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HYDRATE RESEARCH ACTIVITIES THAT BOTH SUPPORT AND DERIVE FROM THE MONITORING STATION/SEA-FLOOR OBSERVATORY, MISSISSIPPI CANYON 118, NORTHERN GULF OF MEXICO

Submitted by:

CENTER FOR MARINE RESOURCES AND ENVIRONMENTAL TECHNOLOGY
111 OLD CHEMISTRY BUILDING, UNIVERSITY, MS 38677

Principal Author: Carol Lutken, PI

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PREPARED BY THE MANAGEMENT TEAM
Carol Blanton Lutken and Dianne R. Welch
CENTER FOR MARINE RESOURCES AND ENVIRONMENTAL TECHNOLOGY
111 OLD CHEMISTRY BUILDING, UNIVERSITY, MS 38677
(CONTACT: CAROL LUTKEN)

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PHASE 1 Subcontractors and Tasks for FY 2006:

Paul Higley, Specialty Devices, Inc., 2905 Capital Street, Wylie, TX 75098
  Task 1: Design and Construction of four Horizontal Line Arrays

Bob A. Hardage, Bureau of Economic Geology, John A. and Katherine G. Jackson School of Geosciences, University of Texas at Austin, University Station, Box X, Austin, TX 78713
  Task 2: Seismic Data Processing at the Gas Hydrate Sea-floor Observatory: MC118.

Jeffrey Chanton, Department of Oceanography, Florida State University, Tallahassee, FL 32306
  Task 3: Coupling of Continuous Geochemical and Sea-floor Acoustic Measurements

Peter Gerstoft, Marine Physical Laboratory, University of California at San Diego, 9500 Gilman Drive, La Jolla, CA 92093
  Task 4: Noise-Based Gas Hydrates Monitoring.

PHASE 2 Subcontractors and Tasks for FY 2008:

Camelia Knapp, Department of Geological Sciences, University of South Carolina701 Sumter Street, Columbia, SC 29208.
  TASK 2: Processing and Interpretation of TGS-NOPEC Industry Seismic Data and Integration with Existing Surface-Source/Deep-Receiver (SSDR) High Resolution Seismic Data at MC118, Gulf of Mexico.

Bob A. Hardage, Bureau of Economic Geology, John A. and Katherine G. Jackson School of Geosciences, the University of Texas at Austin, University Station, Box X, Austin, TX 78713-8924.
  TASK 3: Seismic Data Processing at the Gas Hydrate Sea-Floor Observatory: MC118.

Laura Lapham and Jeff Chanton, Department of Oceanography, Florida State University, Tallahassee, Florida, 32306-4320.
  TASK 4: Geochemical investigations at MC 118: Pore fluid time series and gas hydrate stability.

John Noakes, Scott Noakes, and Chuanlun Zhang, The University of Georgia, Athens, Georgia, and Tim Short, SRI International, St. Petersburg, Florida.
  TASK 5: Automated Biological/Chemical Monitoring System (ABCMS) for Offshore Oceanographic Carbon Dynamic Studies.

Rudy Rogers, Department of Chemical Engineering, Mississippi State University, PO Drawer 9595, Mississippi State, MS 39762.
  TASK 6: Microbial techniques to extract carbon from stored hydrocarbon gases.

Ira Leifer, Marine Science Institute, University of California at Santa Barbara, Bldg. 2, Room 3357, Santa Barbara, CA 93103-5080.
  TASK 7: Scoping study using Spatio-Temporal Measurement of Seep Emissions by Multibeam Sonar at MC118.

Paul Higley, Specialty Devices, Inc., 2905 Capital Street, Wylie, TX 75098
TASK 8: Validate high-frequency scatter on SSDR data by acquisition of targeted cores and velocity profiles at MC118 Hydrate Mound.

Sabodh Garg, Science Applications International Corporation, 10260 Point Campus Drive, MS A-3, San Diego, CA 92121.
TASK 9: Recipient shall model carbonate/hydrate mound in Mississippi Canyon 118 using modified version of (THROBS).

PHASE 3 Subcontractors and Tasks for FY 2009:

Camelia Knapp and James H. Knapp, Department of Geological Sciences, University of South Carolina701 Sumter Street, Columbia, SC 29208.
TASK 2: Geological and Geophysical Baseline Characterization of Gas Hydrates at MC118, Gulf of Mexico.

Bob A. Hardage, Bureau of Economic Geology, John A. and Katherine G. Jackson School of Geosciences, the University of Texas at Austin, University Station, Box X, Austin, TX 78713-8924.
TASK 3: Near seafloor geology at MC118 using converted shear-waves from 4C seafloor sensor data.

Laura Lapham and Jeff Chanton, Department of Oceanography, Florida State University, Tallahassee, Florida, 32306-4320.
TASK 4: Geochemical investigations at MC 118: Pore fluid time series and gas hydrate stability.

John Noakes, Scott Noakes, and Chuanlun Zhang, The University of Georgia, Athens, Georgia, and Tim Short, SRI International, St. Petersburg, Florida.
TASK 5: Automated Biological/Chemical Monitoring System (ABCMS) for Offshore Oceanographic Carbon Dynamic Studies.

Ira Leifer, Marine Science Institute, University of California at Santa Barbara, Bldg. 2, Room 3357, Santa Barbara, CA 93103-5080.
TASK 6: Quantification of Seep Emissions by Multibeam Sonar at MC118.

Sabodh Garg, Science Applications International Corporation, 10260 Point Campus Drive, MS A-3, San Diego, CA 92121.
TASK 7: Modeling a carbonate/hydrate mound in Mississippi Canyon 118 using modified version of (THROBS).

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INTRODUCTION / PROJECT SUMMARY

The Gulf of Mexico-Hydrate Research Consortium (GOM-HRC) is in its tenth year of developing a sea-floor station to monitor a mound where hydrates outcrop on the sea floor. The plan for the Monitoring Station/Sea Floor Observatory (MS/SFO) is that it be a multi-sensor station that provides more-or-less continuous monitoring of the near-seabed hydrocarbon system, within the hydrate stability zone (HSZ) of the northern Gulf of Mexico (GOM). The goal of the GOM-HRC is to oversee the development and emplacement of such a facility to provide a better understanding of this complex hydrocarbon system, particularly hydrate formation and dissociation, fluid venting to the water column, and associated microbial and/or chemosynthetic communities. Models developed from these studies should provide researchers with an improved understanding of gas hydrates and associated free gas as: 1) a geo-hazard to conventional deep oil and gas activities; 2) a future energy resource of considerable significance; and 3) a source of hydrocarbon gases, venting to the water column and eventually the atmosphere, with global climate implications.

Initial funding for the MS/SFO was received from the Department of Interior (DOI) Minerals Management Service (MMS, now the Bureau of Ocean Energy, Management, and Enforcement, BOEMRE) in FY1998. Funding from the Department of Energy (DOE) National Energy Technology Laboratory (NETL) began in FY2000 and from the Department of Commerce (DOC) National Oceanographic and Atmospheric Administration's National Undersea Research Program (NOAA-NURP) in 2002 via their National Institute for Undersea Science and Technology (NIUST). Some ten industries and fifteen universities, the United States Geological Survey (USGS), the US Navy, Naval Meteorology and Oceanography Command, Naval Research Laboratory and NOAA's National Data Buoy Center are involved at various levels of participation. Funded investigations include a range of physical, chemical, and microbiological studies. Studies of the benthic fauna will be added in the next cycle of research studies.

EXECUTIVE SUMMARY

In 1999, a consortium was assembled for the purpose of consolidating both laboratory and field efforts of leaders in gas hydrates research. The Consortium, established at and administered by the University of Mississippi's Center for Marine Resources and Environmental Technology (CMRET), has, as its primary objective, the design and emplacement of a remote monitoring station on the sea-floor in the northern Gulf of Mexico. The primary purpose of the station is to monitor activity in an area where gas hydrates are known to be present at, or just below, the sea-floor. In order to meet this goal, the Consortium has developed and assembled components for a station that will monitor physical and chemical parameters of the sea water, sea-floor sediments, and shallow subsea-floor sediments on a more-or-less continuous basis over an extended period of time. The study of chemosynthetic communities, primarily the microbiological components, and their interactions with geologic processes, is a component of the plan for the Observatory; results will provide an assessment of environmental health in the area of the station including the effects of deep sea activities on world atmosphere and, therefore, weather.

Central to the establishment of the Consortium is the need to coordinate activities, avoid redundancies and promote effective and efficient communication among researchers. Complementary expertise, both scientific and technical, has been assembled; collaborative research and coordinated research methods have grown out of the Consortium and design and construction of most instrumentation for the sea-floor station is essentially complete.

Following much scientific research, consideration and discussion, the Consortium selected Mississippi Canyon 118 (MC118) as the site of the MS/SFO. Criteria for selection included evidence of gas hydrates on the sea-floor, active venting and availability. MMS placed a research restriction on the unleased block so Observatory research might continue even if the block should subsequently be leased, as is now the case. CMRET regularly conducts research cruises to MC118 to enable investigations of the site and to test and deploy instruments/components of the SFO.

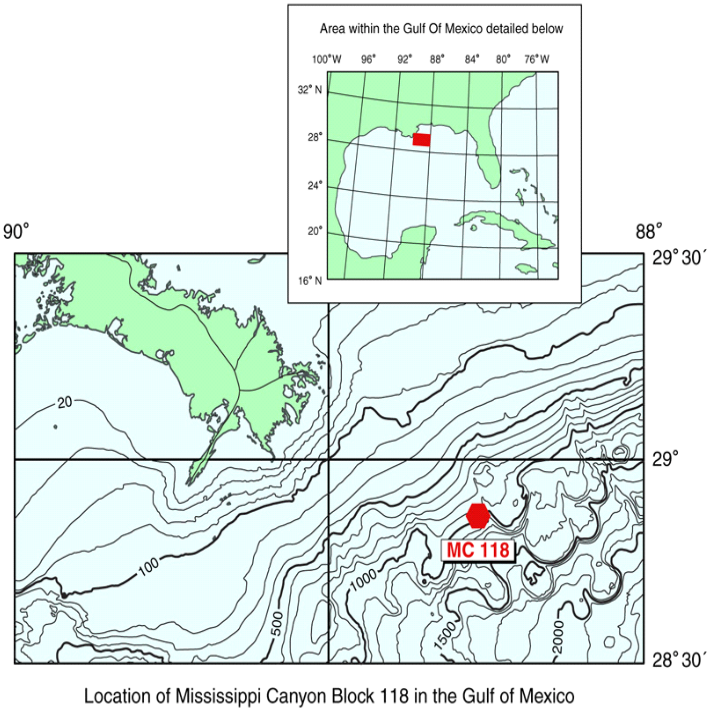


Figure 1. Location of Mississippi Canyon Block 118 in the Gulf of Mexico.

Initial components of the observatory were deployed at MC118 in May of 2005. In spite of a variety of delays, including the effects of several severe hurricanes, follow-up surveys and deployments, continue to take place.

The centerpiece of the observatory (Figure 2) is a series of vertical and horizontal line arrays of sensors (VLA, HLAs) designed to detect shifts in the hydrate stability zone (HSZ). The VLA is to be moored to the sea floor and extend approximately 200 meters into the water column. Sensors in the VLA include hydrophones to record water-borne acoustic energy (and measure sound speed in the lower water column), thermistors to measure water temperature, tilt meters to sense deviations from the vertical induced by water currents, and compasses to indicate the directions in which deviations occur. The horizontal water-bottom arrays consist of hydrophones laid upon, and pressed into, the soft sediment of the sea-floor, and arranged into a cross with four 500m-long arms: two perpendicular arrays, the length of each approximating the water depth at the observatory site. This seismic array design will enable the use of natural surface noise (*via* hydrophone) and microseism noise from salt movement (*via* accelerometer). The goal is to use these passive seismic sources for long-term monitoring of structural and hydrocarbon fluid dynamics in a way analogous to conventional reservoir monitoring. The system will be incorporated into the SFO at the hydrate mound/salt dome complex at MC118, providing the capability of long-term, continuous seismic monitoring that is marine mammal friendly through the elimination of the traditional seismic energy source.

The sea-floor arrangement of arrays will be accomplished by means of the Station Service Device (SSD), the remotely operated vehicle (ROV) especially designed to service the Observatory. The SSD has been used to effect deployments and recoveries and will be used in array deployment to unspool cable. It is anticipated that accelerometers will be implanted in the vicinity of the HLAs in the future, making it possible to image the HSZ to greater depths and to see interstitial space occupied by gas (shown by hydrophone data, which do not travel through gas). The MMS-funded sled will be used as a seismic source of compressional and shear waves for calibrating the accelerometers.

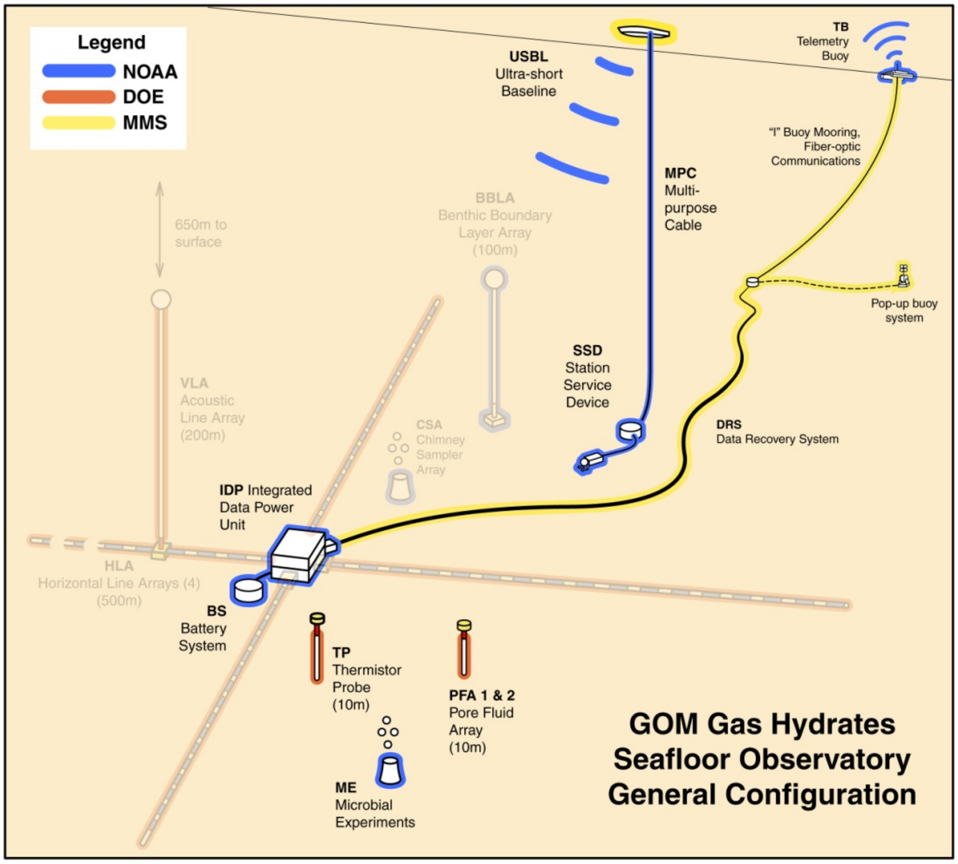


Figure 2. Monitoring Station/Sea-floor Observatory hardware with funding sources. Components already deployed are highlighted. The VLA, BBLA, CSA and additional experiments have been deployed to collect data in test mode, recovered, data analyzed and adjustments made in preparation for permanent deployment.

The MMS-funded Sea-Floor Probe (SFP) has been used several times to retrieve core samples from MC118. These samples are used in the effort to select sites appropriate for deployment of microbial experiments and thermistor and geochemical probes. Images recovered during a C&C Technologies autonomous underwater vehicle (AUV) survey in 2005, have been reprocessed and the results (Figure 3) used in analyses and selection of sites for further study. The NIUST AUV, *Eagle Ray*, has been used to resurvey MC118 (multibeam) and the photomosaic-capable AUV, *Mola Mola*, is scheduled to survey the site in 2010.

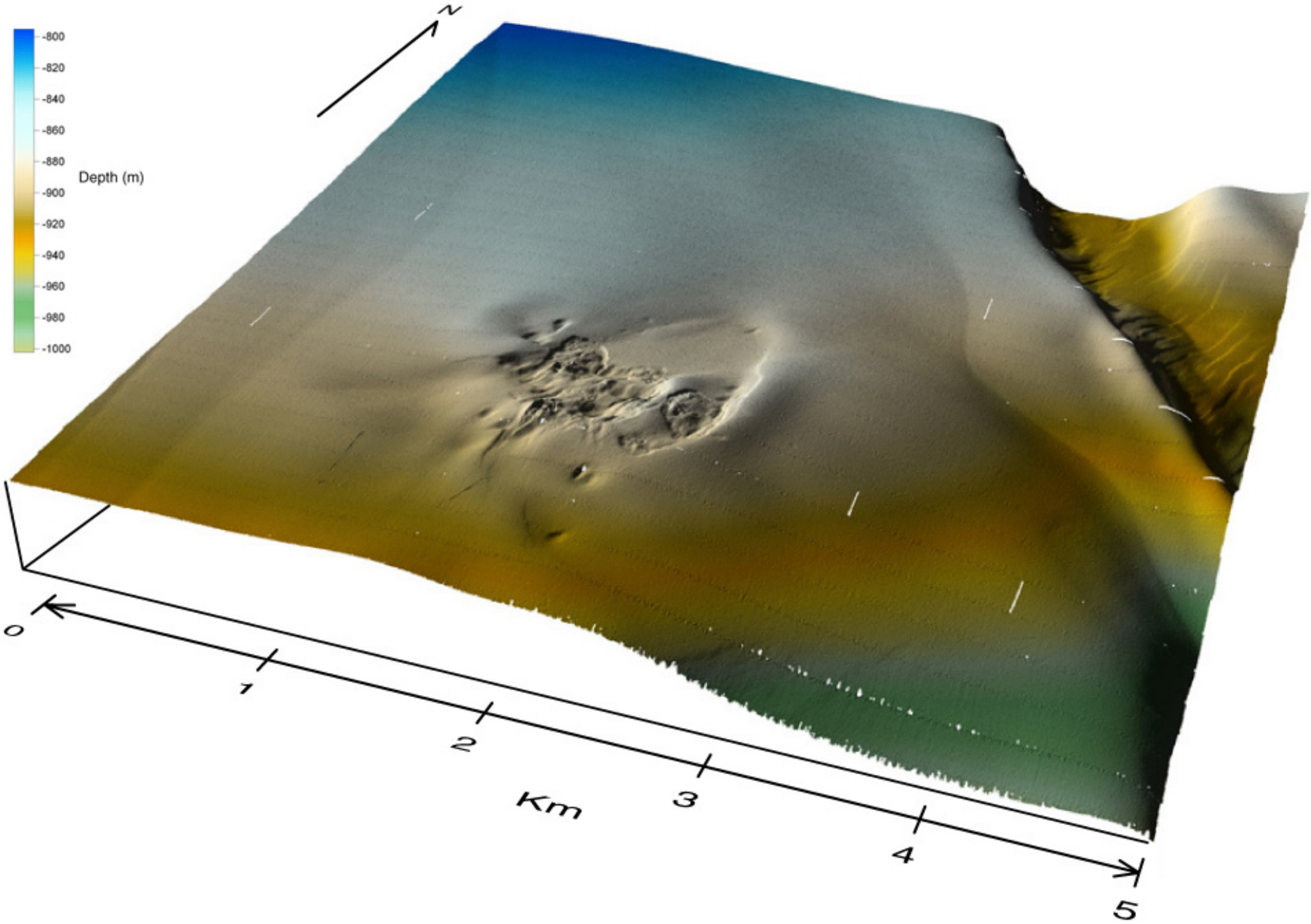


Figure 3. Bathymetry at MC118 as revealed in reprocessed multibeam data. The mound complex includes three crater complexes: a northwestern complex, a southwestern complex and a southeastern complex.

A complete surface-source/deep-receiver (SSDR) survey of the mound at MC118 has been made. The resultant 109 profiles of very high resolution seismic data have undergone processing to create a 3-D model of the mound, including the application of Empirical Mode Decomposition described by Battista et al. (2007).

Experiments designed to assess water-column geochemistry, microbial communities and activities, hydrate host materials, and composition of pore-fluids have been designed, built and tests run at MC118. Sediments collected from Mississippi Canyon have been studied for effects of parameters possibly involved in hydrate formation. Laboratory analyses show that smectite clays promote hydrate formation when basic platelets slough off the clay mass. These small platelets act as nuclei for hydrate formation. Experiments show an increasing importance of microbial activities surrounding active vents in promoting the formation and stability of seafloor gas hydrates.

Seismic data-processing software has been developed at Exploration Geophysics Laboratory (EGL) of the Texas Bureau of Economic Geology (BEG) that is structured to optimize P-P and P-SV image resolution in the immediate vicinity of 4C seafloor-based seismic sensors. 4C sensor technology and negotiations continue with CGGVeritas, to provide cost-sharing, state-of-the-art, 4C - orthogonal X,Y,Z geophones and a hydrophone seafloor sensor technology that will be used to acquire the 4C data.

Interpretation of the MC118 TGS 3D seismic volume provides evidence of successive temporal movement on a series of at least three main faults genetically related to an underlying salt body. The subsurface structural, stratigraphic, thermal, and fluid flow architecture of MC118, like that of many regions in the Gulf of Mexico, is dominated by the presence of salt. The hydrate mound system at MC118 is situated above one of two major salt bodies beneath the block, and appears to have evolved in close association with the crestal fault system developed above and around a dome-shaped salt body. From the 3D seismic volume, some of the preliminary observations provide evidence that (1) the salt moves upward as it is loaded by sediments, (2) major faults nucleate off of the salt body, (3) the salt flank and the associated faults provide vertical migration pathways for deep basin fluids, and (4) the crestal structure is dominated by a radiating system of arcuate faults.

Preliminary conclusions of this work are that the gas hydrate system at MC118 appears to be controlled by the presence of two temporally and kinematically distinct salt bodies present in the subsurface; the salt-related fault systems provide likely migration pathways for the thermogenic hydrocarbons; locations, orientations, and geometries of crestal faults developed above the salt bodies appear to correlate with the surface structural and microbial activities as well as with the gas hydrate mounds observed on the seafloor.

Current site characterization efforts center about evaluating the TGS data set to make quantitative estimates of the lithologic influence on gas hydrate seismic response by implementing recently developed rock physics models for saturated gas hydrates. Modeled results for seismic velocities as a function of gas hydrate saturation are followed by computation of seismic velocities as a function of depth for synthetic porosity profiles. Models for seismic velocities as a function of free gas volumetric fraction are also made.

Geochemical experiments at MC118 have been seriously impacted by the failure of the SSD to recover the SFP boxes. However, alternative-site experiments and laboratory analyses have produced new information on the formation and dissolution rates – and controls on these rates – of gas hydrates.

Although not prescribed in this contract, changes in geochemistry and water chemistry related to the catastrophic oil spill at MC252 are being included in monitoring at the Observatory site. With obvious – and not-so-obvious – impact possibilities on our work, we feel obliged to do our own monitoring of these parameters at MC118. Results appear in the subcontractors' reports but they agree that hydrocarbon plumes do exist at depth, where we have not detected them in the past (See reports of Phase 3, Task 4 and Task 5).

The marine lander survey system has been reconfigured and is ready for a September deployment with the SRI mass spectrometer, the same instrument used with great success to detect the methane plumes deriving from the Deep Water Horizon spill. In addition, the sonar rotator and field gas chromatograph should be ready for this cruise, making it a hydrates-water chemistry intensive mission.

Work on the model of hydrate stability at MC118 has progressed to the point that a confidential report is being submitted to DOE. The Equation of State has been developed to include the multigas hydrates present as well as their phase behaviors under conditions prevailing at MC118. This includes developing constitutive relations for the gaseous phase for ethane and propane, with profoundly different saturation pressures form methane, indirectly.

A series of cruises was conducted by the GOM-HRC this spring. A March cruise to test the improvements to the station service device (SSD), including a simplified deployment scheme, was largely unsuccessful due to horrible sea state, followed by failure of our new strength/fiber-optic cable. This failure was a tremendous setback but was overcome in time for a very successful April cruise on which we managed to use the SSD to collect targeted push cores and to test all aspects of the HLA deployment. On this cruise we redeployed the integrated data power unit (IDP) that will coordinate station operations. In June, we returned to MC118 prepared to deploy all HLAs. We located the IDP and deployed the HLA pod within 12m of it. We were subsequently confounded by the failure of the SSD communications cards. Although we were able to secure a replacement set, communications failed on the first dive following the installation of the replacements. We are still struggling to determine the cause of the failure. The remainder of the cruise was devoted to water chemistry, with some very important findings.

EXPERIMENTAL/ RESULTS AND DISCUSSION

PHASE 1 Tasks for FY 2006:

Task 1: Design and Construction of four Horizontal Line Arrays

Introduction

The Horizontal Line Array (HLA) design evolved with a change replacing the two arrays of 4C sensor packages to four longer all-hydrophone arrays. New cable designs were developed to meet these program needs. This reporting period has seen the successful testing of the array deployment technique. However, deployment of an array in permanent configuration at MC118 has still not happened due to failure of communications cards in the SSD during the deployment dive(s).

Background

The HLA design was contracted in April 2007 with the plan to build two horizontal 4C arrays utilizing technology developed for these 4C sensors during the Borehole Line (BLA) development project. The project plan for the HLAs included building 2 arrays of 4C sensors, each 400 meters long. This plan was modified to include more than 2,000 meters arrays in the form of four all hydrophone arrays arraigned as an “X” pattern of 500m per leg. In addition to building these arrays, efforts have continued to develop a method to deploy them. The deployment method has evolved based on the SSD ROV. The preliminary concept to deploy all of the HLAs simultaneously has evolved into deployment one at a time using the SSD. The previous simultaneous installation plan utilized an SDI built HLA “POD”. This HLA POD has been modified to accommodate the one-at-a-time approach and several other devices designed to aid in this installation method.

Activities during this period

During the last reporting period, the HLA cables were pressure tested, a repair made to one cable and hydrophones were installed for final integration with the data acquisition and telemetry systems. A repeat pressure test was successfully performed at the Southwest Research Institute in San Antonio, Texas, in early February, 2010. The deployment plan has been altered and refined and a deployment method established that includes the deployment on the seafloor of a modified HLA POD in the proximity of the Interconnection and Data Recovery (IDP) device. This HLA POD is designed to accept one HLA array Data Logger (HLA DATS) at a time in the form of a HLA transporter. The HLA transporter includes an HLA DATS and a spool of cable which allow it to be connected to the IDP. This transporter is designed to be carried down to the sea floor by the SSD ROV with a full HLA cable carried on the back of the SSD deployment cage. This has been done successfully on several dives. Tilt of the SSD has had to be adjusted to accommodate the weight of the HLA. This deployment operation is depicted below. The SSD ROV cage is lowered with a full HLA cable on its deployment spool and a HLA Transporter, with DATS, mounts and connectors, on the front of the SSD cage ready to be installed on the HLA POD. After the DATS is placed, by the SSD arm, the 500m of cable is unspooled using the ship’s navigation. The connection to the IDP is then made when the SSD returns to the POD and unspools the connection (green cable) from the POD to the IDP.

Figure 4. Deployment of the POD that will support the four 500m horizontal line arrays of hydrophones.

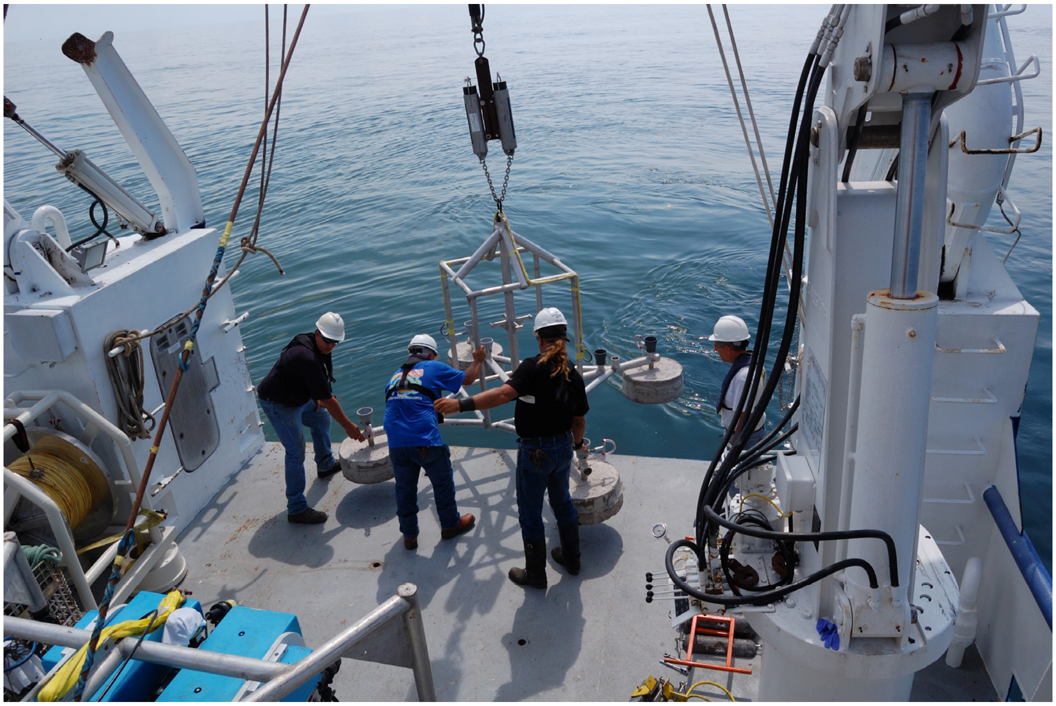


Figure 5. Position of the POD on the seafloor at MC118, south of the northwest vent complex. Note the receivers for the DATS units.

Figure 6. The SSD configured to carry the HLA, DATS and connectors.

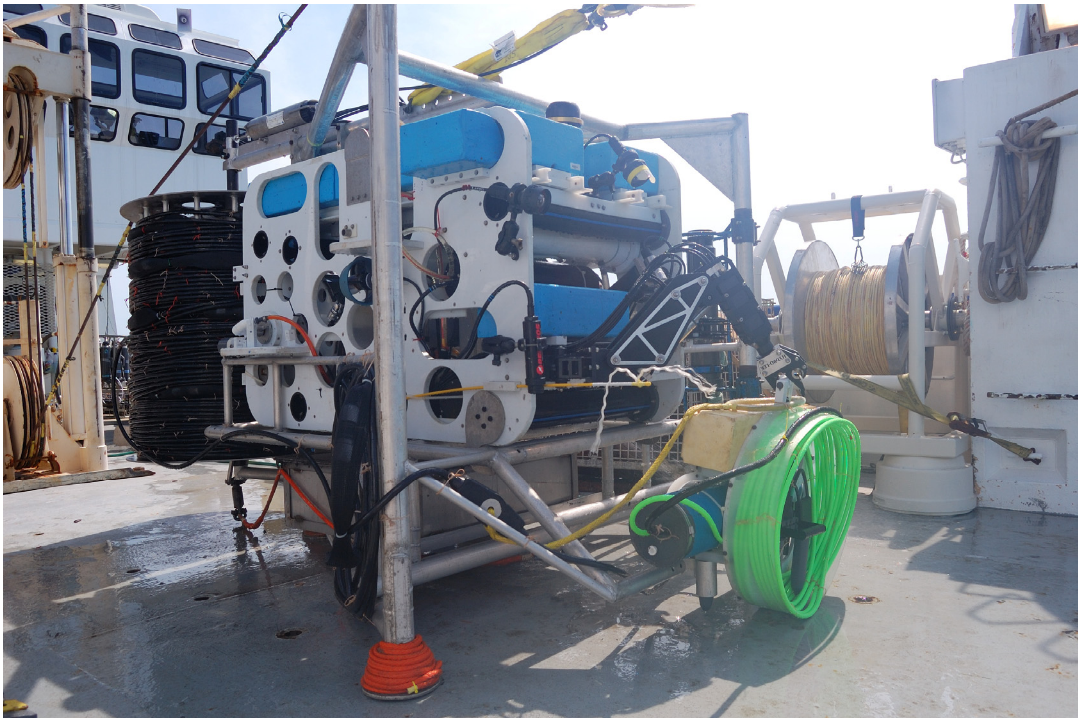


Figure 7. Matt Lowe bands the leading loops of the cable to the SSD so that they ride smoothly to the seafloor, 900m down, ready to begin unspooling.

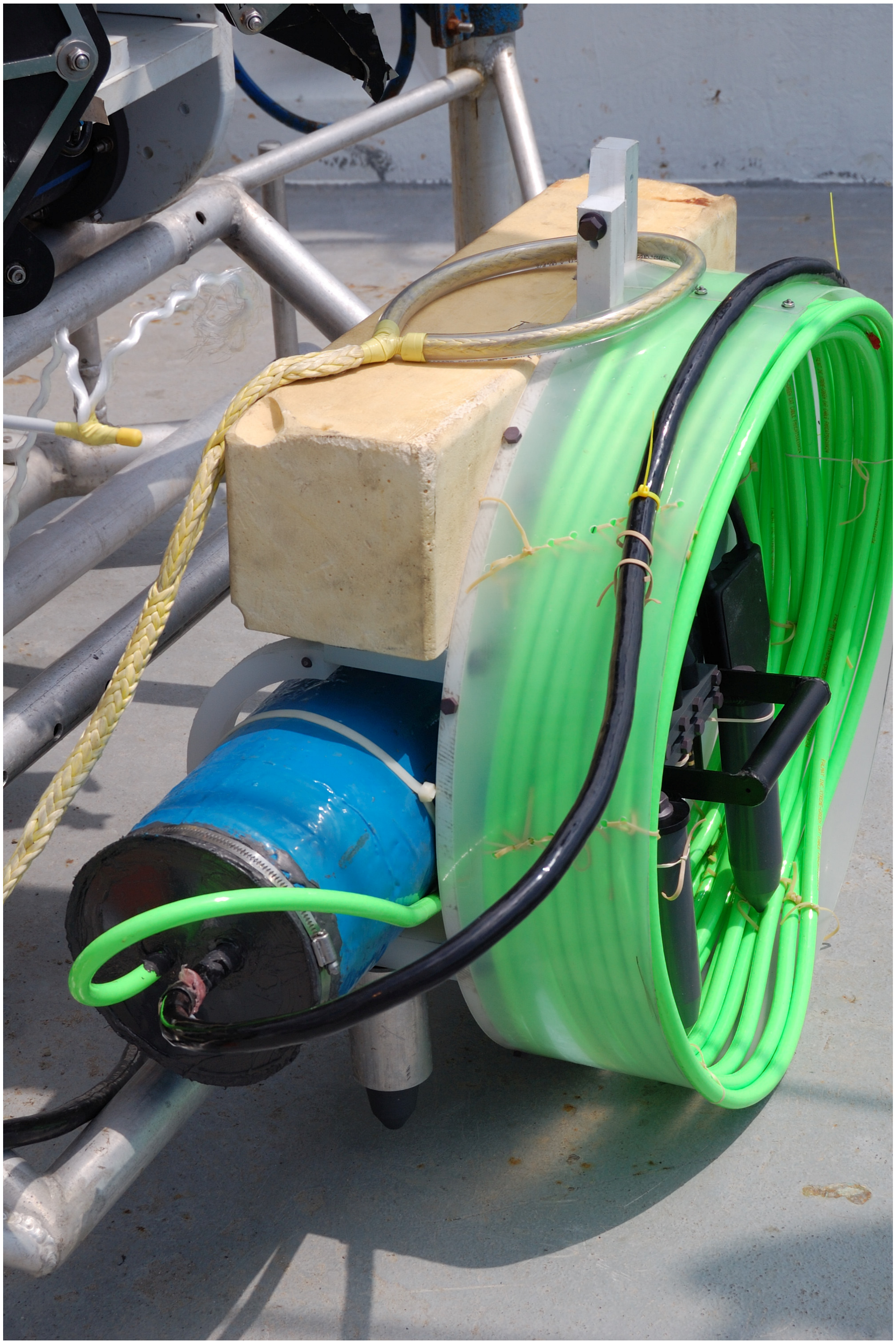
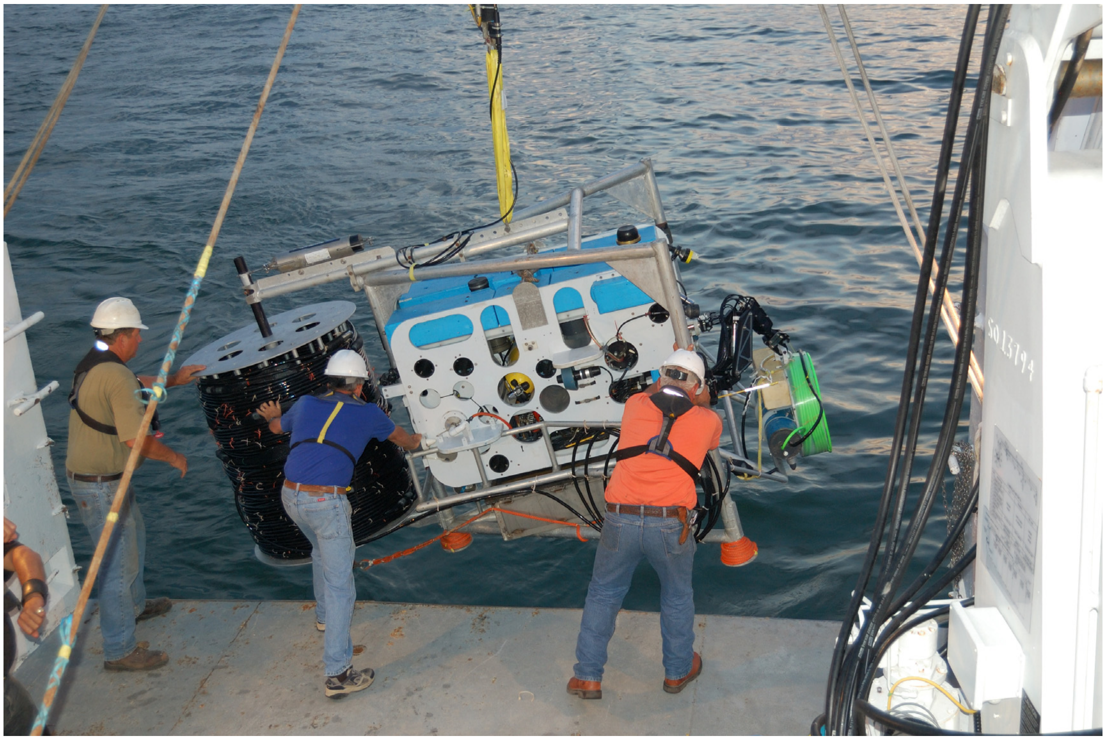


Figure 8. Close-up of the DATS and connectors (to the IDP) ready to ride to the seafloor. The transporter includes the make and break underwater ROV compatible connector which mates the HLA DATS to the IDP.

Figure 9. The SSD being sent to deploy the HLA, the DATS and connectors to connect the HLA to the IDP for data transmission.



Summary

The HLA cables and final integration of the HLA cables with the rest of the data acquisition system has been completed. The deployment method has been tested. The 4 arrays await deployment in permanent configuration.

Task 2: Seismic Data Processing at the Gas Hydrate Sea-floor Observatory: MC118.

This task has been completed: software has been written, tested on data from another hydrates location and awaits data from the MS/SFO.

Task 3: Coupling of Continuous Geochemical and Sea-floor Acoustic Measurements

Phase 1 of this project is complete but the project continues under Phases 2 and 3.

Task 4: Noise-Based Gas Hydrates Monitoring.

Monitoring of gas hydrates at Mississippi Canyon 118 is possible using ambient noise as a sound source. The goal is to attempt to apply passive methods to supply information similar to that supplied by active sources, but on a continuous basis, as passive sources, such as wave-noise, are ever-present at MC118.

By using ambient noise-based methods with dense networks, passive monitoring of gas hydrates is possible. Making use of ambient-noise cross correlation function of diffuse fields between two receivers, information can be recovered that is similar to that recovered using an active source.

The goal of this project is to apply passive methods to supply information similar to that supplied by active sources, but on a continuous basis, as passive sources, such as wave-noise, are ever-present at MC118.

The data recovered from the HLAs will be used to validate the techniques described in earlier progress reports. As the attempts to deploy said arrays and recover test data from them have, thus far, been unsuccessful, we are as yet unable to report on the application of the field techniques and data treatment at the observatory site. HLAs are scheduled for deployment in September, 2010, if GOM weather cooperates.

PHASE 2 Tasks for FY 2008:

TASK 1: Project Management Plan

This task is complete.

TASK 2: Processing and Interpretation of TGS-NOPEC Industry Seismic Data and Integration with Existing Surface-Source/Deep-Receiver (SSDR) High Resolution Seismic Data at MC118, Gulf of Mexico.

This task includes processing and interpreting industry seismic data collected and provided by TGS-NOPEC, Inc. Geophysical Company and integrating them with existing Surface-source/ Deep-receiver (SSDR) high resolution seismic data at from Mississippi Canyon Block 118, Gulf of Mexico (GOM), in order to image and understand the complex geologic structures at the Observatory site and how they relate to gas hydrate formation and dissociation. This work has been focused on the (1) refinement of the structural interpretation of the TGS-NOPEC seismic data, (2) interpretation and mapping of the high-amplitude reflectors identified as possible bottom simulating reflectors (BSRs), (3) integration of this dataset with the high-resolution SSDR single-channel seismic data, (4) preparation and submission of a proposal to the Integrated Ocean Drilling Program (IODP), and (5) initiation of a thorough analysis of the rock physics properties of the inferred gas hydrates at the study site.

The characterization of the subsurface geology – particularly the structure of the carbonate-hydrate mound and how it relates to and impacts hydrate formation and dissociation – has been essentially completed. Integration of the data from the nearby ARCO-1 deep well was a major accomplishment of this phase. The proposal submitted to the IODP supports this effort and has progressed to the full proposal stage but is not expected to develop into a project until 2013, at the earliest. The proposal is to drill borehole(s) to define the subsurface geology at MC118 and to provide the ability to monitor the subsurface at the site, continuously, into the future.

To date, findings of this effort support the inferences that the structure, stratigraphy and thermal and fluid-flow architecture at MC118 are dominated by salt structures, the mound having evolved in association with a crestal fault system that formed over a domed salt body. Depth conversions have been performed and horizons on TGS records correlated with picked horizons in the ARCO-1 well. AVO analysis was performed on one of the TGS inlines. The results included the identification of an interpreted accumulation of free gas beneath the base of gas hydrates. A request for an additional seismic line in raw form – one that crosses the middle of the mound - was made to substantiate this find and to determine how wide-spread the reflector might be. TGS agreed to provide the line.

USC researchers began deriving an impedance volume from the TGS seismic data to be used in porosity calculations and in calculations of gas hydrate saturations.

In their request for continued funding for this project, USC has included funds to purchase an additional, deeper, 3-D dataset from WesternGeco. Further accomplishments are summarized in the Phase 3 sections.

TASK 3: Seismic Data Processing at the Gas Hydrate Sea-Floor Observatory: MC118.

Since no 4-C data have been acquired, no work has been done on this subcontract. Negotiations continue with CGGVeritas for the acquisition of ~60 of their 4-C nodes. This prospect is discussed further in the Phase 3 section.

TASK 4: Geochemical investigations at MC 118: Pore fluid time series and gas hydrate stability.

Additional instruments have been built and some deployed. Accomplishments of this task are covered in depth in the Phase 3 reports.

TASK 5: Automated Biological/Chemical Monitoring System (ABCMS) for Offshore Oceanographic Carbon Dynamic Studies.

The University of Georgia (UGA) and SRI International (SRI) research team have developed a unique survey instrument capable of surveying the methane rich seafloor and collecting biomass and suspended sediment samples on demand. This project is extended into Phase 3 and progress is covered more fully in that section of this report.

TASK 6: Microbial techniques to extract carbon from stored hydrocarbon gases.

ABSTRACT

Gas hydrates form in a crystallization process that is a surface phenomenon whose kinetics depends upon nucleate induction time followed by catastrophic agglomeration after critical cluster size attainment. The goal of this research is to establish mechanisms and kinetics of seafloor hydrate formations/dissociations. The work strives to understand seafloor hydrate accumulations and to foresee seafloor hydrate stability as influenced by microbial activity. Ultimately, the results will help in locating and producing methane gas from gas hydrates. The work supports the Gas Hydrate Observatory at MC-118.

INTRODUCTION

We believe understanding and modeling of microbial activities are necessary to accurately anticipate stabilities of the complex environment around seafloor gas hydrates. Such a model will be an important component of eventually producing methane from the accumulations or even sequestering carbon dioxide. As more experimentation is done, it becomes apparent to us that the microbial influence on seafloor gas hydrates far exceeds what was considered only a few years ago.

The many sediment samples from MC-118 made available to us have helped immensely in these studies. Cultures have been made of in-situ microbes from the MC-118 sediments and compared to *Bacillus subtilis* species obtained from ATCC. Also, this work delves into the effects of the cell masses themselves on hydrate formation, and the results are reported.

Our previous laboratory findings of smectite clays and biosurfactants promoting hydrates in the laboratory were substantiated when we evaluated MC-118 sediments and their indigenous microbes. (Rather than bulk clays, here we refer to the individual, basic smectite clay platelet in a role of hydrate crystal nucleation.) More importantly, how the bacterial cell masses fit into this scheme of clay-surfactant interaction to form hydrates is for the first time determined.

We believe the findings help explain the stability and longevity of seafloor gas hydrate accumulations. The proliferation of microbes in seafloor sediments depends to a great extent on a carbon source. Contained in the gas hydrate accumulations are relatively massive accumulations of carbon. It is not surprising, therefore, when our data indicate how microbes access this carbon source and seemingly thrive on the interior in interstitial spaces between hydrate crystals of seafloor hydrates. Their activity may govern the growth or deterioration of the mounds on the seafloor.

RESULTS AND DISCUSSION

Publications

The Principal Investigator was invited guest speaker at the Gordon Research Conference on Natural Gas Hydrates, Waterville, Maine, June 6- June 10, 2010. The topic of the presentation was based on research under DOE Award DE-FC26-02NT42877 concerning the impact of sediments, organic matter, and microbes on the nucleation and persistence of gas hydrates in natural systems. The title of the presentation was the following: “The importance of microbe/mineral/hydrate interactions in the formation and decomposition of gas hydrates in ocean sediments.”

Other articles that derive from this grant are being prepared for submission.

Funded Support During Current Report Period

Grant funds during this report period supported two part-time undergraduate students in the Spring Semester and one part-time undergraduate during the present summer term. Some part-time endeavors of Research Assistant Professor Zhang were supported by these funds, but the bulk of his time and work on the project during this report period were gratis. The P.I. time and effort during this report period were also donated gratis. Some supplies were provided from the grant.

Research During Current Report Period

In the previous semi-annual report, we detailed publication of our work on microbial influences on gas hydrate formation in seafloor sediments. That publication was the following:

Radich, J., Rogers, R.E., French, W.T.., Zhang, G., 2009. “Biochemical Reaction and Diffusion in Seafloor Gas Hydrate Capillaries: Implications for Gas Hydrate Stability,” *Chemical Engineering Science*, **64**, Issue 20, 4278-4285.

The publication presents a mathematical model of biochemical reactions, smectite clay influences, and hydrate capillary diffusion of nutrients-bioproducts that greatly determine the rate of formation and decomposition of gas-hydrate outcrops on the floor of the Gulf of

Mexico. It is the first such publication that includes microbial effects on hydrates in a mathematical model, and it is believed that other published models not including these effects entail serious error.

The limited work of the current report period is being consolidated and analyzed. Some loose ends of the research that needed additional data are being addressed to the extent allowed by the small amount of funding that remains.

CONCLUSIONS

The experiments performed under this grant have been the first to show the great importance of microbial activities surrounding gas hydrate mounds, hydrocarbon-rich sediments, and natural gas vents in the formation and stability of seafloor gas hydrates. The effect is so important that we believe predictive models of seafloor hydrate formations and decompositions must include these microbial effects. A first such predictive model was developed by us, and it was published in *Chemical Engineering Science* during the previous report period.

In the current report period, the work has been limited by funding, but time and effort have been donated to bring all of the results into publishing articles and possibly patents, which will be concluded in the near future.

TASK 7: Scoping study using Spatio-Temporal Measurement of Seep Emissions by Multibeam Sonar at MC118.

The multibeam scanning sonar project is continued under Phase # and progress is reported in that area of this report.

TASK 8: Validate high-frequency scatter on SSDR data by acquisition of targeted cores and velocity profiles at MC118 Hydrate Mound.

In order to characterize sediments hosting gas hydrates at MC118 researchers must be able to measure the velocity of these sediments. The successful installation of the Pore Fluid Array (PFA) and Temperature Array (TA) with sensors installed to depths nearly 10m below the seafloor at MC118 opened the possibility of installing acoustic sensors on a similar probe as a method of measuring sediment velocity.

The concept includes developing a series of acoustic sensors that can be attached to this type of a probe, survive the installation trauma and operate at sufficient depths to allow this concept to work. This also requires developing a data acquisition package that can survive these conditions and is capable of driving and communicating with acoustic sensors to achieve accuracy sufficient to meet the needs of the studies at MC118. SDI has acquired some of the software and instrumentation development system for use on this project. The development of the probe has not advanced due to the priority given by SDI to completing and deploying the HLAs.

TASK 9: Recipient shall model carbonate/hydrate mound in Mississippi Canyon 118 using modified version of (THROBS).

This preliminary examination of the hydrate phase at MC118 implies that it will be necessary to develop a multi-component simulator in order to model the observed gas and hydrate phase compositions at the Hydrate Mound. The computer program (CSMHYD.exe) developed by Dendy Sloan (Colorado School of Mines) was used to establish the appropriate stability curve, i.e., hydrate dissociation pressure as a function of temperature and salinity.

Since the vent gas at the Hydrate Mound is mostly methane, it was decided to use the methane PVT properties for the "equivalent" gas phase. Other required hydrate properties (e.g. density, compressibility, thermal expansion coefficient, specific heat, heat of formation) were estimated based on published data.

THROBS was modified (January to April 2009) to include the stability curve for Structure II hydrate as deduced from the computer Program (CSMHYD.exe).

SAIC has performed parametric calculations to examine the following aspects of hydrate formation/decomposition at Hydrate Mound:

1. Gas influx rates required for hydrate formation.
2. Effect of salinity on hydrate distribution.
3. Effect of temperature gradient
4. Conditions required the co-existence of 3-phases (hydrate, gas, liquid) and for gas venting at the sea-floor.

This project continues into Phase 3.

TASK 10. Administrative oversight of the Monitoring Station/Sea-floor Observatory Project.

Administration of the Consortium is the responsibility of the University of Mississippi and includes formal Project Proposals to federal funding agencies, Technical Progress Reports, Final Project Reports, informal monthly updates, reports of Consortium meetings, cruise reports, participation in national meetings, organizing meetings between researchers, organizing and participating in program reviews, organizing and participating in research activities, including research cruises. This responsibility was completed for FY08 with the completion and acceptance of the year-end report to DOE, 42877R12. Further administrative duties and responsibilities are addressed in Phase 3.

PHASE 3 Tasks for FY 2009:

TASK 1: Project Management Plan

This task is complete.

TASK 2: Geological and Geophysical Baseline Characterization of Gas Hydrates at MC118, Gulf of Mexico

Introduction

Motivated by the value of marine gas hydrates as a potential energy resource and their potential influence on climate (Buffett, 2000), we are engaged in a study to characterize gas hydrates in the Gulf of Mexico as part of the Gulf of Mexico Hydrates Research Consortium (GoM-HRC). The locations of marine gas hydrates are commonly inferred by the presence of a distinctive Bottom Simulating Reflector (BSR) which typically marks the base of the gas hydrate stability zone (GHSZ) in seismic records (Trehu et al, 2006). Yet lithology, as defined through sediment composition, grain size, and particle shape, is also critical in their emplacement and growth.

Recently, GoM-HRC observations have been complemented with the analysis of an industrial 3-D seismic reflection survey (TGS-Nopec survey covering the entire MC-118 block) and integration of information from an industry well (ARCO-1) drilled within the block in 1989. Here, we report on initial efforts to quantitatively estimate (and understand) the lithologic influence on gas hydrate seismic response. To do so, we are implementing recently developed rock physics models for saturated gas hydrates (Helgerud et al, 1999; Helgerud et al, 2000; Helgerud, 2001).

We present forward modeling results for seismic velocities as a function of gas hydrate saturation, and then compute seismic velocities as a function of depth for synthetic porosity profiles. We also include models for seismic velocities as a function of free gas volumetric fraction.

Physics-Based Models for High Porosity Sediments

Helgerud (2001) presents several physics-based models to describe the elastic properties of hydrate-sediment systems. The models, for clay rich, high porosity ocean-bottom sediments, are described here for implementation and application to the MC118 site. First described is a baseline model applicable for water saturated sediments. The elastic properties of the sediment are described as a function of rock porosity, the mineral and fluid moduli of the rock, as well as the effective pressure. In addition, two variations of the baseline model are presented to include gas hydrate. In the first variation, gas hydrate is modeled as a component of the pore fluid; in the second, gas hydrate is modeled as part of the sediment-frame.

Baseline Model

The baseline model for water saturated sediments is from Helgerud (2001, p. 220-223). The starting point is the calculation of dry-frame effective moduli for the dense packing of identical elastic spheres described using Hertz-Mindlin Contact Theory. Then the equations for effective dry-frame moduli at arbitrary porosity, using modified Hashin-

Shtrikman bounds, are given. Subsequently, Gassmann's equations for saturated conditions (Dvorkin et al, 1999; Helegerud et al, 1999) are applied to the model. First we review the Hertz-Mindlin contact theory, then review an adaptation of this theory using modified Hashin-Shtrikman bounds. Discussion of the baseline models concludes with application of Gassmann's equations. [Alternative Last Sentence of This paragraph: We refer the reader to Helgerud (2001, p. 220-223) for details, and only provide details of the modifications, also from Helgerud (2001, p. 223-224)].

Hertz-Mindlin contact theory:

At critical porosity ϕ_c the effective dry-rock bulk moduli is given by the Hertz-Mindlin contact theory (Mindlin, 1949; Dvorkin et al, 1999b, eqn. 1, p. 1781; see also, Dvorkin and Nur, 1996, eqn. 4, p. 1365 [sic 1366]; Mavko et al, 2009, p. 246-247, 258-262)

$$K_{HM} = \left[\frac{n^2(1-\phi_c)^2G^2}{18\pi^2(1-\nu)^2}P_{eff}\right]^{1/3}$$

Similarly, the effective shear moduli (Dvorkin et al, 1999, eqn. 1, p. 1781) is

$$G_{HM} = \frac{5-4\nu}{5(2-\nu)}\left[\frac{3n^2(1-\phi_c)^2G^2}{2\pi^2(1-\nu)^2}P_{eff}\right]^{1/3}$$

Lower bounded dry-frame model for porosity lesser than critical porosity:

Dvorkin and Nur (1996, eqn. 5, p. 1366) and Dvorkin et al (1999b, eqn. 2, p. 1782) proposed a heuristic modification for porosities below the critical porosity (i.e., $\phi < \phi_c$); explicitly, the effective dry-rock modulus is

$$K_{Dry} = \left[\frac{\phi/\phi_c}{K_{HM}+\frac{4}{3}G_{HM}} + \frac{1-\phi/\phi_c}{K+\frac{4}{3}G_{HM}}\right]^{-1} - \frac{4}{3}G_{HM}$$

The effective shear modulus is

$$G_{Dry} = \left[\frac{\phi/\phi_c}{G_{HM}+\frac{G_{HM}}{6}\left(\frac{9K_{HM}+8G_{HM}}{K_{HM}+2G_{HM}}\right)} + \frac{1-\phi/\phi_c}{G+\frac{G_{HM}}{6}\left(\frac{9K_{HM}+8G_{HM}}{K_{HM}+2G_{HM}}\right)}\right]^{-1} - \frac{G_{HM}}{6}\left(\frac{9K_{HM}+8G_{HM}}{K_{HM}+2G_{HM}}\right)$$

Upper bounded dry-frame model for porosity greater than critical porosity:

For porosities $\phi > \phi_c$, the effective dry-rock moduli are modified (Dvorkin et al, 1999b, eqn. 3, p. 1782); now, the effective dry-rock bulk modulus is

$$K_{Dry} = \left[\frac{(1-\phi)/(1-\phi_c)}{K_{HM}+\frac{4}{3}G_{HM}} + \frac{(\phi-\phi_c)/(1-\phi_c)}{\frac{4}{3}G_{HM}}\right]^{-1} - \frac{4}{3}G_{HM}$$

The effective dry-rock shear modulus is

$$G_{Dry} = \left[\frac{(1-\phi)/(1-\phi_c)}{G_{HM}+\frac{G_{HM}}{6}\left(\frac{9K_{HM}+8G_{HM}}{K_{HM}+2G_{HM}}\right)} + \frac{(\phi-\phi_c)/(1-\phi_c)}{\frac{G_{HM}}{6}\left(\frac{9K_{HM}+8G_{HM}}{K_{HM}+2G_{HM}}\right)}\right]^{-1} - \frac{G_{HM}}{6}\left(\frac{9K_{HM}+8G_{HM}}{K_{HM}+2G_{HM}}\right)$$

Saturated conditions:

In saturated sediments the bulk and shear moduli are obtained from applying Gassmann's equations (Helegerud, 2001, p. 222, eqns. 6.8 and 6.9; Dvorkin et al, 1999, eqn. 4, p. 1782; Mavko et al, 2009, p. 275; Gassmann, 1951);

$$K_{Sat} = K\frac{\phi K_{Dry} - (1+\phi)\frac{K_f K_{Dry}}{K} + K_f}{(1-\phi)K_f + \phi K - \frac{K_f K_{Dry}}{K}}$$

$$G_{Sat} = G_{Dry}$$

The elastic wave velocities (Helgerud, 2001, p. 222, eqns. 6.10 and 6.11) are related through

$$V_p = \sqrt{\frac{K_{Sat} + \frac{4}{3}G_{Sat}}{\rho_B}}$$

$$V_s = \sqrt{\frac{G_{Sat}}{\rho_B}}$$

where ρ_B is bulk density (Helgerud, 2001, p. 222, eqn. 6.12) calculated from

$$\rho_B = \phi\rho_f + (1-\phi)\rho_{solid}$$

The elastic constants for complex mineralogy are obtained through Hill's average formulas (see Dvorkin et al, 1999, p. 1783, eqn. 5, Helgerud, 2001, p. 222, eqn. 6.13)

$$K = \frac{1}{2}\left[\sum_{i=1}^{m} f_i K_i + \left(\sum_{i=1}^{m}\frac{f_i}{K_i}\right)^{-1}\right]$$

$$G = \frac{1}{2}\left[\sum_{i=1}^{m} f_i G_i + \left(\sum_{i=1}^{m}\frac{f_i}{G_i}\right)^{-1}\right]$$

Modifications for Gas Hydrate as a Component of the Pore Fluid

The approach to model gas hydrate as a component of the pore fluid is taken from Helgerud (2001, p. 223). See also Helgerud et al (1999, Approach A), Xu et al (2004, Model 4), Dai et al (2004, Model 4). The presence of gas hydrate in marine sediments is accounted for by assuming that gas hydrate is part of the pore fluid; thereby the stiffness of the dry frame is unaffected. Equations to represent the bulk modulus of the fluid and the bulk density of the rock sample are revised. Given the volumetric concentration of gas hydrate in the pore space as

$$S_h = \frac{C_h}{\phi}$$

we assume the gas hydrate and the pore fluid are homogeneously mixed. Then the effective bulk modulus of the composite pore fluid is written as the Reuss average of the water and gas hydrate bulk moduli, i.e.

$$K_f = \left[\frac{S_h}{K_h} + \frac{(1-S_h)}{K_f}\right]^{-1}$$

The composite fluid bulk density becomes

$$\rho_B = \phi\left[(1-S_h)\rho_f + S_h\rho_h\right] + (1-\phi)\rho_{solid}$$

The saturated bulk modulus is calculated from the Gassmann equation,

$$K_{Sat} = K \frac{\phi K_{Dry} - (1+\phi)\frac{K_f K_{Dry}}{K} + K_f}{(1-\phi)K_f + \phi K - \frac{K_f K_{Dry}}{K}}$$

The saturated shear modulus is $G_{Sat} = G_{Dry}$; furthermore, $G_f = 0$.

Modifications for Gas Hydrate as a Component of the Sediment-Frame Rock Matrix

The approach to model gas hydrate as a component of the sediment-frame rock matrix is taken from Helgerud (2001, p. 224). See also Helgerud et al (1999, p. 2022, Approach B), Xu et al (2004, Model 3), Dai et al (2004, Model 3). The presence of gas hydrate in marine sediments is accounted for by assuming that gas hydrate is a component of the dry frame which reduces the porosity and alters the solid phase elastic properties. The original porosity ϕ is used to calculate a reduced porosity,

$$\bar{\phi} = \phi - C_h$$

This changes the effective mineral modulus by adding an additional component to the sediment-frame rock matrix, thereby increasing the volume occupied by the solid matrix. The associated volume fractions for the rock matrix are revised,

$$\bar{f}_i = f_i \frac{(1-\phi)}{(1-\bar{\phi})}$$

The volume fraction associated with the individual gas hydrate component is

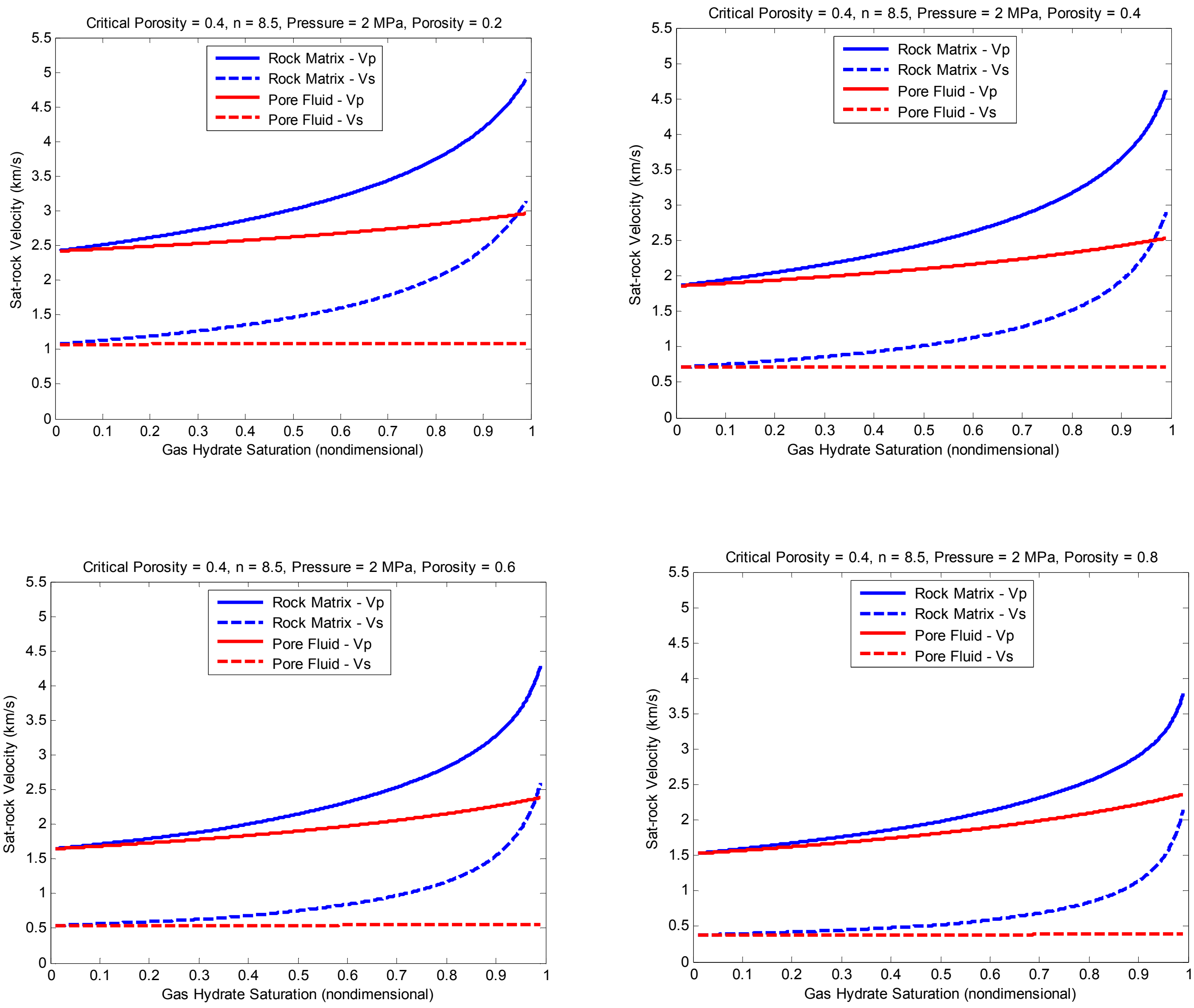
$$\bar{f}_h = \frac{C_h}{(1-\bar{\phi})}$$

The reduced porosity and the revised volume fractions are used in the equations for the baseline model in place of the original porosity and the unrevised volume fractions.

[The equations given here for $\bar{f}_i$ and $\bar{f}_h$ vary from those in Helgerud (2001, p. 224, eqs. 6.17 and 6.18) because of what is believed to be a typo].

Seismic Velocities as a Function of Gas Hydrate Saturation

Both versions, a) the sediment-frame rock matrix model and b) the pore fluid model, are run for a quartz-clay rock by varying the critical porosity and the average number of contacts per grain. With porosity held constant (0.20, 0.40, 0.60, 0.80) for each plot in Figure 10, the models show the response of compressional and shear wave velocities as a function of gas hydrate saturation level. The parameters fixed include critical porosity = 0.40; average number of grain contacts = 8.5; effective hydrostatic pressure = 2.0 MPa (depth approximately 128 m). The rock matrix composition is fixed at Quartz = 0.60 and Clay = 0.40.


Critical Porosity = 0.4, n = 8.5, Pressure = 2 MPa, Porosity = 0.2

Critical Porosity = 0.4, n = 8.5, Pressure = 2 MPa, Porosity = 0.4

Critical Porosity = 0.4, n = 8.5, Pressure = 2 MPa, Porosity = 0.6

Critical Porosity = 0.4, n = 8.5, Pressure = 2 MPa, Porosity = 0.8

Figure 10: Saturated-rock velocities versus gas hydrate saturation; Upper left plot, porosity of 0.2; upper right plot, porosity of 0.4; lower left plot, porosity of 0.6; lower right plot, porosity of 0.8.

Seismic Velocities as a Function of Depth for Synthetic Porosity Profiles

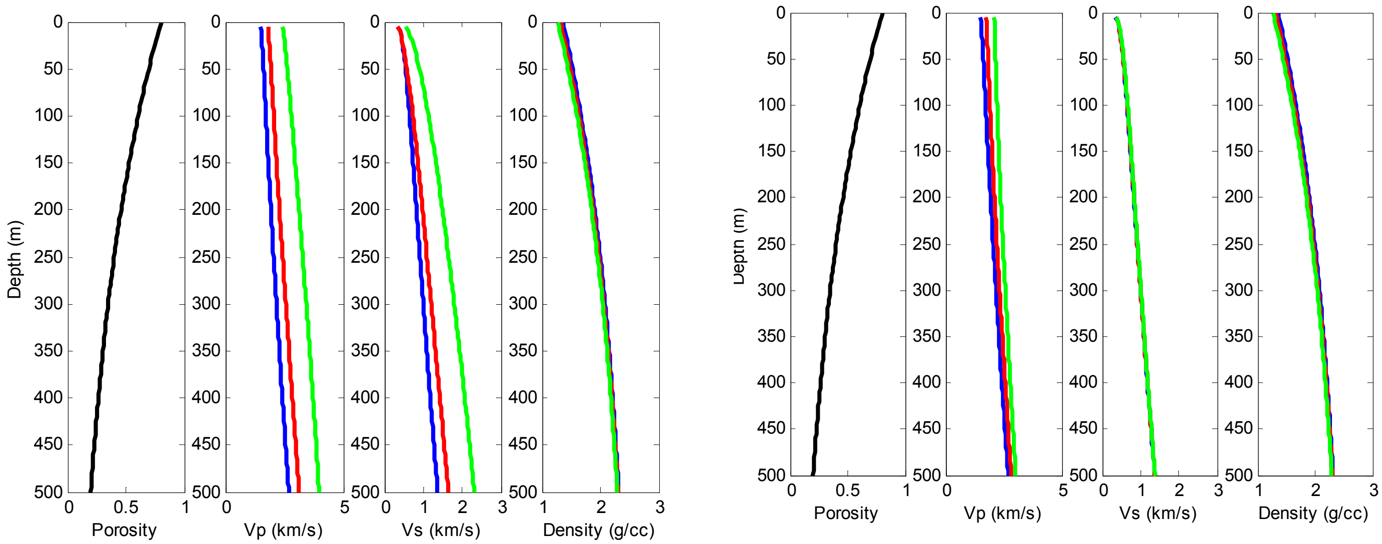
To explore the models further, we again use a quartz-clay rock, and compute a synthetic porosity profile as a function of depth below the ocean bottom. The porosity profile is computed with Athy's law (Athy, 1930) by specifying the porosity at the ocean bottom to be 0.80 and selecting a compaction coefficient such that the porosity is 0.20 at 500 m below the ocean bottom. Compressional and shear wave velocities, and bulk density of the rock, are computed as a function of depth for each of the two models at three different gas hydrate saturation levels (0.00, 0.40, 0.80).

In results for the rock matrix formulation of the model in Figures 11 and 12, both compressional and shear wave velocities are clearly separated as the gas hydrate saturation level is increased as the gas hydrate contributes to stiffness of the sediment-frame. The results are significantly different for the pore fluid formulation of the model in Figures 11 and 12. The compressional wave velocities show some increase as the gas hydrate saturation level is increased, but the increase is significantly less than in the rock matrix model. The shear wave velocities show only a slight increase as the saturation level is increased.

As would be expected, there is a modest decrease in the bulk density as the saturation level is increased due to the lower density gas hydrate replacing the higher density pore fluid. Low (Figure 11) and high (Figure 12) values for the bulk moduli, as shown in the Table below, were run.

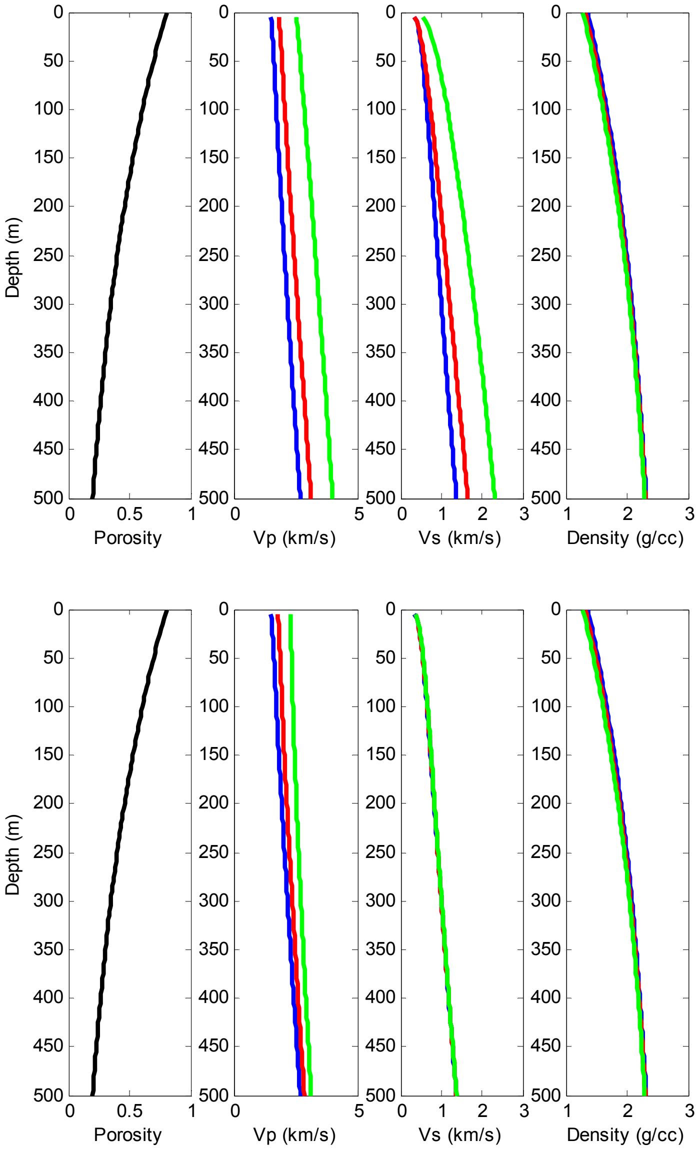
Table: Material Properties

Material	Bulk modulus, K (GPa)	Shear modulus, G (GPa)	Density (g/cc)
Low Hydrate, sI	5.6	2.4	0.90
High Hydrate, sI	8.1	3.3	0.91
Quartz (60 percent)	36.0	45.0	2.65
Clay (40 percent)	21.0	7.0	2.60
Fluid	2.25	0.0	1.04



Rock Matrix Model

Figure 11: Pore Fluid Model
Low hydrate bulk and shear moduli (K and G) from Table above for critical porosity = 0.40, n = 8.5; Blue, satHyd = 0.0, Red, satHyd = 0.40, Green, satHyd = 0.80.: Left plot, rock matrix model (Model 3); right plot, pore fluid model (Model 4).



Rock Matrix Model

Figure 12: Pore Fluid Model. High hydrate bulk and shear moduli (K and G) from Table above for critical porosity = 0.40, n = 8.5; Blue, satHyd = 0.0, Red, satHyd = 0.40, Green, satHyd = 0.80; Left plot, rock matrix model (Model 3); right plot, pore fluid model (Model 4).

Seismic Velocities as a Function of Partial Free Gas Saturation

In areas with gas hydrates, free gas may be trapped in the sediments beneath the base of the gas hydrate stability zone (Helgerud, 2001, p. 228). Curves for the equations of two models (Helgerud, 2001, p. 229-230), as modifications of the baseline model, are described here and plotted in Figure 13. The curves for the velocities are plotted versus water saturation where $S_w = 1 - S_g$. This approach is divided into homogeneously distributed gas (soft condition) and occurrence of gas patches much larger than the average pore size (stiff condition), fully surrounded by water-saturated sediment. These models, modifications of the Baseline model, are also from Helgerud (2001, p. 220-223).

Homogeneous Gas Saturation Model

This first partial gas saturation model assumes the free gas evenly distributed throughout the pore space (Helgerud, 2001, p. 228). To account for the presence of free gas in the fluid, the composite fluid bulk modulus is calculated as the Reuss average of the water and free gas bulk moduli.

$$K_f = \left[\frac{S_w}{K_w} + \frac{(1 - S_w)}{K_g}\right]^{-1}$$

This new fluid bulk modulus will be used in Gassmann's equations to calculate saturated bulk and shear moduli. The new bulk density becomes

$$\rho_B = \phi\left[(1 - S_w)\rho_g + S_w\rho_w\right] + (1 - \phi)\rho_{solid}$$

According to Helgerud (2001, p. 229), small amounts of free gas can have a dramatic effect on compressibility of the composite pore fluid because compressibility of free gas dominates.

Patchy Gas Saturation Model

To estimate an upper limit for the amount of free gas in the sediment at a given wave speed, Helgerud (2001, p. 229-230) presents the patchy gas saturation model. In patches, much larger than the scale of individual pores, the sediment is 100 percent saturated with either free gas or pore fluid. Therefore, the effective saturated bulk modulus is written

$$K_{Sat} = \left[\frac{S_w}{K_{SatW} + \frac{4}{3}G_{Dry}} + \frac{1 - S_w}{K_{SatG} + \frac{4}{3}G_{Dry}}\right]^{-1} - \frac{4}{3}G_{Dry}$$

where S_w is the average water saturation. The parameters K_{SatW} and K_{SatG}, for fluid and gas, respectively, are calculated from Gassmann's equations to represent the bulk moduli of the fully saturated sediment. The parameters are written

$$K_{SatW} = K\frac{\phi K_{Dry} - (1 + \phi)\frac{K_w K_{Dry}}{K} + K_w}{(1 - \phi)K_w + \phi K - \frac{K_w K_{Dry}}{K}}$$

$$K_{SatG} = K\frac{\phi K_{Dry} - (1 + \phi)\frac{K_g K_{Dry}}{K} + K_g}{(1 - \phi)K_g + \phi K - \frac{K_g K_{Dry}}{K}}$$

The equations from the homogeneous free gas saturation model, for bulk density and bulk modulus, are also used here.

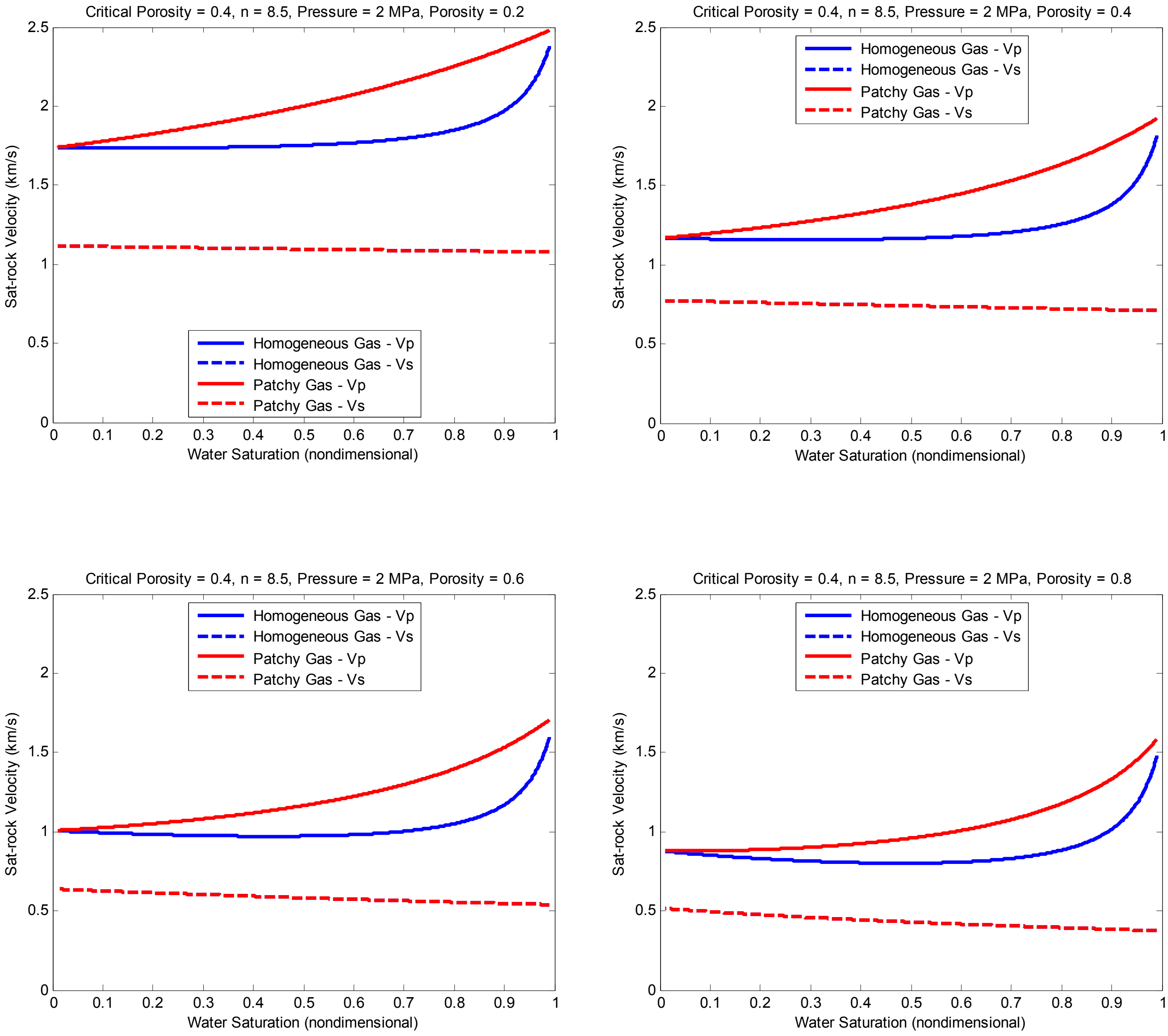


Figure 13: Saturated-rock velocities versus water saturation for a composite pore fluid that is a mixture of water and free methane gas; Upper left plot, porosity of 0.2; upper right plot, porosity of 0.4; lower left plot, porosity of 0.6; lower right plot, porosity of 0.8.

Directions for Seismic Inversion and Microfracture Analysis

For our analysis and evaluation of the MC118 site we will rely on the approach outlined in three recent papers (Xu et al, 2004; Dai et al, 2004; Dai et al, 2008). This approach is aimed at quantifying the presence of gas hydrates from seismic data in the absence of core and logging data. The steps of this approach follow petroleum systems engineering practices, and will include seismic impedance inversion and rock physics modeling of gas hydrates. We will follow that approach, and later will include analysis of the seismic data cube for microfractures.

Compute Porosity Profiles from Interval Velocities

Inputting seismic interval velocities into the model, we will first use the model to calculate a vertical porosity profile by assuming that the sediment does not contain gas hydrate or free gas; we will further analyze departures of the porosity profile from a monotonically decreasing porosity with depth, to assess whether the presence of free gas and / or gas hydrate have been detected.

Perform Seismic Inversion for Impedance

Perform full-waveform pre-stack inversion (using a genetic algorithm to guide parameter selection for modeled synthetics and evaluated fitness values for convergence) to recover 1D high resolution elastic property profiles (for P-wave velocities, Poisson's ratio, and density; i.e. generation of pseudo-well logs).

Microfracture and Fault Analysis

Pre-stack inversion results will also be targeted for use with enhanced attribute analysis to delineate fracture networks and fault structures.

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TASK 3: Near seafloor geology at MC118 using converted shear-waves from 4C seafloor sensor data.

Since no 4C data have been collected from the MC118 site, this task has not progressed visibly. However, an offer has been made by CGGVeritas, through the Texas Bureau of Economic Geology (BEG) for the use of their 4C nodes, no longer being used in their surveys. They are willing to donate the nodes to the Consortium for use in the 4C experiment as well as in future work. The dollar value of this industry cost sharing will be approximately $2.4 million (about $40,000 per module). BEG also located the engineer who has the most experience in operating these OBS modules. The services of this engineer now at Geokinetics, will have to be retained to provide training for CMRET personnel in the use of these nodes. Both the training and the transfer of the nodes are being investigated to determine if the time and resources required can be budgeted for completion of this project. While the nodes will have to be transported and refurbished and a deployment strategy established, this is a likely direction we will pursue in order to accomplish this task.

TASK 4: Geochemical investigations at MC 118: Pore fluid time series and gas hydrate stability.

Introduction

Monitoring geochemical constituents over time is an essential task to determine gas hydrate stability and to quantify the flux of methane from the hydrate reservoirs. Hydrate stability is controlled by high pressure, low temperature, moderate salinity, and saturated gas content. While the first three variables are often defined in studies of hydrate deposits, *in situ* CH_4 concentrations have not been reported. Pore-fluids surrounding gas hydrates are greatly under-saturated with respect to CH_4, indicating hydrate instability (Lapham et al., in press). Dissolution rates calculated from the *in situ* CH_4 data are significantly below those predicted by assuming thermodynamic equilibrium. These results indicate that seafloor hydrates are meta-stable and support the hypothesis that kinetic factors, such as oil coatings, biofilms, or the hydrate structure, control their stability. Such information is critical to truly evaluating the stability of worldwide hydrate deposits. We have conducted a series of lab studies to address these questions.

To carry out this investigation, several seafloor instruments have been designed and deployed to measure in situ methane gradients in both space and time. The Pore-Fluid Array (PFA) was developed to work in conjunction with geophysical techniques (Lapham et al., 2008). Two PFA'S are currently deployed at the MC-118 site. We have evidence that geophysical temporal variability is reflected in geochemical variability. Assessing geochemical variability will define and give meaning to observed acoustic anomalies. Data from the first PFA deployment show that dissolved methane concentrations vary over time and are sensitive to tectonic activity Prior to this deployment, such information was speculative. We have also built smaller, SSD-deployable pore-water instruments called peepers.

Hypothesis 1: Geophysical temporal variability will result in geochemical variability. By monitoring geochemical variability over time we can determine what is causing geophysical variability.
Approach 1: For 2009-2010, we requested funds to allow us to continue monitoring the two PFA devices installed at MC-118.
Progress to date: We have been unable to retrieve the PFA samplers at MC 118 due to issues with the SSD. However we have developed two new mini-PFAs and deployed and recovered them at a secondary site.

A secondary goal is to develop better osmo-samplers and test them as opportunities arise. We constructed two newly designed mini-PFAs that contain osmosamplers. Towards that end we participated in a John Tully Cruise in the Pacific Northwest and deployed these newly designed osmo-samplers.

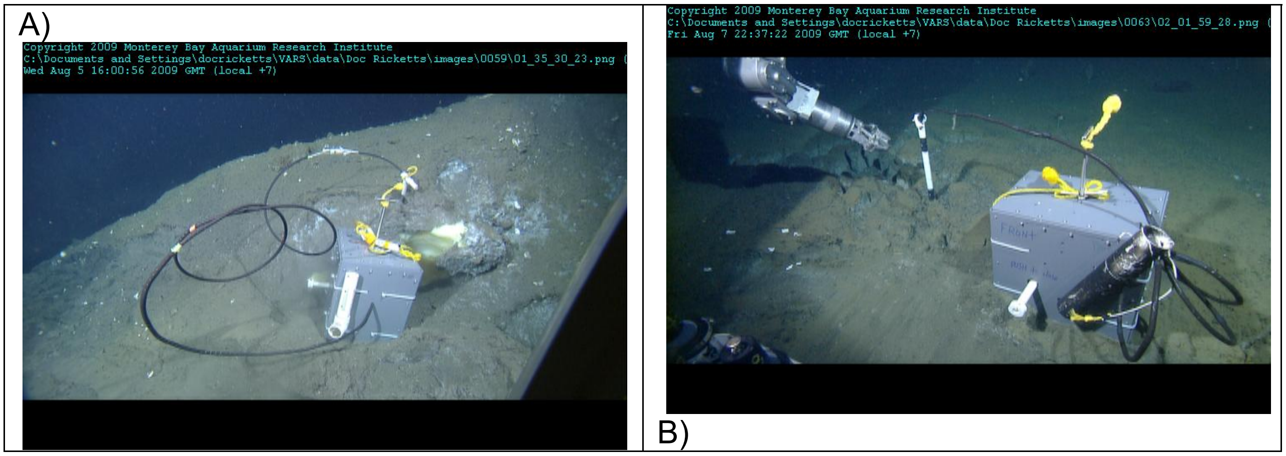


Figure 14: Seafloor pictures of mini-PFAs. Both were deployed with ROV Doc Ricketts (MBARI) and retrieved with ROV ROPOS. A) Barkley Canyon and B) Bubbly Gulch.

Design of the mini-PFAs. The mini-PFAs are essentially the same as the larger PFAs deployed at MC 118. There are four OsmoSampler pumps within the gray box in Figure

14. Each pump is attached to a port along a probe tip. The difference with this probe tip, compared to the larger PFA, is that it is short and can sample different sediment depth ranges from 2cm to 60cm. This allows for a more quantitative assessment of the methane flux coming out of the sediments. The samplers are capable of storing up to ten months of water samples. We can analyze them in sections providing a 6day resolution of the geochemical variability at the site over the previous ten-month period.

Test deployment. Two of these newly designed mini-PFAs were deployed off Vancouver Island in a gas hydrate site in August 2009 (Figure 15). In May 2010, using the ROV ROPOS, we retrieved them and are now currently processing the pore-fluids contained within the copper coils. Along with the OsmoSamplers, the mini-PFAs are equipped with bottom water temperature probes; temperature data from both instruments are shown in Figure 16. We have analyzed a section of one of the pumps (7.5cm sediment depth) for methane (Figure 17), ethane, and propane concentrations as well as for methane δ^{13}C (Figure 18).

In summary,

•2 mini-PFAs were deployed off Cascadia Margin in Aug 2009 and recovered in April 2010. Each had 4 OsmoSamplers each, with ~300 meters of copper tubing per sampler.

•One was placed at Barkley Canyon (850m water depth) to determine saturation state of methane within 4 cm of the hydrate surface.

•One was placed at a new site "Bubbly Gulch" (1250 m water depth) where the seafloor was bulging, creating cracks in the sediments that bubbles escaped from.

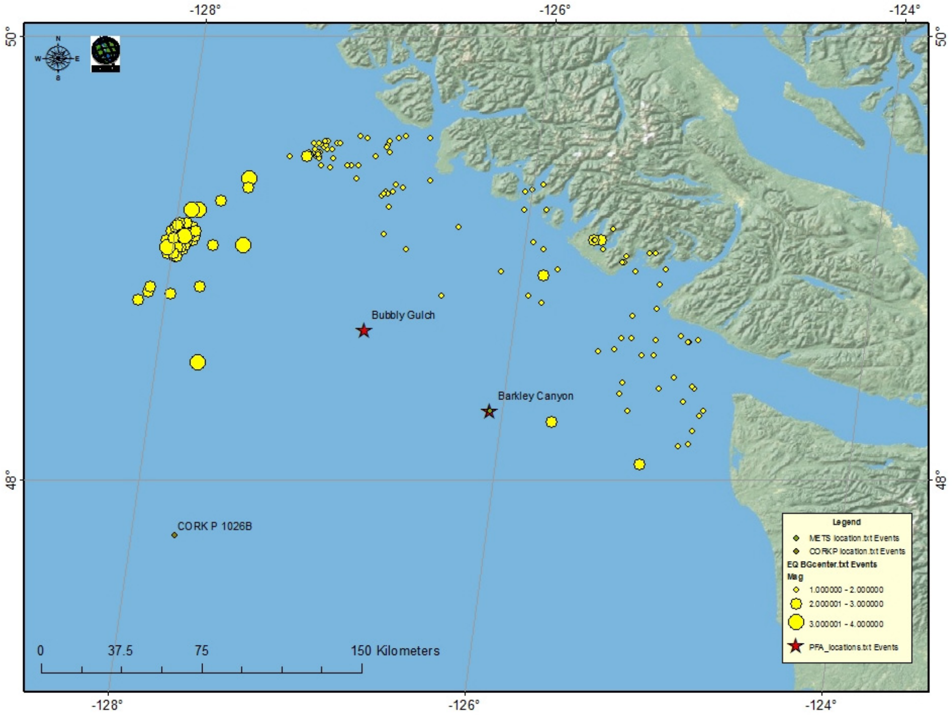


Figure 15: Location map of two mini-PFAs deployed offshore Vancouver Island (stars). The yellow circles show seismic activity within a 100km radius of the sites. The size of the yellow circle is proportional to earthquake magnitude. The location of the IODP CORK P is also shown.

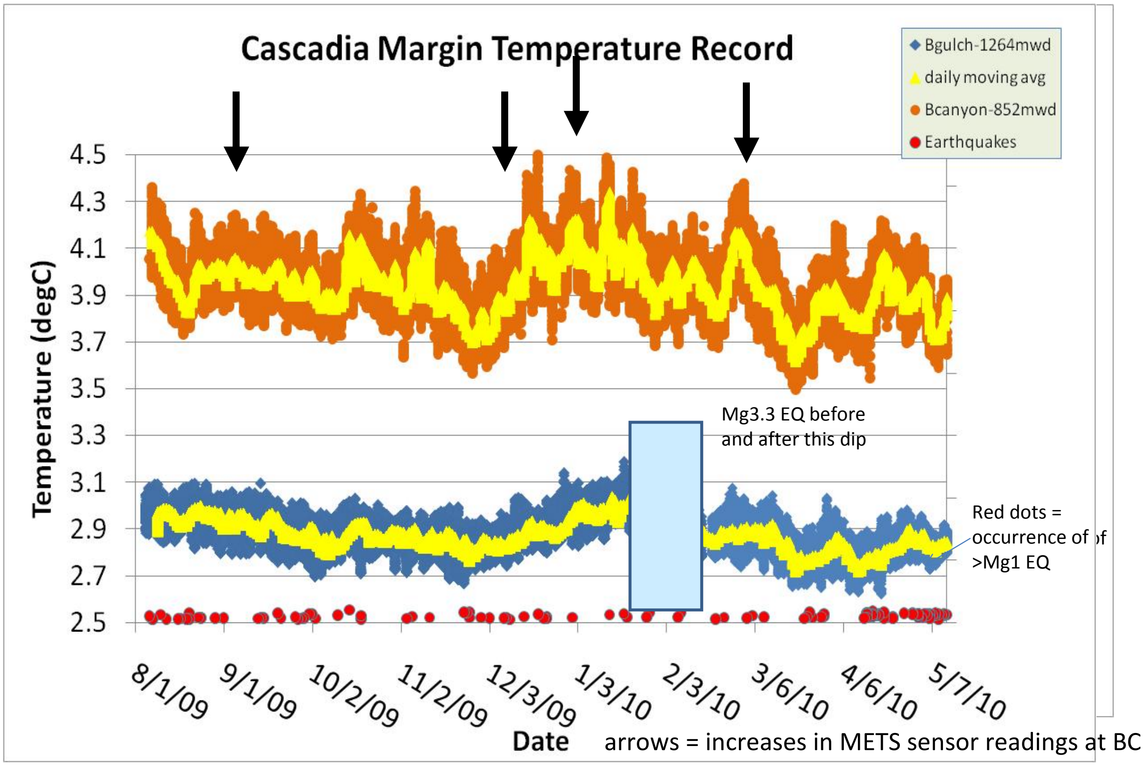


Figure 16. Data from both bottom water temperature probes deployed off Cascadia margin.

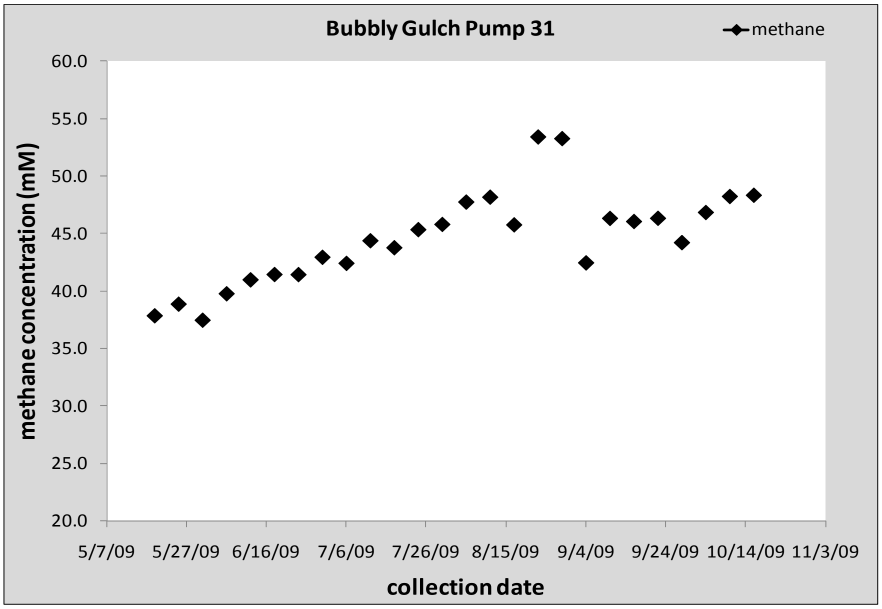


Figure 17: Methane concentrations over time.

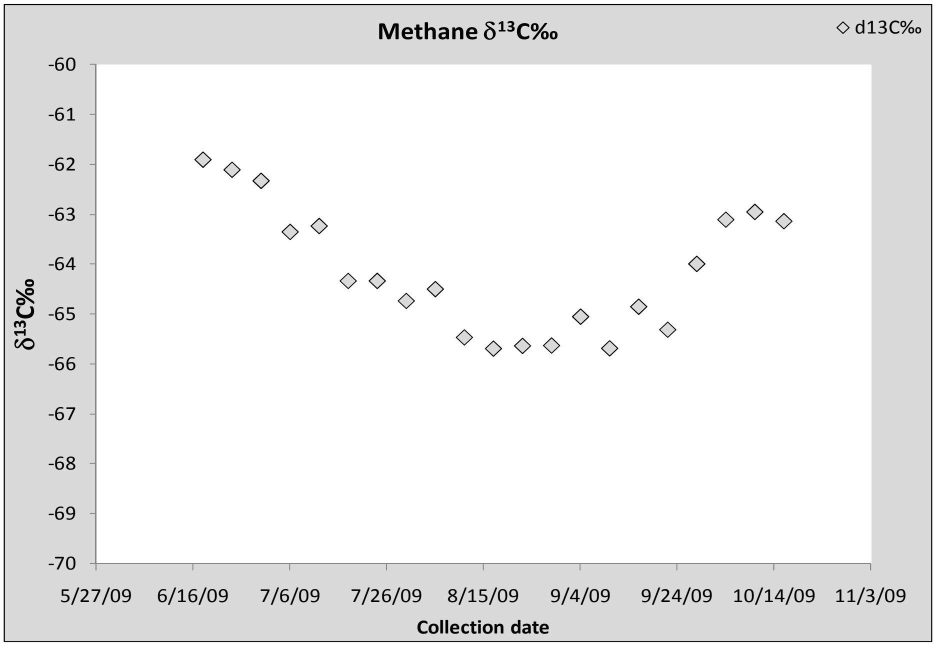


Figure 18: Methane stable carbon isotopic composition over time.

These results demonstrate that these instruments are capable of capturing geochemical variability at these sites with a resolution of approximately 6days. Such geochemical variability has been shown to be related to geophysical variability giving an indication of geophysical changes that may be occurring at this site (Lapham et al. 2008). The methane concentrations measured in these samples approach expected methane saturation values for this site (~70mM). To our knowledge this is the first time such high concentrations of methane have been measured from natural environments. While the methane $\delta^{13}C$ values that we measure at the test site are consistent with biogenic methane (ca. -64‰), we expect methane $\delta^{13}C$ from the MC118 deployment to indicate the contribution of thermogenic methane in this system, as has been seen during previous deployments (Lapham et al. 2008).

June 2010 Field work at MC-118.

We participated in an evaluation of three approaches for measurement of dissolved methane concentration in seawater overlying MC-118. These approaches were
1. Vial collection, storage and subsequent gas chromatography analysis on shore. Jeff Chanton
2. In situ Quadrapole Mass Spectrometry (Conducted by Tim Short and Ryan Bell, USF)
3. In situ Contros IR methane sensor, Ken Sleeper and Jeff Chanton
The results are presented in the Figures below:

Gas Chromatography

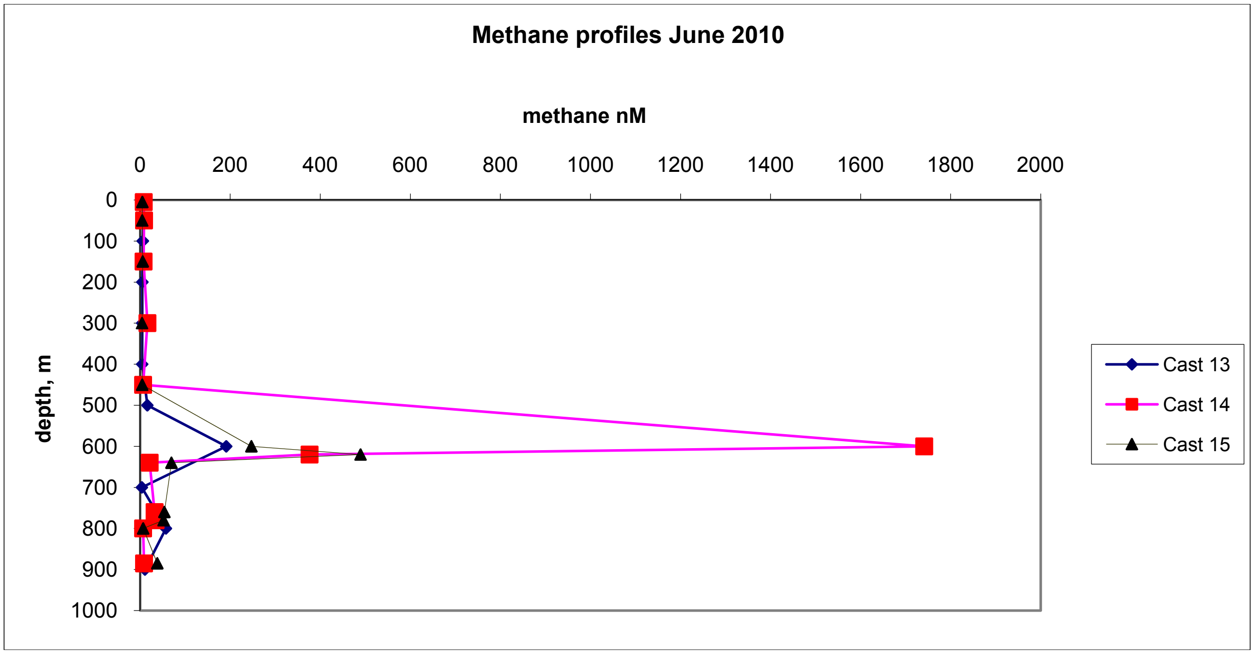


Figure 19a. Methane profiles (nM x axis) in the water column over MC-118 vx depth m on the y axis. As determined by vial collection and gas chromatography.

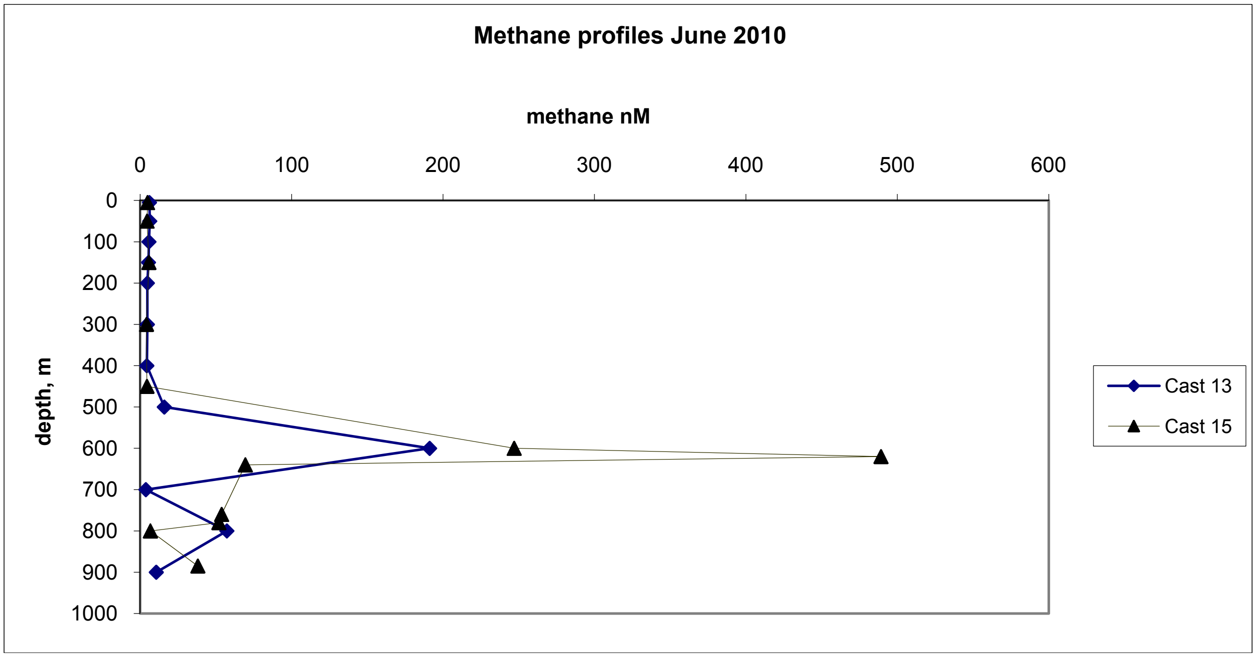


Figure 19b. Same as Fig 6a, but with full scale set at 600 nM.

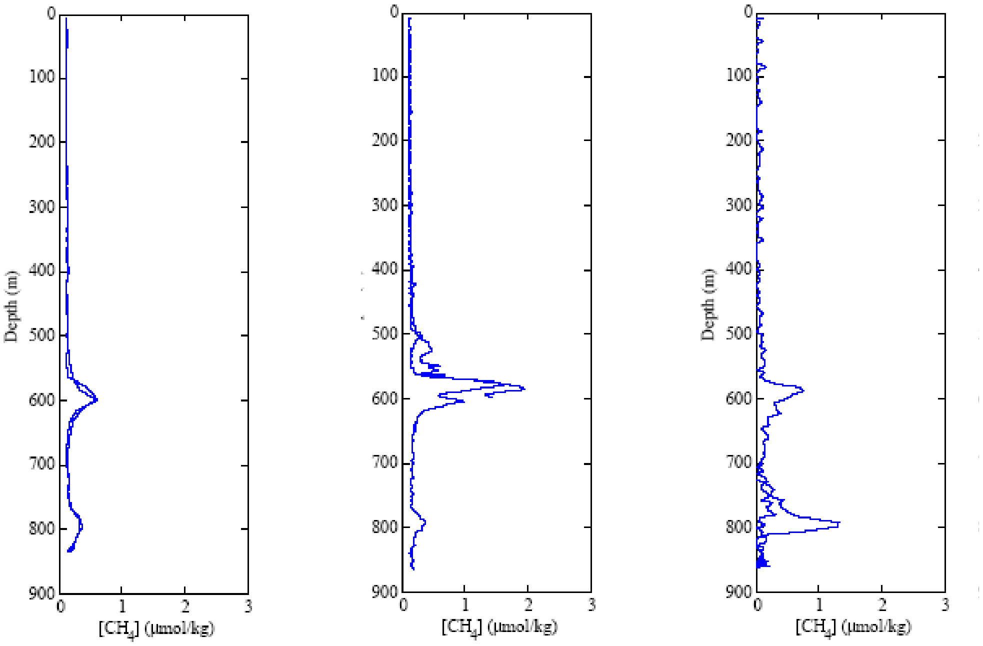
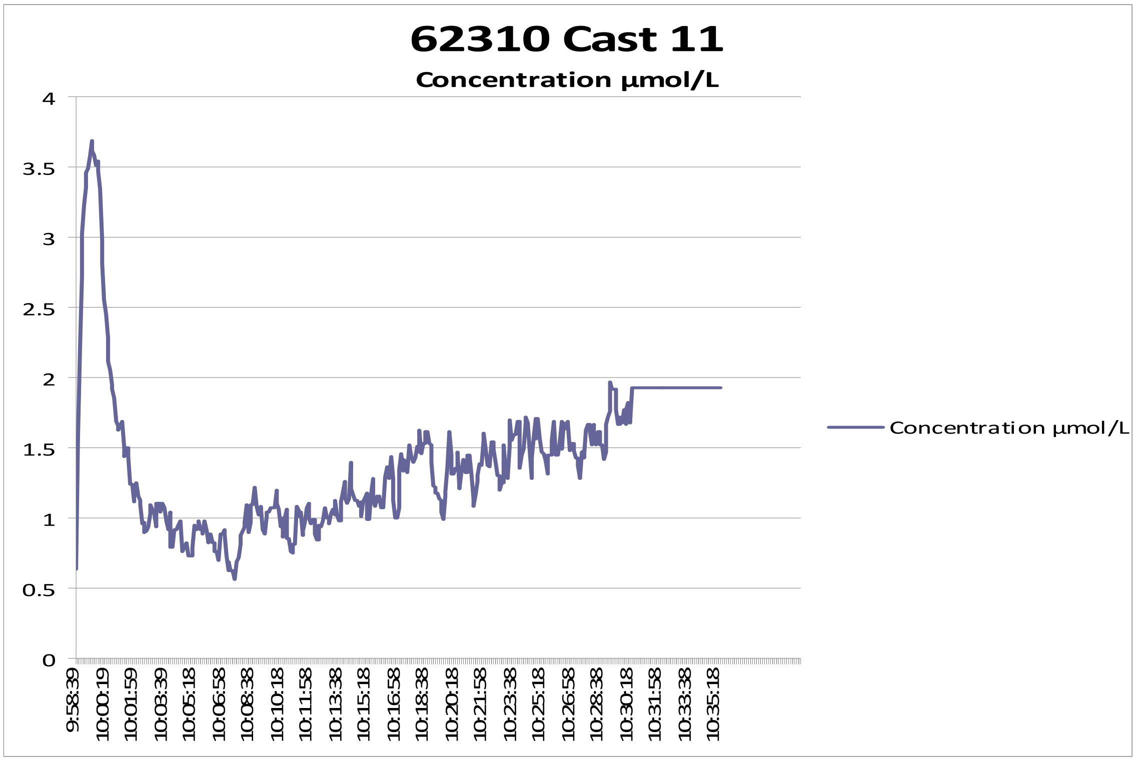
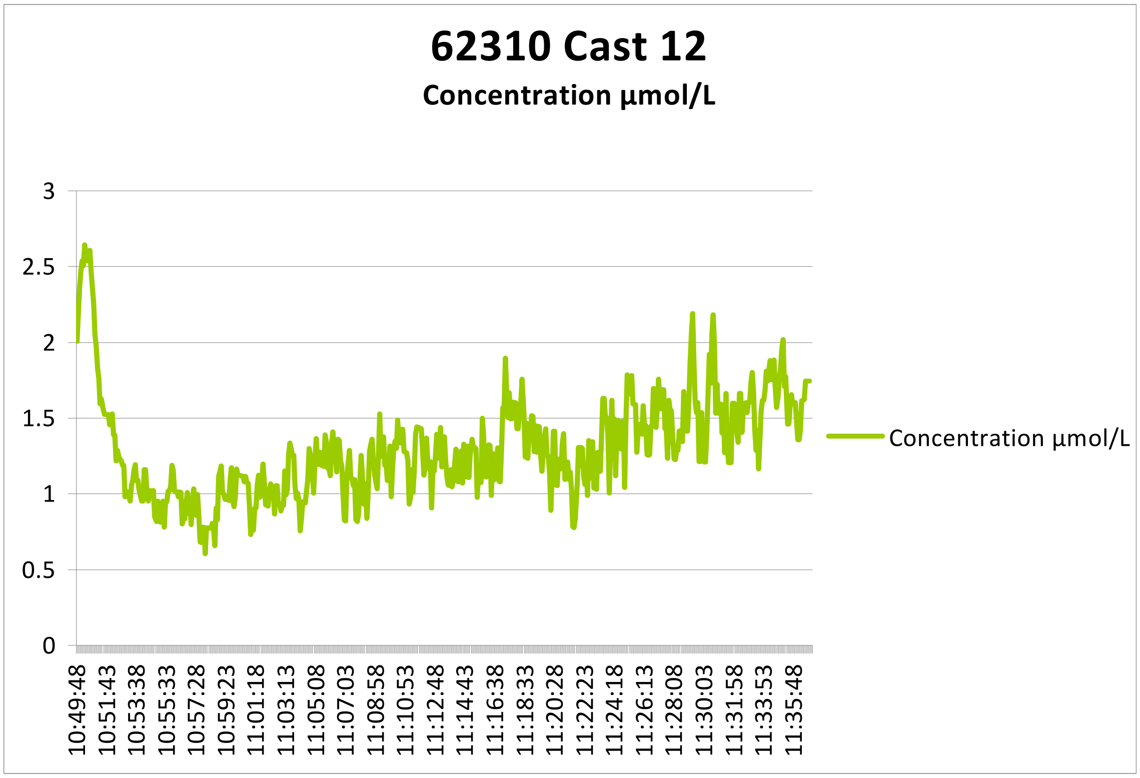
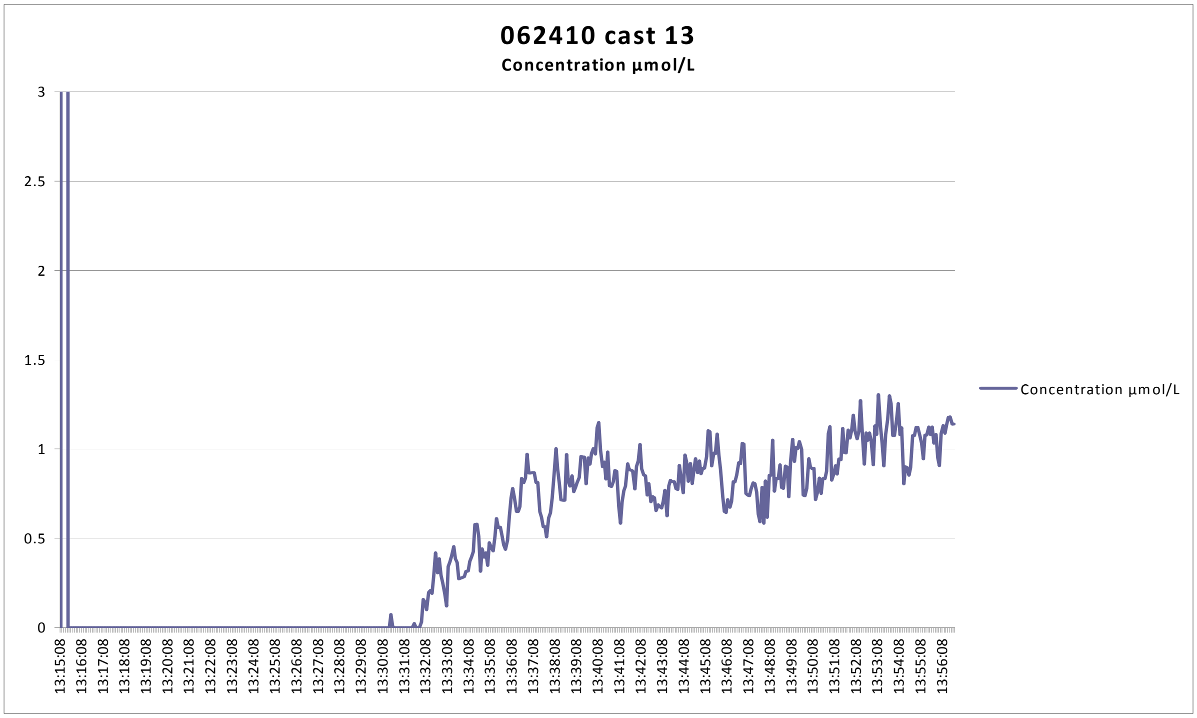


Figure 20. Three water column profiles were collected with Short and Bell's (USF) mass spectrometer on the same days. Depth in meters is on the y axis and concentration in uM is on the x-axis.

We also measured methane concentration in the water column with the new Contros Sensor. These figures follow:




62310 Cast 12
Concentration µmol/L
3
2.5
2
1.5
1
0.5
0
10:49:48
10:51:43
10:53:38
10:55:33
10:57:28
10:59:23
11:01:18
11:03:13
11:05:08
11:07:03
11:08:58
11:10:53
11:12:48
11:14:43
11:16:38
11:18:33
11:20:28
11:22:23
11:24:18
11:26:13
11:28:08
11:30:03
11:31:58
11:33:53
11:35:48
Concentration µmol/L


062410 cast 13
Concentration µmol/L
3
2.5
2
1.5
1
0.5
0
13:15:08
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Concentration µmol/L

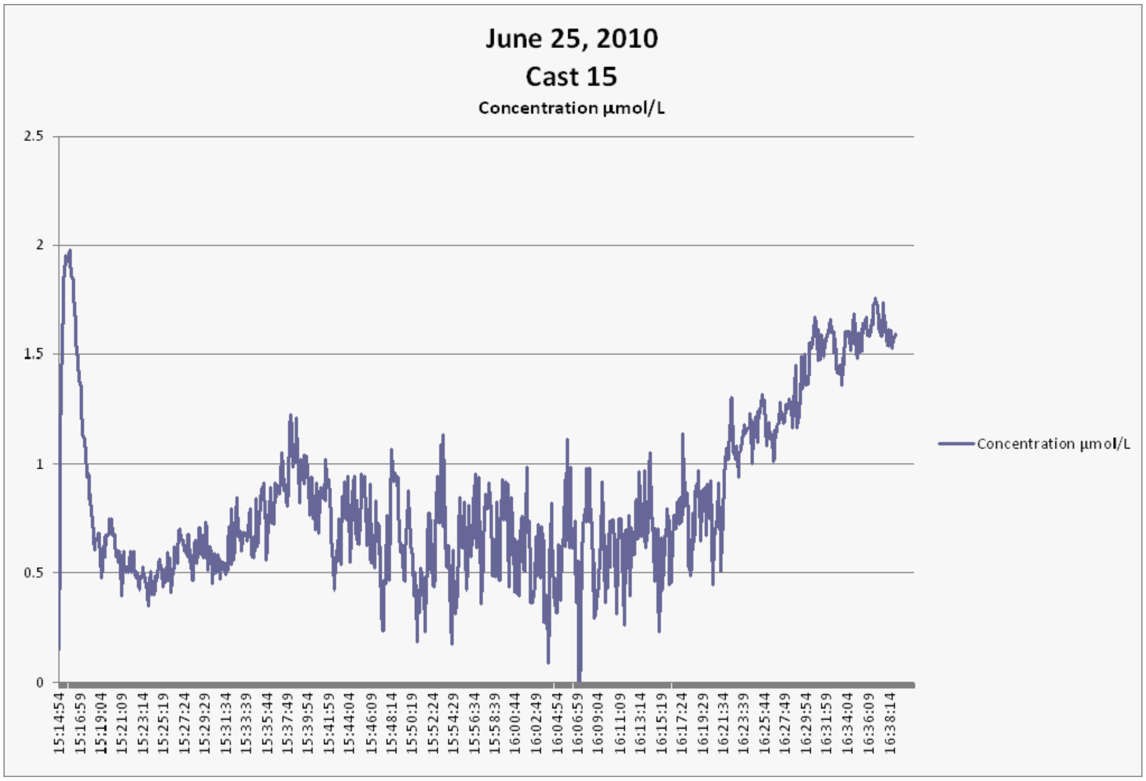
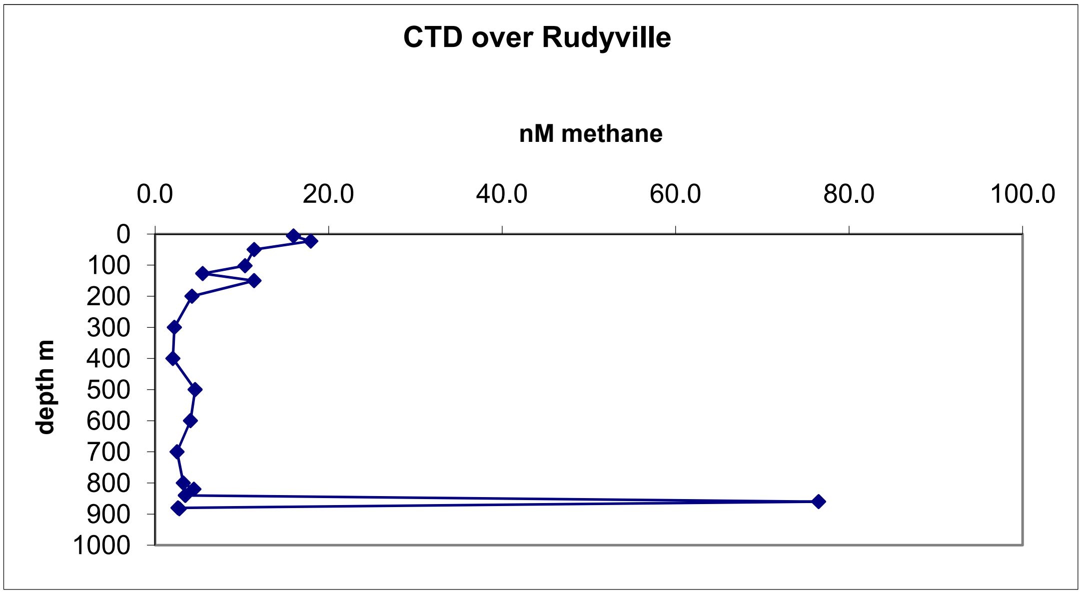


Fig. 21 a, b, c d. Contros methane sensor data. On the Y axis on these plots is methane concentration in uM, and on the x axis is time, which is related to depth as the sensor was lowered over the side over time mounted on the Rosette.

Agreement between the vial gas chromatograph approach and the mass spec is quite good. Both show nM concentrations in the water column and a spike approaching 1000 nM (1 uM) at about 600 meters. The Contros sensor generally shows greater concentrations (0.5 to 3 uM) and the shape of the profiles is different, showing maximum concentrations near the surface.

Concentrations at MC-118 were greater than they have been in past years, due to the oil and gas blow out at MC-252, about 8 nautical miles to the southeast. Figure 22 shows typical profiles from 2009 over a seep site (Fig 22a) and over background area (Fig. 22b).



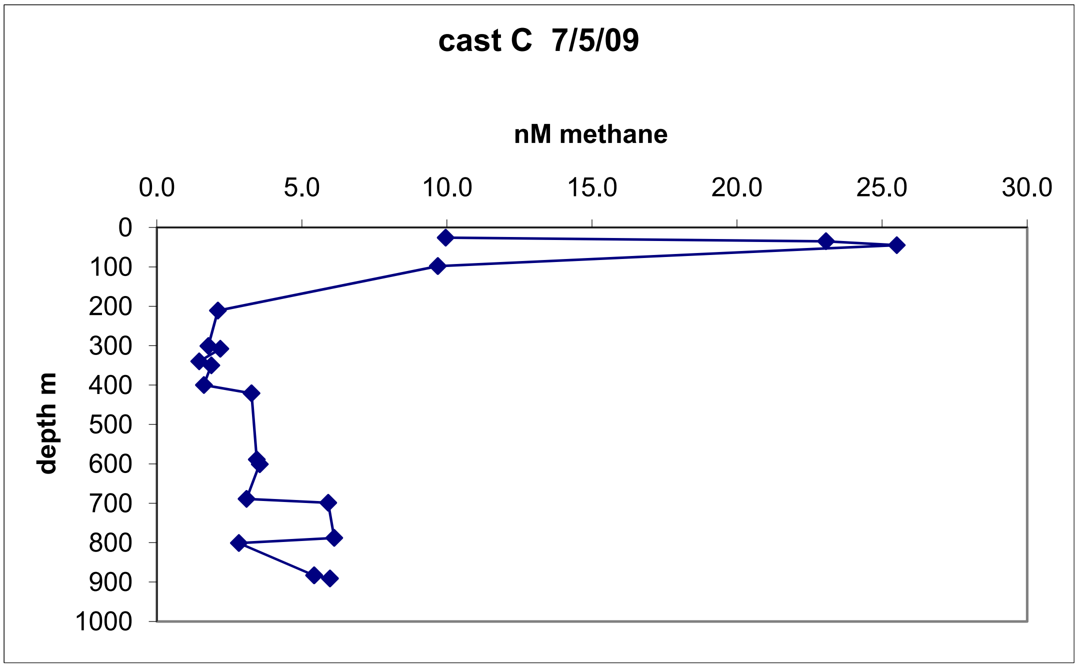


Figure 22. Water column methane concentrations from 2009 exhibit significantly lower concentrations.

Hypothesis 2: While within the appropriate temperature and pressure field hydrate deposits are "meta-stable" when exposed to in situ CH_4 *concentrations which are well below saturation. Under these conditions they dissolve at rates significantly below those predicted by thermodynamic equilibrium.*

The distinction between Disassociation and Dissolution.

There are three primary factors that control the stability of gas hydrates: pressure, temperature, and the concentration of the guest molecules in the surrounding environment. Pressure and temperature govern the stability of hydrate structure. When pressure regimes are too low or temperatures are raised too high hydrate becomes unstable and decomposes by **dissociation**. Dissociation is a relatively fast, often violent form of decomposition that results in the release of methane gas bubbles ($CH_{4\ (g)}$) to the surrounding water. If the pressure and temperature regime are within the range of hydrate stability, but the concentration of the guest molecule in the surrounding water is below saturation, the hydrate will become unstable and decompose by **dissolving** into the surrounding water. In this case, decomposition is typically at a slower rate and in a less spectacular manner than that observed during dissociation. It is the mechanisms that control dissolution in natural environments that are of most interest in the current proposal.

Rehder et al. (2004) and Hester et al. (2009) used artificially produced hydrate in natural conditions to measure the dissolution rate of hydrates in regimes where temperature and pressure conditions would not result in dissociation of the hydrate. Using synthetic hydrate in under-saturated seawater conditions resulted in dissolution rates for both experiments exceeding 100 cm/yr. However, observations of natural hydrate formations do not support such high rates of dissolution in under-saturated water conditions. Bush Hill is a large gas hydrate pingo located on the seafloor in the Gulf of Mexico in 570 m of seawater. The pressure at this site is ~840psi and temperature averages 7.9°C (MacDonald et al. 2005). These values are within the hydrate stability field, thus we would not expect hydrate dissociation to be occurring at this site. However, the surrounding seawater is under-saturated with respect to methane concentrations, thus we would expect that the hydrate outcrop should be dissolving into the surrounding seawater. Video equipment installed by MacDonald et al. (2005) monitored the Bush Hill hydrate formation over the period of a year. Despite changes in microbial mat cover and inhabitation by marine life, over the observation period, the shape and size of the hydrate formation remained relatively little changed, and certainly was not dissolving at a rate of 100 cm/yr. Similarly, a hydrate outcrop observed at Barkley Canyon (Cascadia Margin) was observed first in 2004 and again revisited in 2006, photographs of the hydrate formation indicate little change in the size over the two year period indicating that dissolution rates at this site are also less than 100 cm/yr. Lapham et al. (*in press*) provides further evidence of slow dissolution rates at a Barkley Canyon site. In their study, Lapham et al. (*in press*) estimated hydrate dissolution rates of outcropping hydrate to be ~3.5 cm/yr based on observations of an opening fissure in the hydrate formation. This value is approximately an order of magnitude lower than the calculated dissolution rate given the concentration of methane in the surrounding seawater assuming diffusion controlled dissolution (30cm/yr). They also provided dissolution rates for buried hydrates based on flux calculations from measured concentration gradients in water surrounding buried hydrates and found dissolution rates two orders of magnitude lower than those estimated from outcrops (Lapham et al *In press*).

Two mechanisms have been proposed to account for observed stability of hydrate in conditions where under-saturated methane concentrations should result in rapid dissolution of hydrate formations. The first proposed mechanism is the so-called “push-pop” model in which the dissolution of hydrate from the top of the formation is being approximately balanced by resupply of hydrate formation from the bottom as gas migrating upward through the sediment enters the hydrate stability zone (HSZ) and begins to form hydrate from the bottom of the formation. However, Lapham et al. (*in press*) measured methane concentrations in the porewater of the sediment drape overlying the hydrate formation at the Barkley Canyon and Mississippi sites. They found uniformly low methane concentrations (~0-5 mM). Thus it does not seem that the hydrate formations are rapidly shedding methane to the overlying seawater, indicating that the "apparent" natural hydrate stability at these sites is not the result of resupply of hydrate from below approximately balancing dissolution of hydrate to the overlying seawater. Using sulfate concentrations and $\delta^{13}C$ values to constrain anaerobic methane oxidation rates, Lapham et al. (*In press*) found that although microbial methanotrophy was likely occurring at these sites, even accounting for this consumption of methane the porewaters surrounding the hydrate are still highly under-saturated with respect to methane. The second hypothesis to explain the apparent stability of natural hydrate in under-saturated water is that conditions in or components of natural hydrate are acting to slow the dissolution rate below what would be expected by pure diffusion controlled dissolution.

Laboratory Component

In summary, studies examining dissolution of artificial hydrates have found rates in excess of 100cm/yr (Hester et al. 2004, Bigalke et al. 2009, Rehder et al. 2009), however observations of natural hydrate formations have given rise to estimates of dissolution rates an order of magnitude lower (MacDonald et al. 2005; Lapham et al. *in press*). We wish to examine factors that could be acting to inhibit dissolution of gas hydrates to understand the controls on dissolution in the natural environment.

We initially hypothesized that the gas composition of natural hydrates could be acting to slow dissolution rates. We know that incorporation of ethane and propane into the hydrate structure (str-II) act to stabilize the hydrate, we were interested in discovering if this enhanced stability also contributes to slow dissolution of the hydrate. In order to test this possibility we measured the dissolution rate of pure methane (str-I hydrate) in the lab. We calculated a flux of 0.14mM/hour as the average of two experiments (Figure 19a) which gives us a dissolution rate of 30cm/yr. We then measured the dissolution rate of a mixed-gas (C_1-C_3; str-II) hydrate to measure whether the increased stability of str-II hydrates would also result in slower dissolution rates. However, we calculated a similar dissolution rate of 27 cm/yr (Figure 19b).

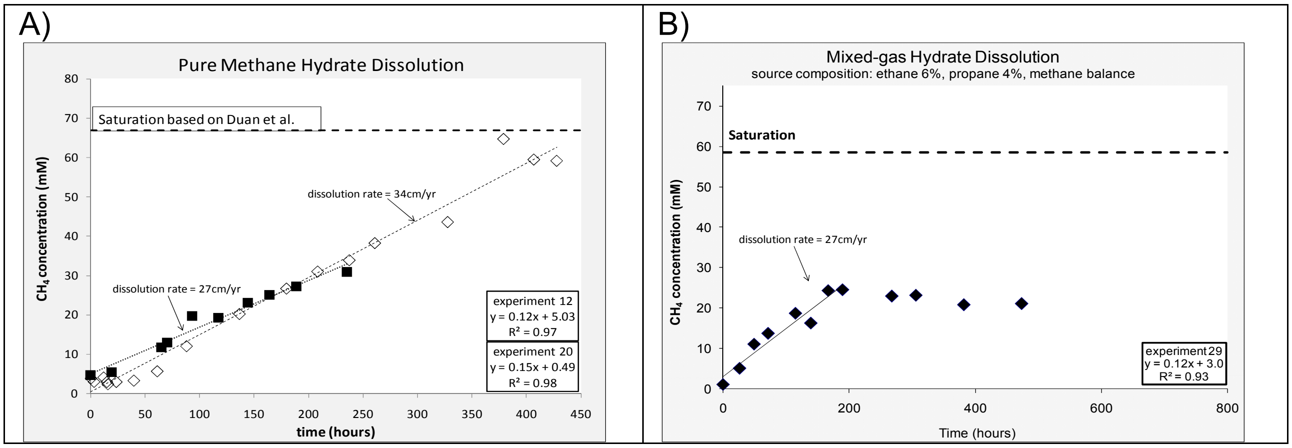


Figure 23. Results of Dissolution Experiments Comparing Dissolution Rates of Str-I and Str-II hydrates. In panel A are the results of two (replicated) experiments measuring the dissolution rate of methane (strI) hydrate in the lab. Panel B gives the results for str-II (mixed-gas) hydrate.

Thus, we failed to find any difference in dissolution rates of mixed-gas and pure methane hydrates formed in the lab demonstrating that the presence of C_2 and C_3 hydrocarbons does not slow the dissolution rate of hydrate.

Another potential factor that could be inhibiting hydrate dissolution is the presence of oils. Such oils on the surface of hydrate could act as “armoring agents” to slow dissolution rates. We are currently conducting experiments to determine dissolution rates of hydrates coated in an oil slick. We intend to compare dissolution results to those we obtained from oil-free samples to evaluate whether such armoring has a significant impact on dissolution rates.

Publications

Lapham, L.L., J .P. Chanton, R. Chapman, and C.S. Martens. Methane under-saturated fluids in deep-sea sediments: Implications for gas hydrate stability. Accepted for publication Earth and Planetary Science Letters. In press.

Lloyd K*., G*. Lloyd, D. B. Albert, J.F. Biddle, J.P. Chanton, A. Teske. Spatial Structure and Activity of Sedimentary Microbial Communities Underlying a *Beggiatoa* spp. Mat in a Gulf of Mexico Hydrocarbon Seep. PLoS ONE, Volume: **5** Issue: **1** Article Number: **e8738** Published: JAN 15 2010

Luzinova, Y, G. T. Dobbs, L. Lapham, J. Chanton, B. Mizaikoff. Detection of cold seep derived authigenic carbonates with infrared spectroscopy. Submitted to Marine Chemistry, July, 2010.

Cruise participation

August 2009. Laura Lapham to deploy mini-Pore Fluid Arrays offshore Vancouver Island- testing of instruments to be deployed at MC118

March 2010. Rachel Wilson, James Nelson to MC 118 to retrieve and replace PFA sampler box. Not successful in getting to site.

June 2010 Jeff Chanton to MC 118 to retrieve and replace PFA sampler box. Not successful in getting to site. Water column work successful.

April 2010, to Rachel Wilson to Cascadia Margin to recover osmo samplers, as part of the mini-PFAs. Two instrument packages were picked up, which verified new design usefulness. These mini-PFAs can now be deployed at MC 118, possibly from the surface with a camera relay.

Meetings

DOE hydrate programs meeting, Atlanta, January 2010. Lapham, L.L., J. P. Chanton, C.S. Martens, A. Teske, P. Higley, R. Camilli, N. Farr, J. Noakes, S. Noakes, T. Short, R. Bell, S. Joye, M. Bowles, and MC 118 consortium geochemistry group. Update on geochemistry of MC 118. Oral presentation.

DOE hydrate programs meeting, Atlanta, January 2010. Lapham, L.L., J. P. Chanton, R. Wilson, R. Bell, T. Short, I. R. MacDonald, and C.S. Martens. Gas hydrate dissolution: In situ and laboratory experiments. Poster presentation.

AAPG meeting April 2010. Lutken, C. B., L. Macelloni, L. Lapham, S. Caruso, M. Lodi, R. Camilli, V. Asper, A. Dierks, C. Knapp, and J. Knapp. Monitoring seafloor morpho-geological evolution of the MC 118 hydrate/carbonate mound via multiple AUV missions.

ASLO February 2010. Holmes, B, L.L. Lapham, J. H. Knapp, C.C. Knapp, C.A. Brunner, L. Macelloni, C. Lutken, and J.P. Chanton. Correlation of microbial activity and methane sources with shallow faults in the Gulf of Mexico. Poster presentation.

Gordon Research Conference on Gas Hydrates, New Hampshire June 2010. RM Wilson, LL Lapham, RT Short, RJ Bell, and JP Chanton. Using continuous mass spectrometry to monitor dissolution of artificial methane and mixed-gas hydrates. Poster presentation by Wilson.

Goldschmidt June 2010, Knoxville, Tennessee, Lapham, L, Wilson, R., Short, T, Bell, R and Chanton, J. Mechanisms Influencing Hydrate Dissolution Rates in Under-saturated Systems. Oral presentation by Wilson.

International Geoscience & Remote Sensing Symposium 2010. Garcia-Pineda, O., I. MacDonald, W. Pichel, X. Li, B. Zimmer, and L. Lapham. Using SAR to estimate spatial and temporal variability of oil output from natural hydrocarbon seep formations. Abstract submitted.

Gulf Coast Association of Geological Societies 2010 Conference. Macelloni, L., L. Lapham, S. Caruso, C. Lutken, and J. Chanton. Seafloor bio-geological and geochemical processes spatial distribution as proxy to evaluate fluid flux regime and time evolution of a complex carbonate/hydrates mound, northern Gulf of Mexico, submitted abstract.

TASK 5: Automated Biological/Chemical Monitoring System (ABCMS) for Offshore Oceanographic Carbon Dynamic Studies. Development of a Marine Lander Survey Vehicle for Gas Hydrate Research

The University of Georgia has assigned the University of Mississippi/DOE grant number 037757-02 (November 2009). In addition, a contract has been established (January 2010) between the University of Georgia (UGA) and SRI International (SRI) to support SRI effort in the integration of in situ mass spectrometry with microbe sampling for gas hydrates research. The beginning and end dates of the project period are November 2009 through August 2010, respectively. General schematics have been drawn for the

Lander components which include the underwater mass spectrometer and multi filtration system. The Lander and surface vessel will be linked by the same fiber optic cable as the SSD ROV. Design specifications for the electronics interfacing the fiber optic cable and Lander instrumentation have been finalized and the components are now being tested.

Individual filter assemblies, or packs, have been constructed (Figure 24) and will be installed in the Lander in groups of 30. Over 60 filter packs have been constructed to allow two complete filter groups to be deployed (one at a time) prior to disassembly, cleaning and reloading. The filter packs will be prefilled with distilled water to prevent contamination from surrounding water during deployment. Once deployed and upon pump activation, the distilled water will be displaced with seawater at the desired depth and location. The pump will continue to move seawater through the filter until the desired volume has been reached or the filter has been clogged. After collecting a sample, the pump injector can move from one filter pack to another so that multiple filters can be collected with varying pore sizes per sampling location. Upon recovery, the filter packs have pressure relief valves that will aid in equalizing the internal pressure that could potentially build as a result of deep water sampling.

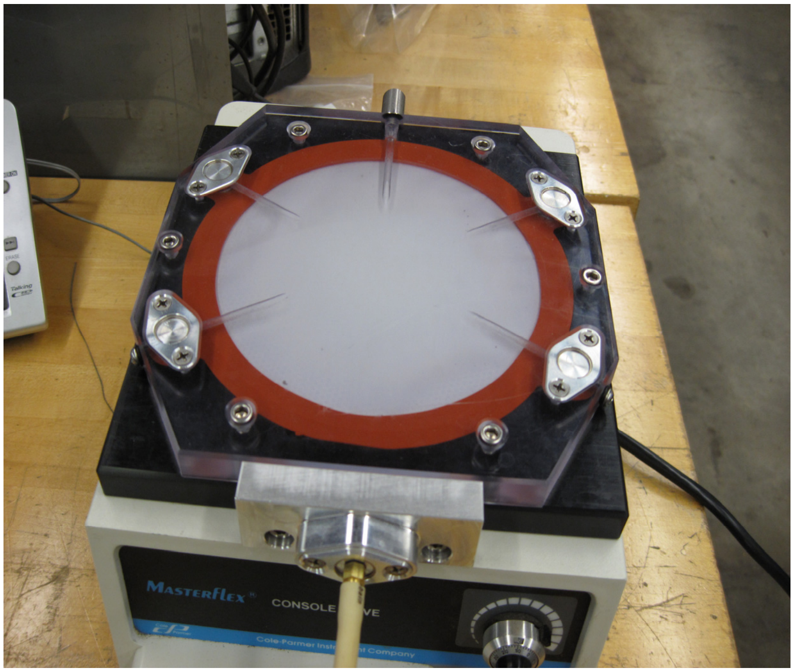


Figure 24. Filter assembly mounted on distilled water pumping station.

SRI has coordinated with UGA to ensure that their existing underwater mass spectrometer (UMS) will be compatible with the new Lander system. The existing UMS will mount into the Lander frame and communication will plug directly into the Lander electronics pressure housing. From there, communications with the UMS will be through the fiber optic cable. SRI has also begun to investigate methods to improve detection limits for methane using UMS analysis by implementing a cold trap system between the membrane inlet and the ion source of the mass spectrometer. Major components have been identified and orders are currently being placed.

To further test the UMS for methane detection, SRI deployed the UMS at MC118 in June, 2010 to investigate potential changes in dissolved gas and volatile organic concentrations in the water column that may be due to the Deepwater Horizon spill. Data from three vertical profiling casts were collected, and in each case the data indicate elevated concentrations of methane (over previous profiling casts performed before the spill in approximately the same area) at approximately 600 m and 800 m depths. Figure 25 shows raw UMS data (shown as a time series of intensity of m/z 15, diagnostic of methane) for the one of the profiling casts at a site within MC118.

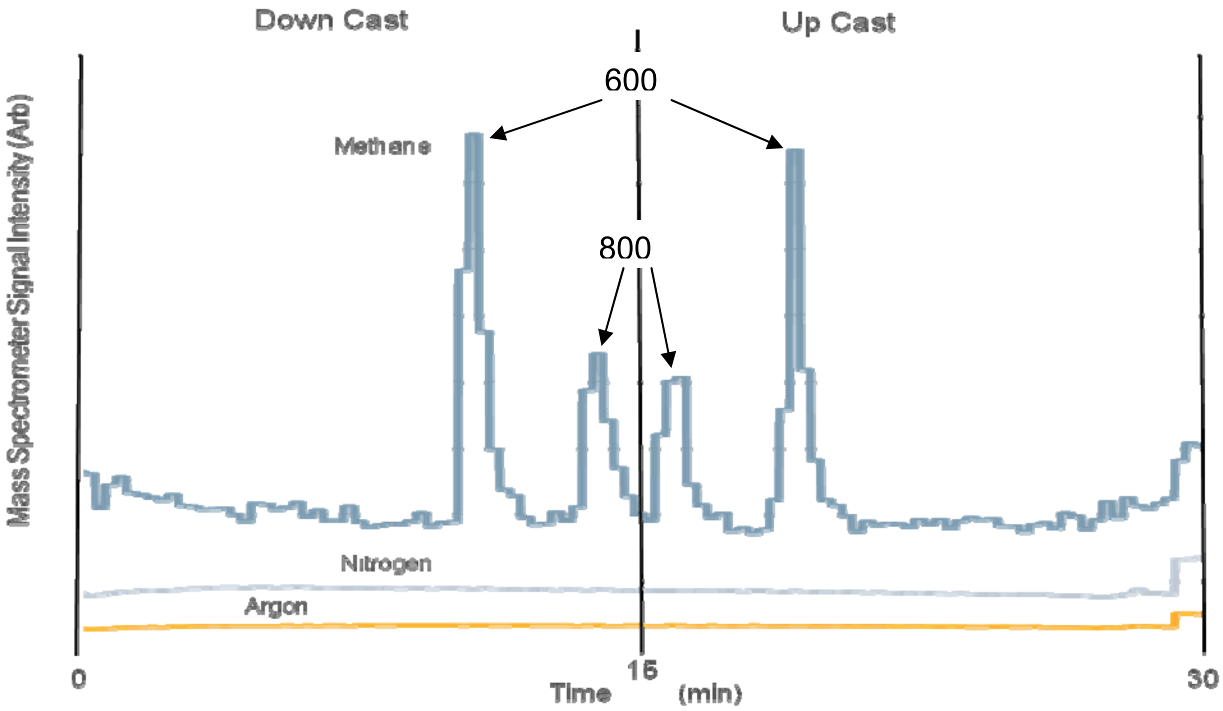


Figure 25. Time series UMS data for m/z 15 (diagnostic for methane) for a vertical profiling cast at MC118. Also shown are concurrent data for nitrogen and argon. The time period for the down cast and up cast are noted on the figure.

TASK 6: Quantification of Seep Emissions by Multibeam Sonar at MC118.

In preparation for a late September cruise, the field GC has been set up to measure methane and other n-alkanes from a sample pump on the laboratory roof. This allows continuous monitoring and improvement of the gas chromatograph’s performance, which now allows better than 1% accuracy on methane, ie, the system can detect methane concentrations of 10 ppb above ambient. We are collecting these data to better understand the diurnal transport of hydrocarbons from the seep fields by sea breezes and night circulation.

In addition, work has continued on the equilibrator, to allow real-time aqueous methane measurements simultaneous with gas chromatography measurements of atmospheric methane. The high efficiency of the equilibrator created a problem where the extracted gas was too low pressure for injection through a check valve into the gas chromatograph. A new system has been designed and built using an air pot (a piston valve) with a solenoid actuator to compress the equilibrator output and therefore increase the sample pressure to allow injection into the gas chromatograph.

Analysis of sonar rotator data collected in the Arctic continues, and student Chris Stubbs, is close to finishing his thesis. The rotating multibeam sonar scanner (ROSSCAN) currently is ready for the field deployment with testing planned for late August. A compass has been added to the system to provide precise direction information, previously this pointing information had to be derived from the rotator. In shallow water, the system can be deployed on a lander in Pogo mode to navigate ROSSCAN towards the target for observations. Although we are hoping ROSSCAN will be ready for autonomous deployment and recording, this is pending renewal funding for embedded computer purchase. An alternate approach, which will be implemented in any case, is to interface ROSSCAN with the ROV and pipe the data shipboard. This approach will be used in the first deployment to ensure that data is in fact being collected.

If time permits, we will deploy an excitation-emission matrix fluorometer system in the Gulf of Mexico; the spectrometer is available; however, funding is necessary for the housing and thus is pending. The excitation-emission matrix fluorometer will allow simultaneous measurement of CDOM, oil, and chlorophyll, either at the seabed or from a total platform near the sea surface.

TASK 7: Modeling a carbonate/hydrate mound in Mississippi Canyon 118 using modified version of (THROBS).

Introduction

The hydrate mound in Mississippi Canyon Block 118 (MC 118), as described by McGee et al. (McGee, T. et al., 2008. Structure of a carbonate/hydrate mound in the northern Gulf of Mexico, paper to be presented at the International Conference on gas Hydrates, Vancouver, Canada, July 6-10, 2008), contains mostly Structure II thermogenic hydrates formed by gases upflowing along a nearly vertical fault system extending from a salt diapir that underlies several hundred meters beneath the hydrate mound. The surface of the hydrate mound is characterized by several crater clusters; these crater clusters have been grouped into three major complexes based on topographic relief and gas venting (McGee et al., 1998). At present, the SE complex exhibits no venting activity; the NW complex has moderate activity, and the SW complex shows moderate to high venting activity. The venting activity has most likely changed over time. In addition to variable venting activity over time, the following observations are relevant to the modeling of hydrates at this site:

1. Salinities as high as 5 times that of sea-water have been recorded around the vents in the NW complex. High salinity and gas venting suggests the presence of 3-phase conditions (gas + hydrate + liquid).

2. Chemical composition of vent gas is different from that of the hydrate. It has been suggested that the difference is due to molecular fractionation (Roger Sassen, quoted

by McGee et al., 2008). Treatment of this aspect will require a “compositional” simulator.

3. Presence of multiple BSRs. It is possible that this is due to the existence of gas hydrates that are stable to greater depths (higher temperatures?) than that encountered above the “shallowest” BSR. Clearly, a compositional simulator is needed for modeling this phenomenon.

4. Acoustic wipeout zones, observed in seismic profiles, have been interpreted to indicate the possible presence of free gas (“chimney” flow) and/or other inhomogeneities (e.g. carbonate/hydrate blocks in the sediments). Modeling of chimney flow and/or other inhomogeneities can only be done by a multi-dimensional hydrate simulator.

Prior to the start of Year 1 (2008-2009) of SAIC effort, our hydrate simulator (THROBS) was restricted to one-dimension and Structure I methane hydrate. It was recognized that THROBS will have to be generalized in several respects in order to treat the phenomena of interest. Required changes include:

1. Incorporation of the stability curve and other hydrate properties (heat of melting, hydration number, and thermomechanical properties) for structure II hydrates.

2. Replacement of methane gas equation-of-state (EOS) and gas solubility relationship by an EOS and solubility curve that reflects the gas composition.

3. Development of a multi-dimensional version of THROBS.

Given the fiscal constraints, SAIC undertook a limited research effort during the first year (2008-2009). Specifically, we incorporated structure II hydrate stability curve and relevant properties (item 1 above) into THROBS simulator. The gas mixture forming the hydrate was represented as a single gas. The modified THROBS simulator has been used to model (1) the hydrate distribution above the shallowest BSR, (2) presence of high salinity fluids within the hydrate stability zone, and (3) gas venting at the sea-floor. The work performed during Year 1 is described in a report by Garg and Pritchett (S. K. Garg and J. W. Pritchett, Modeling Studies of Hydrate Mound, Mississippi Canyon 118, Gulf of Mexico, Report submitted to the University of Mississippi, September 2009).

As previously mentioned, a “compositional” (i.e. multi-gas) simulator is needed to account for the various gas components present in MC 118 hydrates; such a treatment for the gas composition is necessary for modeling phenomena such as molecular fractionation and multiple BSRs. During Year 2 (2009-2010), we initiated the development of a multi-component (methane, ethane, and propane) simulator. Because of funding limitations, this effort will need to be spread over a couple of years. The work has been divided into two parts, i.e. (1) development of a computationally efficient multi-component equation-of-state (i.e. PVT behavior of 3-gas components, water, and salt; phases will include hydrate and precipitated salt as solid phases, water with dissolved gases and salt as a liquid phase, and a gas phase), and (2) modification of the simulator to accommodate the new equation –of-state.

Work performed during the report period

Contract Matters

SAIC subcontract for Year 2 with the University of Mississippi was finalized towards the end of October 2009. Because of late start, we have requested a no-cost extension to the end of October 2010.

Technical Progress

In preparation for the extension of the approach to treat multidimensional problems, we have completed the adoption of the existing (single gas) THROBS equation-of-state for use in the multidimensional STAR simulator. Test calculations have verified that, with the new STAR/HYDCH4 constitutive description, the two codes (THROBS and STAR) produce identical results when used to solve 1-D problems. Since the MC 118 site analysis will eventually require a multidimensional treatment, this is a necessary step in the development. With the existing THROBS constitutive description incorporated into STAR, we can now carry out preliminary multidimensional studies and are in a better position to proceed toward the final goal of a multidimensional, multi-component modeling capability. A description of STAR/HYDCH4 is provided in Appendix A.

During the current report period (January 1, 2010 to June 30, 2010), we initiated work on the development of a multi-component equation-of-state. We are also examining the question: should we incorporate the new EOS into one-dimensional THROBS code or multi-dimensional STAR code (SAIC's geothermal simulator that is similar to TOUGH)? Final decision will depend on the intended applications, and will be made in consultation with the University of Mississippi Hydrates Consortium. The multi-component equation-of-state will be incorporated into the simulator during the next funding period (2010-2011). Two techniques (Ki value method and statistical thermodynamics method) are available for predicting the composition of hydrate composed of multiple gases. Of these two methods, the statistical thermodynamics method is the more accurate; it enables the calculation of cage occupancy in addition to gas composition. Unfortunately, this method is too computationally intensive to be incorporated into the THROBS simulator. The Ki value method relies on graphs and/or algebraic fits to determine the vapor-solid distribution coefficient for each gas component, and is computationally more efficient than the statistical thermodynamics method, and will therefore be adapted for use in the THROBS simulator. Since the Ki charts assume pure water phase (zero salinity), it will be necessary to use an empirical relation to correct for salinity effects on hydrate equilibrium temperature. Development of the compositional version of THROBS will also require PVT properties for all the hydrocarbon gases (methane, ethane, propane), and a generalization of the mass (i.e. accounting for the mass of all the hydrocarbon gases, water, and salt) and energy balance relations.

To-date, we have focused on the PVT properties for the hydrocarbon gases. The problem of formulating a quantitative compositional constitutive relationship for a mixture of H_2O, NaCl, and three hydrocarbon gases (methane, ethane and propane) in as many as four phases (an aqueous brine phase, a solid halite phase, a solid gas hydrate phase, and a gaseous mixture phase) is both complex and tedious. The existing HYDCH4 equation-of-state software package for a simpler system (H2O/NaCl/CH4) consists of 8,123 lines of FORTRAN source code which is subdivided into 64 subroutines. These separate computational modules each accomplishes a particular task; many describe the separate behavior of the various phases which may be present (density, viscosity, specific internal energy, composition, *etc.*) under particular conditions of fluid pressure, temperature, and overall composition. One of the major differences between HYDCH4 and the new compositional description will be the treatment of the gaseous phase, since it will now consist of a mixture of three hydrocarbons instead of a pure substance (methane). Therefore, we elected to begin the new development with a new treatment for the gaseous phase.

The conventional approach to formulating a quantitative constitutive relationship for a particular phase (in this case, the gaseous phase) is to use a straightforward "mixing model" to combine the properties of the individual constituents. Unlike methane (CH4; molecular weight 16), however, both ethane (C2H6; molecular weight 30) and propane (C3H8; molecular weight 44) in pure form can exhibit two-phase behavior under the pressure-temperature conditions of present interest. The critical points of the three pure substances are as follows:

Methane	*Pcrit* = 44.8 bars	*Tcrit* = –82.6°C
Ethane	*Pcrit* = 48.7 bars	*Tcrit* = +32.2°C
Propane	*Pcrit* = 42.5 bars	*Tcrit* = +96.7°C

The saturation pressures for ethane and propane (*i.e.,* the pressure above which the pure substance will be a liquid, not a gas) vary as follows with temperature in the region of interest for hydrate stability:

	Ethane	Propane
Temperature	*Psat*	*Psat*
0°C	23.87 bars	4.75 bars
5°C	26.89 bars	5.51 bars
10°C	30.18 bars	6.37 bars
15°C	33.76 bars	7.32 bars
20°C	37.66 bars	8.37 bars

The reason why ethane and propane can be present in the gaseous phase in the range of interest (temperatures from 0°C to 20°C or so; pressures of several tens to a few hundred of bars) is that they are not present as pure substances, but are relatively dilute constituents in a gas mixture that consists primarily of methane. This means, however, that the individual properties (density, viscosity, specific internal energy, aqueous phase solubility, *etc.*) of pure ethane and propane as functions of pressure and temperature are unavailable from standard references (except at relatively low pressures) for use in conventional "mixing" models. Accordingly, it has been necessary to try to develop constitutive relations for the gaseous phase indirectly, using various sorts of inferential methods.

For example, assuming that the mass fractions of ethane and propane are relatively small in the gaseous mixture, it should be permissible to model the gas-phase specific internal energy in terms of the (known and predominant) specific internal energy for methane alone at the pressure and temperature in question, modified by "deviation" terms for the other two minor constituents:

$$E\,(P,T) = E_{methane}\,(P,T) + C_{ethane} \times \delta E_{ethane}\,(P,T) + C_{propane} \times \delta E_{propane}\,(P,T)$$

where *Cethane* and *Cpropane* (both presumably << 1) are the mass fractions of the minor constituents in the gas mixture and where, without loss of generality, *Emethane*, *δEethane* and *δEpropane* are all set to zero at $P = 0$, $T = 0°\text{C}$. The pure methane specific internal energy (*Emethane*) is well-known over the pertinent range; the behavior of *δEethane (P,T)* and *δEpropane (P,T)* may be estimated by examining the behavior of the pure substances in the regions where they are gaseous (at low pressures for all temperatures, and at temperatures above the critical temperature for all pressures). This is the approach taken in the present work.

For gaseous-phase mass density ρ, the approach taken previously in the THROBS simulator (pure methane) was to use a modified ideal gas law:

$$\rho = P\,m \,/\, Z\,R\,T$$

where m represents molecular weight (~16 for methane), R is the universal gas constant, T is absolute temperature, and the dimensionless "compressibility factor" Z is a function of pressure and temperature (which approaches unity in the limit as P approaches zero). In the present work, a similar approach is being taken, except that (1) m now represents an appropriate "mean molecular weight" for the mixture (usually somewhat greater than 16) and that (2) Z now depends on three parameters – pressure P, temperature T, and mean molecular weight m. A similar approach may be taken for viscosity, or perhaps the gas-mixture viscosity will be taken as the same as that of methane gas alone at the same pressure and temperature.

Future Plans

Work on the multi-component equation-of-state will be continued during the remainder of Year 2 (i.e. until the end of October 2010).

Task 8: Administrative oversight of the Monitoring Station/Sea-floor Observatory Project.

Administration of the Consortium is the responsibility of the University of Mississippi and includes formal Project Proposals to federal funding agencies, Technical Progress Reports, Final Project Reports, informal monthly updates, reports of Consortium meetings, cruise reports, participation in national meetings, organizing meetings between researchers, organizing and participating in program reviews, organizing and participating in research activities, including research cruises. For this reporting period, these include:

- The MMRI/CMRET/STRC has a new Director, Dr. Greg Easson, whose expertise is in remote sensing and Geoinformatics Systems (GIS). Greg's tenure with the Consortium began, officially, January 2010.
- UM Consortium members Carol Lutken, Leonardo Macelloni, Ken Sleeper, Dianne Welch and Greg Easson participated in DOE's information exchange sessions in Atlanta, January 25-29, hosted by the Georgia Institute of Technology. Consortium work presented during this 4.5 days of formal and informal presentations, poster sessions and discussions: Geochemistry and Microbiology: Laura Lapham (presenter), with Jeff Chanton, Ian MacDonald, Marshall Bowles, John Noakes; Geology and Geophysics: Jim Knapp (presenter), Camelia Knapp, Leonardo Macelloni; Major Project Overview: Carol Lutken (presenter), Leonardo Macelloni (presenter), Ken Sleeper, Dianne Welch, Greg Easson; several posters.
- UM completed the justifications for requesting continued Congressional funding in January, 2010 (FY2011).
- In February, MMRI/CMRET shop personnel travelled to Wylie, TX, to confer and work with Specialty Devices, Inc., on the completion of the new cable for use on the March cruise and to prepare the HLAs (Horizontal Line Arrays) and SSD (Station Service Device). All cables and SSD passed the pressure testing at Southwestern Research Institute in preparation for the March cruise.
- Much administrative effort was invested in plans for a March 1-7 cruise aboard LUMCON's R/V *Pelican*, designed to be an engineering cruise for the Station Service Device. Unfortunately, during an on-board test of the new Cortland cable, the outer member(s) stretched revealing a (presumed) failure in the inner optic-fiber member and the cable was deemed unsafe and unusable for any of the proposed missions. Following the cable's "return" to non-stressed state, it continued to pass light but at a severely reduced level. Later, all optic capability was lost.
- Immediately upon return to Oxford, contact was made with Cortland Cable Co. and Matt Lowe and Brian Noakes drove the cable to Cortland (Cortland, NY) where they and Cortland crews examined, tested, reterminated, pulled and otherwise stressed the cable and its components. They concluded that the cable did what they promised it would do: work with a load of up to 4500lbs; however, this is well below the stress that we know the cable may be subjected to if it is challenged (snagged, tangled, etc.) at depth. We had additional tests run at other facilities to determine what the cable's remaining capabilities were. We decided that we could not trust this cable with the SSD but that, having both strength and optic members, it could be used to deploy the IDP (master data-logger) and serve as the main line of the data recovery system.
- Leo Macelloni provided support to NAVO in preparing for their DTAGS cruise to MC118 in the form of maps and other images including some that have been post-processed by him and his students.
- Missions for the April 20-29 cruise included deploying the station service device (SSD) to conduct video surveys of some lesser-known portions of the MC118 mound

and vicinity and affording opportunities for additional personnel (beyond SDI) to operate the SSD, deploying a mock-horizontal line array to test the proposed technique (including deploying the seafloor pod, attaching a data-logger to it, unspooling the array and attaching it to the IDP), redeploying the IDP, recovering push-cores for geochemical and microbial studies, attempting to recover the osmobox from the pore-fluid array deployed at the NW crater complex, recovering one or both of the bio-batteries deployed in 2006. Nearly all missions were achieved in spite of horrible weather and the explosion of the DeepWater Horizon rig just 10 miles from our site. We tested the new carousel for push-coring set-up, learning much about this carousel (8 core-tubes with quivers, mounted on a carousel on the SSD) and how it works. We collected 3 good intact cores (see photo, Figure 26) from Mandy Joye's requested coring site south of the exposed crater complexes. With the onset of horrible weather (8-12' seas and 25-30kt winds), we headed for Pensacola Bay and calmer waters to continue testing the deployment system for the arrays. Three dives here gave us opportunity to allow other operators time at the SSD controls. We deployed the pod, swam the SSD with the data-logger aboard, placed the Transporter on the pod and deployed and partially unspooled a mock-up array. Visibility deteriorated so much that by Monday evening we headed back to MC118. Back on site we were able to work in fairly rough seas – well enough to deploy the IDP. When the seas calmed, we were surrounded by slick. We had a 100% functional SSD and had hoped to complete another dive to recover instruments and collect additional push-cores as well as documentation of locations but were not willing to risk the SSD by putting it through the oil/chemical-dispersant that was getting thicker by the minute.

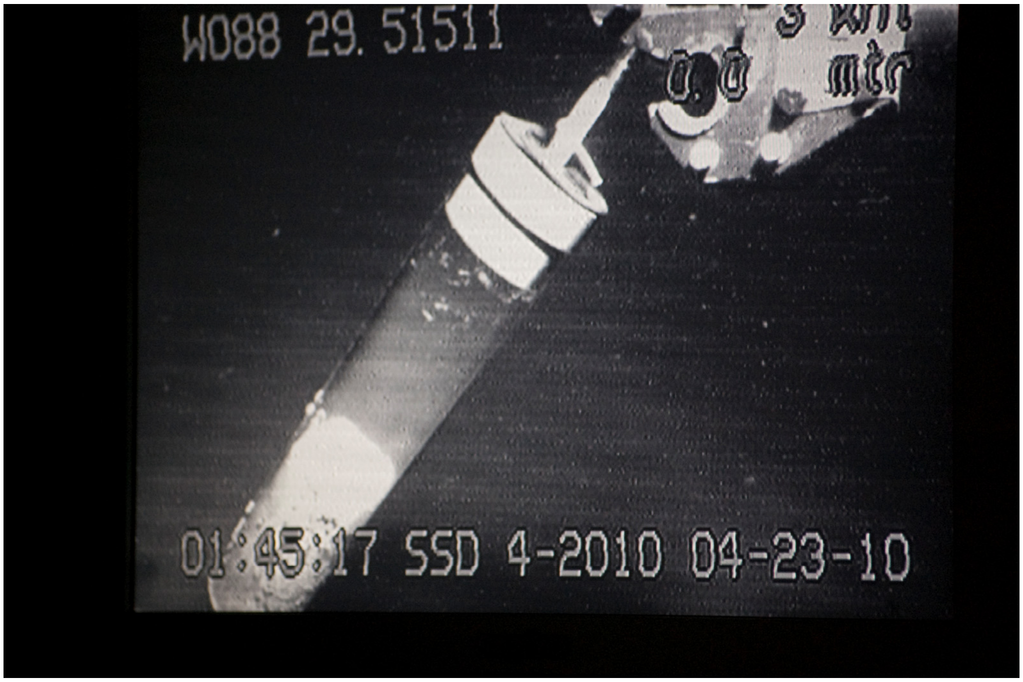


Figure 26. The SSD collecting targeted a push-core.

- Several abstracts were submitted by Consortium members to present results of recent Consortium-related research at the Annual Convention of the American Association of Petroleum Geologists in New Orleans, Louisiana, April 11-14, 2010. Carol Lutken, Antonello Simonetti and Marco D'Medio attended this meeting from the University of Mississippi. Although Jim and Camelia Knapp had abstracts accepted, they were unable to attend the meeting so the UM representatives presented much of their work. Since Antonello had performed much of the geophysical processing and analyses, this worked well. Adrian Addison, Camelia's student, was also present to present the poster. Simona Caruso, now with Fugro, Aberdeen, was able to attend the meeting, and was the primary presenter of the Lutken, et al. poster while Lutken presented the Knapp, et al. talk in the hydrates session.
- In addition to participation in the technical sessions at AAPG, much important work was accomplished at this meeting. Gary Humphreys, Fugro–Houston, spent about an hour with Carol and Simona discussing the prospects of a Fugro-drilled borehole at MC118. Carol met with Jim Brooks and got an oral commitment from him to do heat-flow work at MC118 in 2010-11. 20m piston cores are also a possibility though they would not be recovered during the same cruise as the heat-flow.
- Additional folks integral to the Observatory effort, past and present, with whom we made contact at this meeting include Harry Roberts (LSU), Bill Shedd (MMS – hydrates point man in New Orleans office), Roger Sassen (hydrates, consultant to oil and gas industry), Art Johnson (Hydrate Energy International and Hydrates session co-chair, Bob Hunter, BP and Hydrates session co-chair), Allen Lowrie (Navoceano and consultant), Craig Shipp (Shell –hazards lead), Paul Godfriaux (MMS, New Orleans), Wenyu Xu (Slumberger, modeler who remains very interested in the project and in our progress modeling the multicomponent hydrate stability zone).
- Particularly during May, but throughout the April – forward time-frame CMRET has been involved ay innumerable levels in the work related to the Deep Water Horizon oil spill at MC252. Andy Gossett and Matt Lowe have been immersed in NIUST work relating to the oil spill. The oil spill has certainly occupied us at MMRI as well since we are part of NIUST and since our Observatory site is within 10 miles of the spill site. The May NIUST cruise time was mostly devoted to collecting samples in the vicinity of the spill and documenting anomalous chemical readings.
- Spill related proposals have been written by many Consortium members and many funded by various agencies. Members of the Consortium have been involved in spill-related work since the explosion, April 20.
- Technical semiannual progress report 42877R14 was completed and submitted to DOE during this reporting period as were regular monthly reports documenting progress of subcontractors and the Consortium in general.
- The Gulf of Mexico Hydrates Research Consortium held a web-ference discussion of the details of the need for a borehole and the pros and cons of different suggestions. This replaced the usual spring meeting and plans are in place for a fall meeting in Oxford in October.
- Proposals for continued Congressional FY11 funding from all three federal agencies – MMS, DOE, and NOAA – have been written and submitted.
- The June deployment cruise accomplishments include: 1. Acoustic contact with the

IDP (master data-logger for the Observatory); communicated with it successfully and regularly for the duration of the cruise; 2. Dive of the SSD on which we managed to locate the IDP within minutes of landing on the seafloor, using the SSD's sonar and, later, visuals; 3. Landing the SSD within 10m of the IDP; 4. Confirmed the location and orientation of the IDP, 5. Determined the direction (NNE) and disposition of the cable from the IDP to the pop-up buoy (the means of transferring data from the station to a surface vessel until a link from the station to land is established); 6. Surveyed the area for pod and HLA deployment possibilities; 7. Successful deployment of the HLA pod 12m from the IDP. The next dive we lost communications and although we managed to secure a replacement set of cards, they continued to fail during deployment so we redirected our efforts to water chemistry and used the rosette as a lander as well as to collect water samples. Our instruments – mass spectrometer and follow up gas chromotography - verify the presence of methane plumes at depth - ~600m and ~800m, apparently as a result of the Deep Water Horizon spill in April. We have never seen readings this high and certainly not up in the water column that far, so distant from the seafloor and any possible vent.

Task 9. Project Summary Updates:

The website updates are the responsibility of the CMRET. An update of our DOE web information is underway, as are updates of our publications and student participants.

Publications are added to the Consortium list as they appear and a revised list of recent publications accompanies this report.

The Consortium has long expressed a desire/need for a website dedicated to the Consortium work and accomplishments associated with the development of the Seafloor Observatory. Marco D'Emidio, whose expertise is GIS (Geoinformatics Systems) as well as geology, has developed the geological and geophysical pages for the website, including core locations and descriptions, cruise reports, online geophysical data collected by the CMRET, reports of meetings and many maps derived from Consortium effort. It is the goal of the Consortium Administration to have the website up and running, though incomplete, by our fall meeting, scheduled for October 26-27.

CONCLUSIONS

This report covers the accomplishments of the eigth six-month period (fourth for the FY08 awards; second for the FY09 awards) of funding of Cooperative agreement Project #DE-FC26-06NT42877, between the Department of Energy and the Center for Marine Resources and Environmental Technology, University of Mississippi. The efforts of the Hydrates Research Consortium are reviewed: cruises to test, deploy and recover instruments have been made, innovative data processing techniques employed to evaluate seismic datasets, both standard and Consortium-developed, and an improved image of the subsurface structure of the carbonate-hydrate mound at MC118 is emerging. Additional proposals for funding are nearly ready for submission. HLA configuration and deployment challenges have been addressed and a new schedule for HLA deployment has been developed for fall, 2010, and additional cruises scheduled for 2011. New constraints on hydrate formation have been established, multibeam technology used effectively to measure both volume and frequency of bubble plumes at vents, a probe that will measure sound speed in situ at MC118 begun to be built, and advanced phases of a hydrate 3-gas model completed. The DOE's Project Management Plan is complete and has been delivered to NETL. Manuscripts have been submitted to peer-reviewed journals and additional papers and presentations have resulted from Consortium research efforts. Additional cruises are scheduled for 2010 and 2011 that include AUV surveys, major deployments, additional test deployments and retrieval of instrumentation that remains on the sea-floor. Every effort has been – and will continue to be – made to maximize Consortium members' access to and benefit from the cruises scheduled for 2010. Additional efforts to monitor developments resulting from the vast amounts of hydrocarbons spilled into the seawater at MC252 are ongoing, with Consortium researchers making significant findings/contributions to unraveling that developing predicament.

ACRONYMS AND ABBREVIATIONS

3-D	3-dimensional
4-C	four component
ABCMS	Automated Biological Chemical Monitoring System
ATCC	American Type Culture Collection
AUV	autonomous underwater vehicle
AVO	amplitude vs. offset
BBLA	Benthic Boundary Layer Array
BEG	Bureau of Economic Geology (University of Texas)
BLA	Borehole Line Array
BOEMRE	Bureau of Ocean Energy Management, Regulation, and Enforcement
BSR	bottom-simulating reflector
C&C	Chance and Chance
CDOM	colormetric dissolved organic material
CGGVeritas	Compagnie Générale de Géophysique (CGG) and Veritas
CH_4	methane
CMRET	Center for Marine Resources and Environmental Technology
DATS	Data Acquisition and Telemetry System
DOC	Department of Commerce
DOE	Department of Energy
DOI	Department of the Interior
DWFS	Deep-Water Filtering System
EGL	Exploration Geophysics Laboratory
EOS	equation-of-state
FY	Fiscal Year
G	shear modulus
GHSZ	Gas Hydrate Stability Zone
GIS	Geoinformatics Systems
GOM	Gulf of Mexico
GOM-HRC	Gulf of Mexico-Hydrates Research Consortium
HLA	horizontal line array
HRC	Hydrates Research Consortium
HSZ	Hydrate Stability Zone

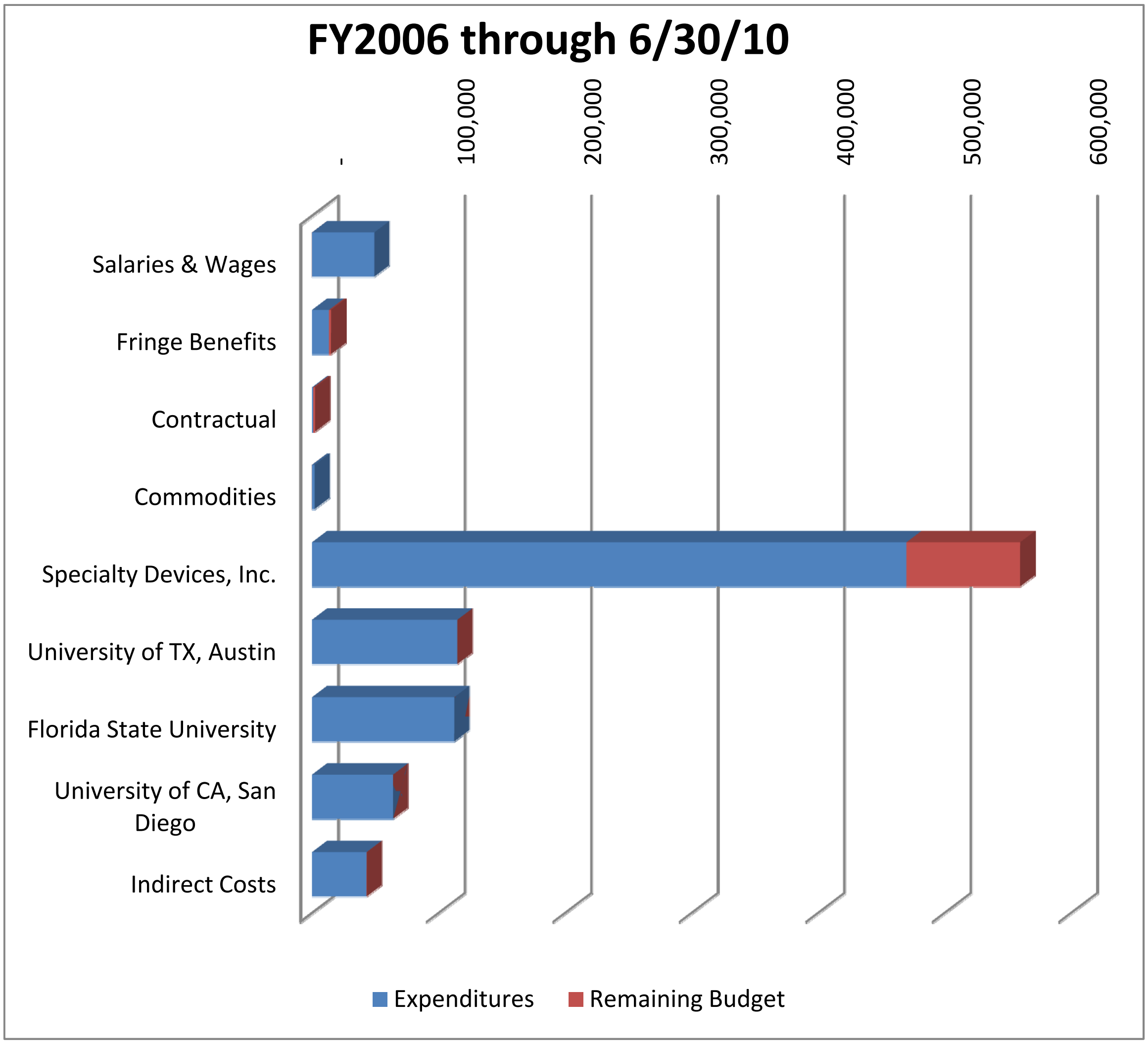
IDP	Integrated Data Power Unit/Interconnection and Data Recovery device
K	bulk modulus
LUMCON	Louisiana Marine Consortium
m	molecular weight
MC	Mississippi Canyon
MMRI	Mississippi Mineral Resources Institute
MMS	Minerals Management Service
uM	micromolar
MS/SFO	monitoring station/sea-floor observatory
NETL	National Energy Technology Laboratory
NIUST	National Institute for Undersea Science and Technology
NOAA	National Oceanographic and Atmospheric Administration
NURP	National Undersea Research Program
OER	Ocean Exploration and Research
P	pressure
PFA (=PCA)	pore-fluid array
PVT	pressure-volume-temperature
R	universal gas constant
ROSSCAN	rotating multibeam sonar scanner
ROV	remotely operated vehicle
R/V	Research Vessel
SAIC	Science Applications International Corporation
SDI	Specialty Devices, Inc.
SFO	Sea Floor Observatory
SFP	Sea Floor Probe
SSD	Station Service Device
SS/DR	Surface-Source Deep Receiver
STAR	SAIC's multidimensional simulator
STAR/HYDCH4	constitutive description
STRC	Seabed Technology Research Center
T	absolute temperature,
TA	thermistor array
TGS-NOPEC	geophysical data (2-D, 3-D) acquisition company
THROBS	SAIC's hydrate simulator
TSS	dynamic motion sensor
UCSB	University of California, Santa Barbara
UGA	University of Georgia
UMS	underwater mass spectrometer
USBL	ultra-short baseline navigation system
USC	University of South Carolina
USF	University of South Florida
USGS	United States Geological Survey
VLA	vertical line array
WesternGeco	Western Geophysical Company
Z	dimensionless "compressibility factor"
ρ	gaseous-phase mass density

COST STATUS

As can be seen in the figures and tables that follow, Phase 1 (FY06) funds are essentially spent, with the exception of those allocated to the Horizontal Arrays, a major Observatory component. The arrays have been completed and pressure-tested at Southwest Research Institute. All four have now passed the pressure-tests and are ready for deployment. We expect to be invoiced soon for the final array and pressure test.

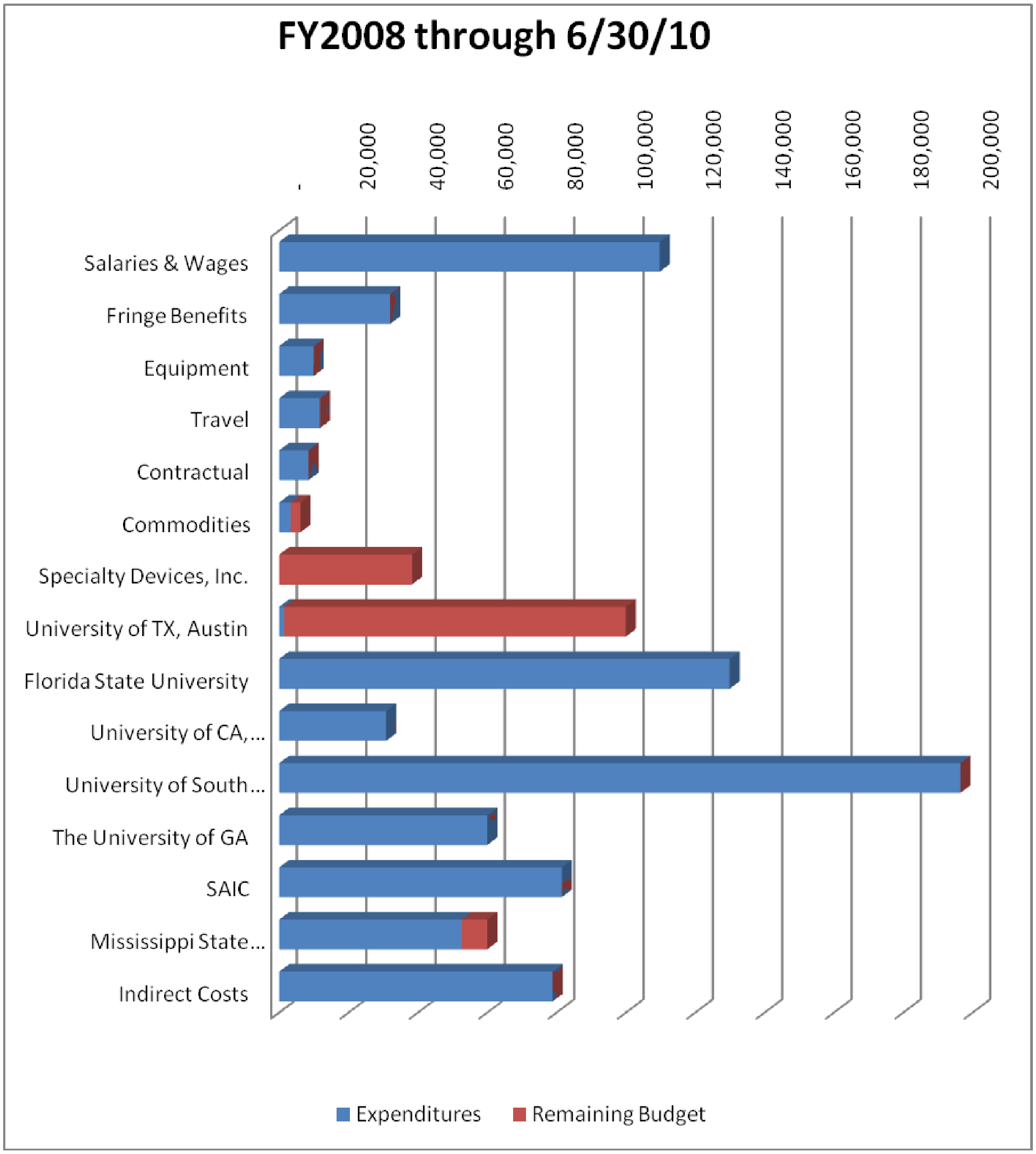
Funds are essentially intact for the Phase 2 4C experiment and the speed-of-sound probe, projects that depend upon the deployment of the HLAs before they can be undertaken. Subcontracts for Phase 3 are underway using these “new” funds.

A no-cost extension has been requested for additional time to complete Phases 2 and 3.



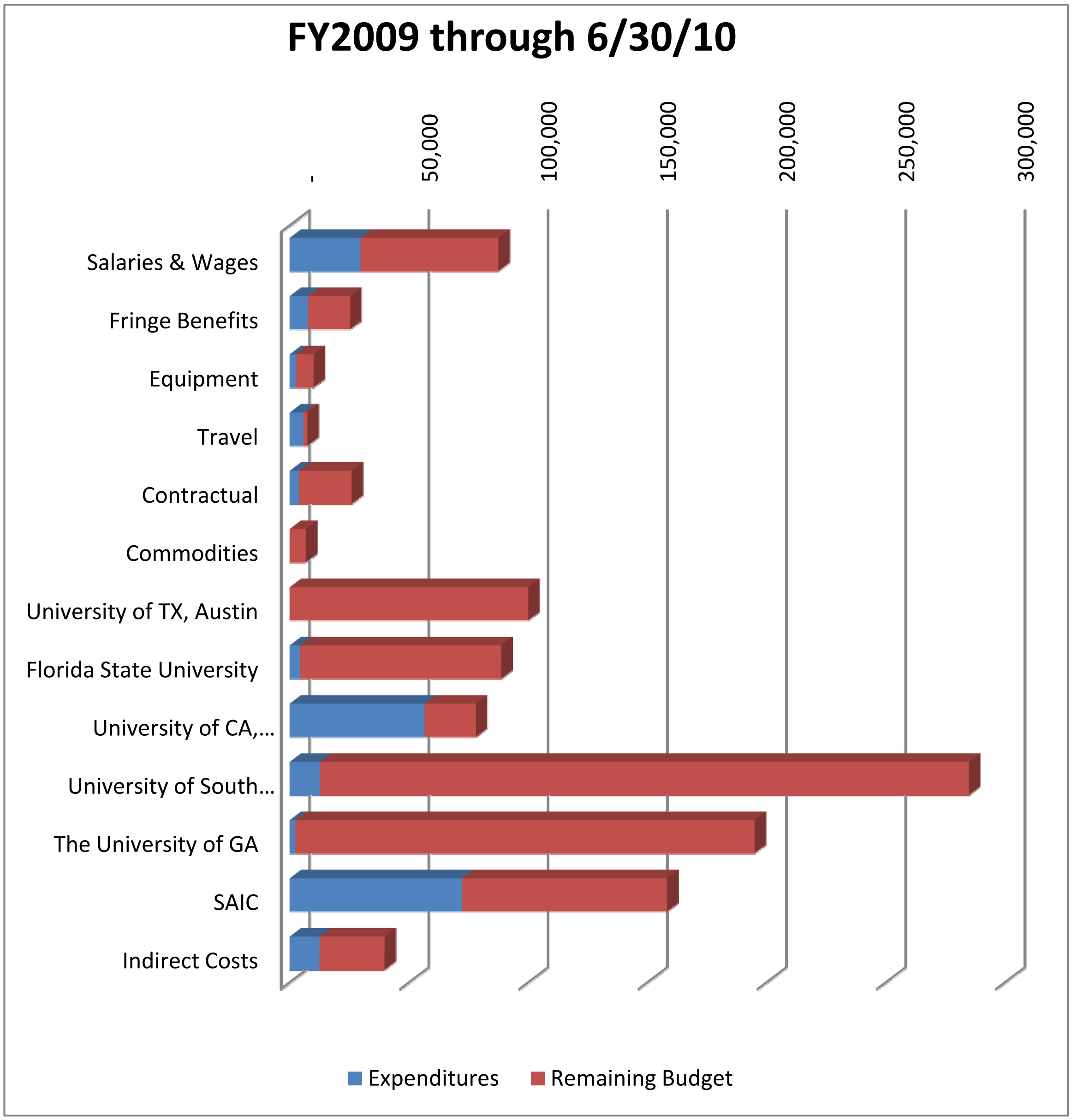
Mississippi Mineral Resources Institute
DOE DE-FC26-06NT42877
Funding Status as of 06/30/2010

FY2006	Expenditures	Remaining Budget
Salaries & Wages	49,309	(229)
Fringe Benefits	13,471	1,646
Contractual	1,026	1,474
Commodities	2,176	(2,176)
Specialty Devices, Inc.	470,000	89,912
University of TX, Austin	114,979	21
Florida State University	112,520	-
University of CA, San Diego	64,113	-
Indirect Costs	43,155	187
Total	870,749	90,835


FY2008 through 6/30/10
-
20,000
40,000
60,000
80,000
100,000
120,000
140,000
160,000
180,000
200,000
Salaries & Wages
Fringe Benefits
Equipment
Travel
Contractual
Commodities
Specialty Devices, Inc.
University of TX, Austin
Florida State University
University of CA,...
University of South...
The University of GA
SAIC
Mississippi State...
Indirect Costs
Expenditures
Remaining Budget

Mississippi Mineral Resources Institute
DOE DE-FC26-06NT42877
Funding Status as of
6/30/2010

FY2008	**Expenditures**	**Remaining Budget**
Salaries & Wages	109,809	-
Fringe Benefits	32,043	-
Equipment	10,000	-
Travel	11,800	-
Contractual	8,500	-
Commodities	3,342	2,811
Specialty Devices, Inc.	-	38,336
University of TX, Austin	1,445	98,555
Florida State University	129,972	-
University of CA, Santa Barbara	30,881	-
University of South Carolina	196,517	-
The University of GA	60,000	-
SAIC	81,527	-
Mississippi State University	52,642	7,360
Indirect Costs	78,860	-
Total	807,338	147,062


FY2009 through 6/30/10
-
50,000
100,000
150,000
200,000
250,000
300,000
Salaries & Wages
Fringe Benefits
Equipment
Travel
Contractual
Commodities
University of TX, Austin
Florida State University
University of CA,...
University of South...
The University of GA
SAIC
Indirect Costs
Expenditures
Remaining Budget

Mississippi Mineral Resources Institute
DOE DE-FC26-06NT42877
Funding Status as of
6/30/10

FY2009	**Expenditures**	**Remaining Budget**
Salaries & Wages	29,729	57,873
Fringe Benefits	7,719	17,686
Equipment	2,692	7,308
Travel	5,822	1,578
Contractual	3,843	22,157
Commodities	-	6,767
University of TX, Austin	-	100,001
Florida State University	4,328	84,397
University of CA, Santa Barbara	56,584	21,534
University of South Carolina	12,666	272,234
The University of GA	2,416	192,613
SAIC	72,329	85,923
Indirect Costs	12,529	27,296
Total	210,657	897,367

MILESTONE STATUS

Milestones identified in the Project Management Plan are discussed below and related to their status.

Milestone 1: *Complete the baseline characterization of the subsurface at the Observatory site, MC118 for presentation to the panelists at the DOE Merit Review.* *Complete Seismic Analysis of data from MC118 including defining features that relate to the occurrence of gas hydrates.*

Baseline character of the Observatory site at MC118, as revealed in several seismic data sets is essentially complete. However, expansion of the site characterization, including a time element, will go forward with the analysis of additional industry standard data from WesternGeco. TGS-Nopec industry standard data, high resolution data (chirp-sonar and surface-source-deep-receiver) have been tied together and referenced to the ARCO well in the block. Improving the site characterization through chemical and AUV surveying has added valuable information to the site baseline characterization. Acquisition of a dataset from MC118 from Western Geco has been negotiated and approved but the dataset has not yet been received by USC. A polarity-preserving chirp system has been received and awaits installation on the NIUST AUV for survey work at MC118.

Milestone 2: Recover instruments from the seafloor and analyze data for baseline geochemistry and microbiology for the model (Task 9).

Most instruments have been recovered from the seafloor at MC118, data recovered and mostly analyzed. However, some instruments remain on the seafloor even after several efforts to retrieve them. Additional attempts to recover instruments are scheduled for September.

Milestone 3: Deploy horizontal line arrays, connect them to the data recovery system and collect test data from the data-logger. *All components of the deployment have been tested successfully(April, 2010).* A deployment cruise for this task has been rescheduled for September, 2010. All four arrays are ready for deployment but will likely be deployed in installments as deck-space and maneuvering have turned out to be even more challenging than anticipated.

Milestone 4: Complete installation of all Observatory components and collect geophysical data for input into model (Task 9). Due to deployment logistics, this milestone will necessarily follow the deployment of the horizontal arrays and collection of geochemical sensors.

Milestone 5: Complete additional surveys – SSDR, Mass spectrometer (STRC-funded), multibeam (NIUST-funded) to provide important updated baseline seismic data prior to the commencement of true monitoring. *Estimated completion is March, 2010.* The multibeam and mass spectrometer surveys are complete. The hydrophone array – necessary for the SSDR survey with the AUV-borne receiver - is in Phase 2 of development by NOAA and is due for testing.

Milestone 6: **Complete 4C survey and analyze data for new software:** This milestone depends upon the coordination of two survey ships and industry standard nodes and source. It depends upon the deployment of the HLAs and relates directly to Task 3. CGGVeritas is in a less motivated state with oil spill related work and legislation, the loss of our key person from their employ. We continue to pursue this vital component of the station.

Milestone 7: Establish a “final” model of the observatory site, from which changes

can be determined and monitoring established. The initial phases of the modeling effort are complete. A confidential report of the integration of the equation of state into the SAIC model will soon arrive at NETL. Real data are needed for input into the final model.

ACCOMPLISHMENTS

Major accomplishments of this reporting period include:
Emplacement of a new Director for the MMRI/CMRET/STRC
Establishment of a deployment scheme for the HLAs; successful test of the plan
Successful proof of concepts and recovery of data in support of CH4 plumes in the water-column near MC118
Successful recovery of targeted push-cores with the SSD
Successfully deployed and communicated with the IDP
Deployed the HLA POD 12m from the IDP
Establishment/renewal of important collaborations
Successful functions added to the SSD's capabilities (push-cores, surveying)
Recovery of geochemical data from the near-seabed and shallow seabed
Coordination of multiple methods of water-column chemical evaluation
Completion of requests for continued federal funding
Completion of request justifications for continued federal funding from all three agencies: BOEMRE, DOE, and NOAA

PROBLEMS/DELAYS

The majority of delays in the program derive from one of two sources, or a combination of the two: weather and electronics at 900m water depth. In addition, the Deep Water Horizon spill has complicated our work and hijacked significant portions of our resources – both time and personnel. Ship time is more difficult than ever to schedule. The deployment of the HLAs has been rescheduled but the projects that are depending upon this critical achievement remain in "stand-by" mode. They are working with other or synthetic data until data can be recovered from the HLAs and, in the case of UT-Austin, have nearly all funds remaining to do the work when the data do become available.

Weather dictates cruise scheduling and successes. Although extra cruises have been scheduled for 2010, weather conditions cannot ever be predicted and we face similar delays in the future. Cruise requests for 2011 have been made and are concentrated in the months known for better weather in the Gulf, but we have not received assurances that we will get these requested times. Since ship time demand is so high, it seems likely that we will have to take at least some marginal days.

Electronics at depth will always be challenging. The SDI/CMRET team has worked diligently to overcome many but anticipate additional difficulties in the future as part of working in extremely challenging environments.

PRODUCTS

Important products of this reporting period are:

1. Early rock physics study results
2. Preliminary modeling

3. Cruise accomplishments and deployments
4. Progress Report from 2009 (July – December)
5. Publications and presentations at national meetings

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National Energy Technology Laboratory

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880

One West Third Street, Suite 1400
Tulsa, OK 74103-3519

1450 Queen Avenue SW
Albany, OR 97321-2198

2175 University Ave. South
Suite 201
Fairbanks, AK 99709

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