showing overall sample texture (left). Detail of cavity in mid-portion of previous photo (right)

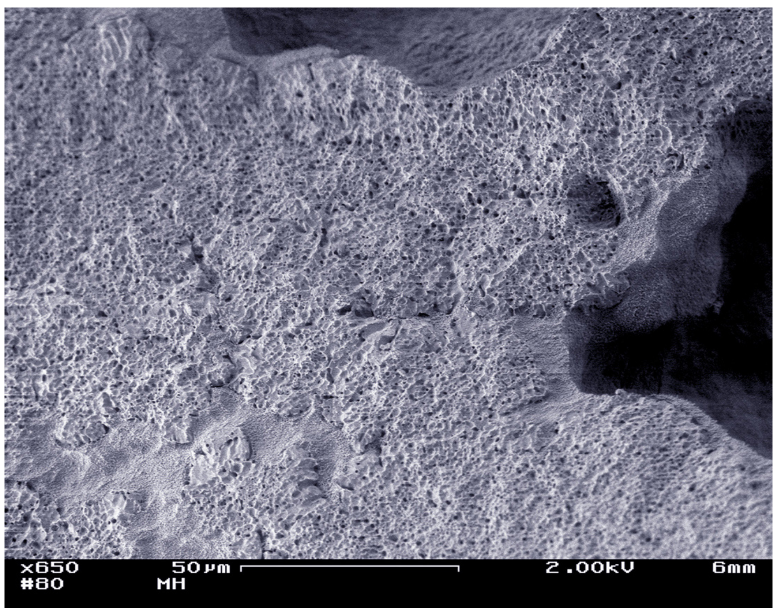

Figure 7: Very late stage surface deterioration.

For run 2 of hydrate synthesis the thermocouples were replaced by Ag-foil electrodes, so that impedence spectra can be generated for this second hydrate sample. The first run took several weeks to achieve 100% reaction of ice to methane hydrate, which may be because the ice was packed tighter then usual and the cell configuration is different from previous hydrate synthesis experiments. To speed up the hydrate synthesis process for run 2 slightly less ice was packed into the cell, but still more than usual because we want a low porosity hydrate sample.

During hydrate formation in run 2 an LCR meter was used to make electrical conductivity measurements on the sample replacing the thermocouple to monitor hydrate formation. Figure 8 shows a cole-cole plot during heating cycle 1 of hydrate synthesis, whereby crushed ice and methane in the pore space is undergoing a change to hydrate, ice, methane and water in the pore space. This impedance spectrum is in good agreement with the confined water and ice samples that were measured in July. There is a temperature dependence in which the colder the sample the larger the real resistance.

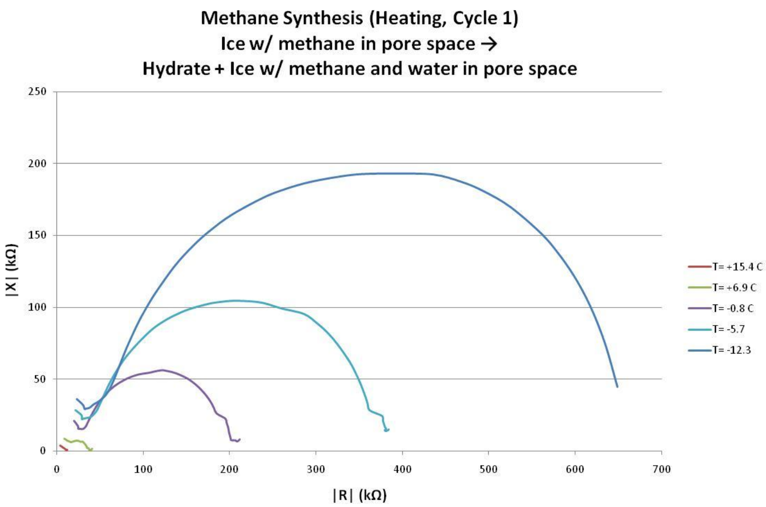

Figure 8: Cole-cole plots during heating cycle 1 where crushed ice and methane in the pore space are undergoing the change to hydrate, ice, methane and water in the pore space for different temperatures.

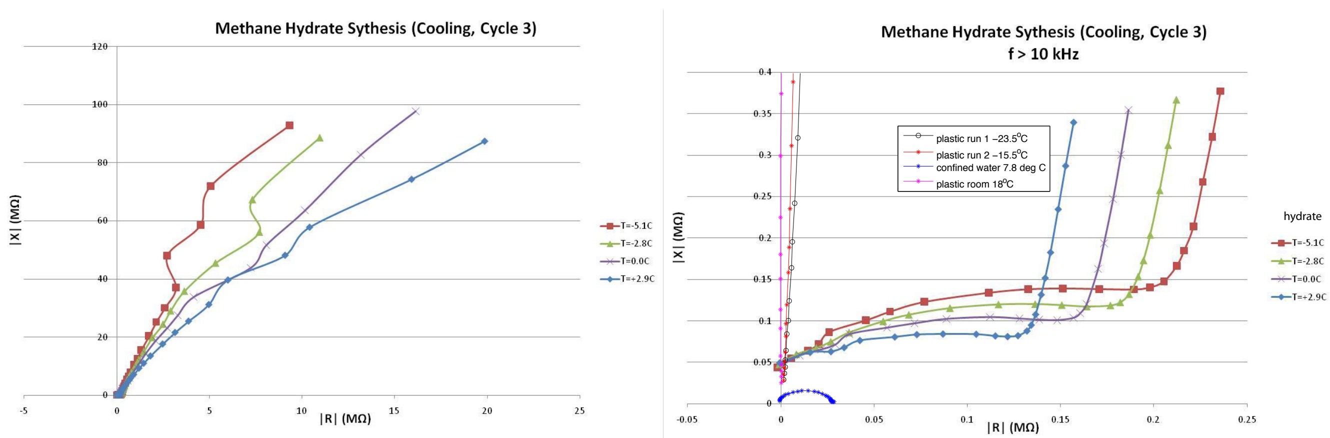

Figure 9: Cole-cole plots during cooling cycle 3 (left) and a close up for frequencies above 10 kHz (right)with overlay of the teflon plug runs and confined water for different temperatures.

Cole-cole plots are shown for the cooling cycle 3 in Figure 9 and the heating cycle 4 in Figure 10. In both figures there is a close up at frequencies above 10 kHz. There appears to be a switch in the temperature dependence and resistance value in low and high frequencies. Low frequency data show higher temperatures generate a larger real resistance, while at high frequencies lower temperatures have a larger real resistance. There is a distinct kink in the cole-cole plots between 0.1 and 0.25 mega-ohms on the real axis for frequency >10 kHz. We think this is a small contribution from some combination of ice/water/methane at grain boundaries.

In Figure 11 a cole-cole plot of impedances is shown during the 4th heating cycle when we were confident that the sample was primarily hydrate. The teflon plug impedances have been plotted on this figure showing that it is more resistive than the sample.

To date, this cell has been successfully used to (1) measure resistivity of ice and other calibration materials, (2) form pure methane hydrate in situ and determine final sample texture (Fig. 1), and (3) measure resistivity of pure methane hydrate for 20 Hz to 2 MHz. Initial results suggest that impedance spectra > 50 kHz is attributed to methane hydrate, indicating resistivity that is similar in magnitude to that of ice ($\approx 10^{-5}$ S/m at

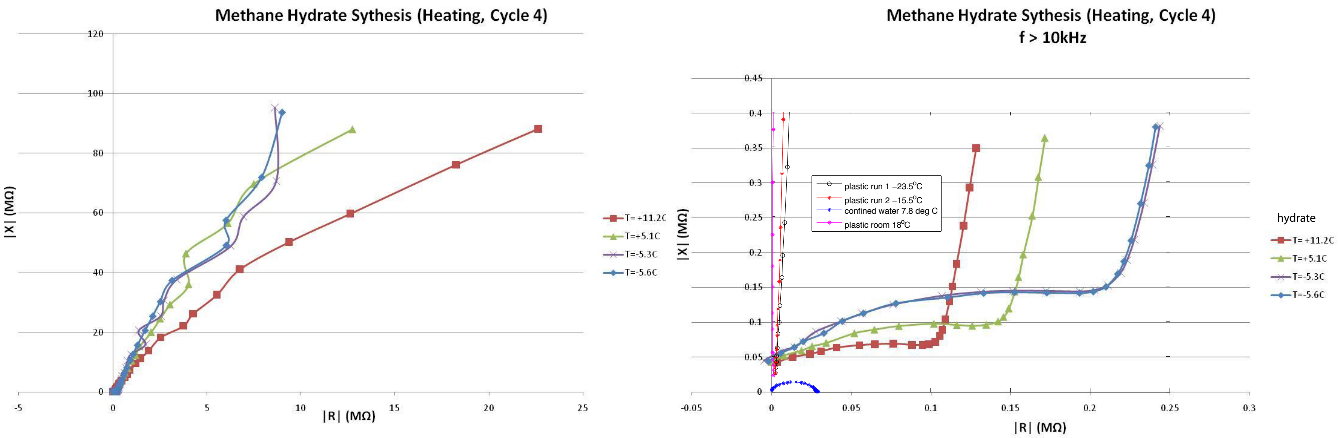

Figure 10: Cole-cole plots during heating cycle 4 (left) and a close up for frequencies above 10 kHz (right) with overlay of the teflon plug runs and confined water for different temperatures.

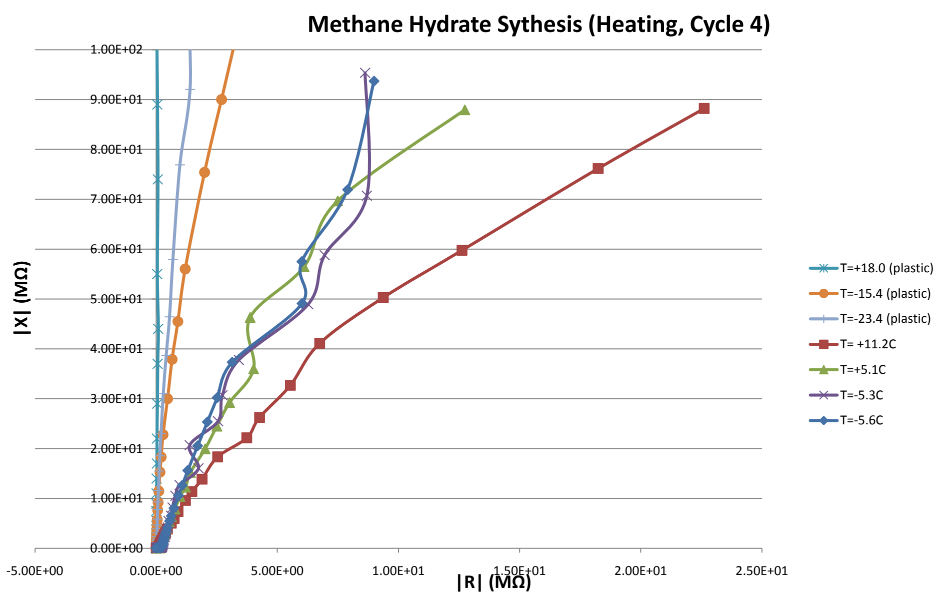

Figure 11: Cole-cole plots of the teflon plug and methane hydrate synthesis for different temperatures.

-8^{o}C). We plan additional measurements on pure gas hydrate as well as on mixtures of hydrate, seawater, and sediments. All current impedance measurements have been done manually and DuFrane is researching how the process can be automated.

Task 7.0: Modeling and Inversion of Field Data. 1D OCCAM inversions for the transmitter navigation are ongoing, with inversions for one survey line taking almost a week to complete. This task has proven to be more difficult then intended and some bugs are still being worked out. In the near future we may have our own in-house 2D inversion capabilities as Kerry Key has made significant progress in developing the inversion component of a 2.5D CSEM finite element forward code by Li and Key (2006). Using this code to invert data is the next logical step for WR 313, GC 955 data. The MC 118 can probably be handled well with 1D.

Task 8.0: Estimate Quantitative Hydrate Volumes from Field Models and Laboratory Studies. This task commences later this year.

Task 9.0: Technology Transfer. The data have been distributed to the sponsors (February, 2009) and preliminary results were presented at the Seafloor Electromagnetics Consortium annual meeting March 18 and 19, 2009. Version 1.0 of the transmitter navigation was distributed to sponsors in early December. At our annual Seafloor Electromagnetics Consortium meeting held March 17 and 18, 2010 Vulcan results at MC 118 were presented and well received. Processed data were distributed to sponsors at the end of March 2010. We have undertaken a project to further develop the Vulcan technique with an industry partner. We have also started a collaboration with Carolyn Ruppell to develop a similar system to be used to map permafrost in the Beaufort sea.

Task 10.0: Final Publication. This task is scheduled for Budget Period 3.

CONCLUSION.

The conductivity cell measurements are going well. We have synthesized hydrate two times in the cell, the first time with thermocouples in place and using the resulting sample to generate SEM photographs of hydrate produced in the cell, and a second time, with Ag-foil electrodes in place to make electrical conductivity measurements during hydrate synthesis. We have the benefit of a new post-doctoral scholar, Wyatt DuFrane, working with Jeff Roberts at LLNL, and who has and will be making the electrical conductivity measurements in Menlo Park. This is helping progress since the field data are proving more time consuming then anticipated. A number of publications and abstracts are in submission, revision, and in press. The Vulcan technology is undergoing further development due to interest from a third party and represents a technology transfer from this DoE project to industry. We have had the opportunity to work with Peter Kannberg, a masters student of Anne Tréhu at Oregon State University, twice during this quarter working up a data set collected at Hydrate Ridge in 2009. The preliminary results are to be presented at the fall AGU.

COST STATUS

Table 1: Project costing profile for Budget Period 2, Quarter 4

Time period	Cost share	DoE Plan	DoE Actual
July 2010	$0	$8000	$7684
August 2010	$0	$8000	$7684
September 2010	$0	$8000	$7684
Totals	$0	$24000	$23052

Salaries:

Karen Weitemeyer, a post-doctorate scholar during the budget review period, charged July, August and September salaries.

MILESTONE STATUS

Milestone log for Budget Period 2.

Milestone 1: Revised Project Management Plan. Task 1.0, completed 3 November, 2008.

Milestone 2: Submission of Technology Status Assessment. Task 2.0, embodied in the original proposal.

Milestone 3: Preparation of marine instrumentation for shipping. Task 3.0, completed 30 September, 2008. Equipment was tested in the laboratory and trucked to Fort Lauderdale. Critical milestone for tasks 5,7,8,9,10.

Milestone 4: Carry out field program in GoM. Task 3.0, completed 26 October, 2008. Field program was completed more than successfully, with one extra survey area covered and 15 more stations than proposed. Critical milestone for tasks 5,7,8,9,10.

Milestone 5: Produce initial cruise report Task 3.0, completed 30 January, 2009.

Milestone 6: Design conductivity and pressure cell. Task 5.0, work completed. Critical milestone for tasks 6, 8, 9, 10.

Milestone 7: Generate merged EM/navigated data set. Task 4.0, work completed. Critical milestone for tasks 7, 8, 9, 10.

Milestone 8: Construct conductivity/pressure cell Task 5.0, work completed. Critical milestone for tasks 6, 8, 9, 10.

Milestone 9: Make calibration tests of cell using water standard Task 5.0, work completed. Critical milestone for tasks 6, 8, 9, 10.

Milestone 10: Install cell in Menlo Park and make initial hydrate measurements Task 5.0, work completed. Critical milestone for tasks 6, 8, 9, 10.

Milestone 11: Preliminary interpretation of field data Task 4.0, work completed.

Milestone 12: Webpage updated Task 9.0, January 30 2009.

Milestone 13: Produce Phase 1 Report Tasks 1-5, completed 2 November 2009. Task 5 given a 6 month extension.

ACCOMPLISHMENTS

• Collection of the Marine CSEM Field Data

• Conductivity cell completed.

• Processing of the data is completed.

• Two Fire in the Ice article were published one in 2009 and the other in 2010.

• Participated in a "Spot Light on Research" article for Fire in the Ice in 2009.

• Raw data and processed data have been distributed to sponsors (2009, 2010).

• Generated merged transmitter navigation with the CSEM data using the Total field navigation program and distributed this version to the sponsors in early December 2009 and March 2010.

• Generated pseudosections for the 0.5 Hz and 6.5 Hz CSEM data transmissions for all 14 tows of the 4 surveyed areas in the Gulf of Mexico 2010.

• Generated pseudosections for Vulcan at MC 118, GC 955, AC 818, and WR 313 and preliminary interpretations of the data, 2010.

• First Break article published this June (2010).

• Completed calibration tests of cell using water standard.

• Installed the cell in Menlo Park, formed hydrate in the cell and produced SEM images of this sample.

• Made a second hydrate sample and have made some initial electrical conductivity measurements.

PROBLEMS OR DELAYS The design and construction of the conductivity was given a six month extension in 2009, and this past quarter we have installed the cell in Menlo Park, produced hydrate in the cell and made initial electrical conductivity measurements on hydrate. Improvements to the transmitter navigation are ongoing and any further 1D and 2D interpretations are stalled until we are satisfied with the transmitter navigation.

PRODUCTS

• Revised Project Management Plan.

• A project website was set up:

http://marineemlab.ucsd.edu/Projects/GoMHydrate/index.html

Cruise Report is available for download.

• Project Summary:

project summary outlining project goals and objectives on the NETL project Web site.

• Collection of Marine CSEM data in the Gulf of Mexico:

Data distributed to sponsors early February.

• Fire in the Ice article published Winter 2009.

• NETL kick off meeting, Morgantown, WV - January 6, 2009

The PI delivered a project overview presentation.

• Talk given at the 2009 MARELEC Meeting - Stockholm, Sweden - July 7-9 2009

Steve Constable presented *Applying marine EM methods to gas hydrate mapping*

• Submitted the first quarter report February 2 2009.

•Steve Constable gave an invited talk at LLNL mid march 2009 called:

Marine Electromagnetic Methods for Mapping Gas Hydrate

• SIO Seafloor Electromagnetics Consortium annual meeting, La Jolla, CA - March 18-19, 2009

Karen Weitemeyer delivered two presentations:

Marine EM for gas hydrate studies, with first results from the Gulf of Mexico

Using Near field data to navigate controlled source electromagnetic data

• Submitted the second quarter report April 2009.

• Karen Weitemeyer gave two invited talks in Australia

Marine EM for gas hydrate studies, with first results from the Gulf of Mexico

• Submitted the third quarter report July 2009.

Steven Constable delivered a presentation in Japan:

Marine Electromagnetic Methods for Mapping Gas Hydrate

• Submitted the Phase 1 report October 2009.

• AGU Poster presentation December 2009 by Karen Weitemeyer and Steven Constable

Marine EM for gas hydrate studies, with first results from the Gulf of Mexico

• DoE Atlanta Hydrate Meeting January 25-29, 2010. A talk and Poster presented by KW and SC

Applying Marine EM Methods the Gas Hydrate Mapping

• Fire in the Ice article published March 2010.

Test of a new marine EM survey method at Mississippi Canyon 118, Gulf of Mexico

• SIO Seafloor Electromagnetics Consortium annual meeting, La Jolla, CA - March 17-18, 2010

Karen Weitemeyer and Steven Constable delivered a presentation:

Results from the GoM gas hydrate studies

• Processed data distributed to sponsors late March, 2010 and early April, 2010.

• First Break Article published this June (2010).

Mapping shallow geology and gas hydrate with marine CSEM surveys

• Attended the 20th Electromagnetic Induction Workshop in Giza, Egypt September 18-25, 2010, and presented a poster.

Mapping gas hydrates and shallow sedimentary structure in the Gulf of Mexico using marine CSEM

• Submitted two abstracts to the 7th International Conference on Gas Hydrates (ICGH7), July 2011.

One by Constable, Du Frane, Pinkston, Weitemeyer, Roberts, Stern, Durham, on

Electrical resistivity of laboratory-synthesized methane hydrate

The second by Weitemeyer and Constable on

The development of marine electromagnetic methods for gas hydrate mapping

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