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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:

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

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

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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.

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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.

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

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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:

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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.

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

PHASE 4 Subcontractors and Tasks for FY 2010

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TASK 2: Integration of Multiple Methods of Geological and Geophysical investigations to advance Shallow Subsurface Characterization at MC118.

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TASK 3: Modeling a carbonate/hydrate mound in Mississippi Canyon 118 using modified version of (THROBS).

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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.

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

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INTRODUCTION / PROJECT SUMMARY

The Gulf of Mexico Gas Hydrates Research Consortium (GOM-HRC) was organized in 1999, with the goal of establishing a monitoring station/sea-floor observatory (MS/SFO) to investigate the hydrocarbon system within the hydrate stability zone (HSZ) of the northern Gulf of Mexico. The intention has been to consolidate research effort and to equip the MS/SFO with a variety of sensors that will enable more-or-less continuous monitoring of the near-seabed hydrocarbon system and to determine the steady-state description of physical, chemical and biological conditions in its local environment as well as to detect temporal changes of those conditions.

The purpose 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, BOEM) 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 nineteen industries and nineteen universities are actively involved in Consortium/Observatory research; the United States Geological Survey (USGS), the US Navy, Naval Meteorology and Oceanography Command, Naval Research Laboratory (NRL) and NOAA's National Data Buoy Center are involved at various levels of participation. Funded investigations include a range of physical, chemical, and biological studies. Studies of the benthic fauna as a proxy for seafloor hydrocarbon venting comprise a recent addition to the emphasis areas of the Consortium.

The project is administered by the Center for Marine Resources and Environmental Technology (CMRET), the marine arm of the Mississippi Mineral Resources Institute (MMRI) of The University of Mississippi.

EXECUTIVE SUMMARY

In 1999, a consortium was assembled for the purpose of consolidating both laboratory and field efforts of leaders in gas hydrates research in the Gulf of Mexico. 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 within the zone of hydrate stability 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. Study of chemosynthetic and other benthic communities and their interactions with geologic processes is a component of 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 are essentially complete.

In October, 2004, Mississippi Canyon 118 (MC118) (Figure 1) was selected by unanimous consensus of the GOM-HRC at their semiannual fall meeting as the location likeliest to fulfill the research needs and goals of the group. Criteria for selection included evidence of gas hydrates on the sea-floor, active venting and availability. Based upon roughly five years of site evaluations, sensor design, fabrication, testing and data collection and evaluation, selection of the site was followed by MMS placing 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. MC118 is the only research reserve in the Gulf of Mexico and the Seafloor Observatory is the only such facility in the Gulf.

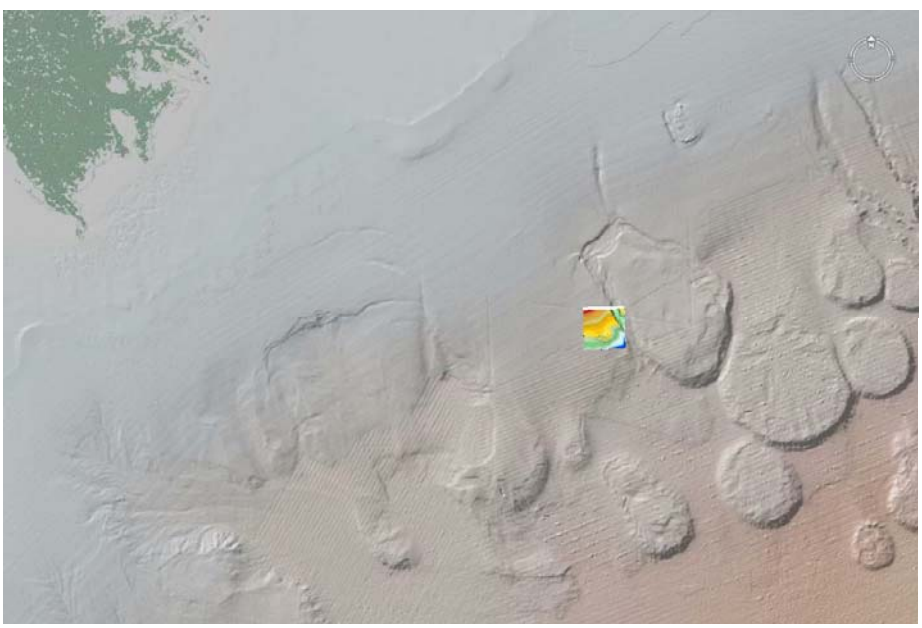

Figure 1. MC118 is located ~30 miles off the toe of birdsfoot delta on the edge of a massive slump.

Since changes in the hydrate stability zone must be in some way measured against an established baseline, a significant effort has been devoted to establishing the baseline geology and chemistry at the site of the MS/SFO at MC118. Characterization and baseline determination commenced in spring, 2005. The First Phase Sea-floor Probe (SFP) installation was completed successfully with two sub-sea-floor arrays emplaced in the sea-floor at MC118; a thermistor array, and a geochemical, pore-fluid chemistry, and pressure sensor array were deployed using the MMS/BOEM gravity-driven SFP. In spite of a variety of delays, including the effects of several severe hurricanes, follow-up surveys and deployments, continue to take place. Geophysicists and geologists at the University of South Carolina and the University of Mississippi have established that the observatory site lies directly over a rising salt dome, that "master faults" extend from the salt body to the seafloor, that the three crater complexes on the mound each reside on the hanging wall of one of these master faults, that swarms of radial faults intersect these master faults providing a conduit system sufficient to supply hydrocarbon fluids from depth to the seafloor and water column. Moreover, resistivity data as well as additional geophysical findings suggest that these conduits are alternately open and closed – possibly by hydrate dissociation or dissolution and formation. 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. Rogers (2001) established a connection between the microbial communities and hydrate formation and recently found through experimental analyses of MC118 microbial consortia that *microbial cell wall material inhibits hydrate formation*, a necessary occurrence for the bacterial cell's survival, as it prevents hydrate formation-heats from being liberated directly onto cell surfaces. Microbes inhibit hydrate formation, thus enhancing their ability to survive the extreme conditions of the deep sea HSZ.

During this reporting period, the CMRET participated in just one cruise to the MS/SFO. In October, we chartered Louisiana Universities Marine Consortium's (LUMCON's) R/V *Pelican* and took several projects to MC118. Major achievements of this cruise included:
1. Successful deployment of the WHOI (Woods Hole Oceanographic Institution) optic modem, Figure 2, to recover data, remotely from the Benthic Boundary Layer Array (BBLA). This method enables data recovery without risk of collision, entanglement, etc. of instruments or recovery to the sea surface. A full data download – 3.5 months of data - was completed in just over an hour's time. From the deck to the site in the water-column and maintaining a 75m watch circle with the vessel, establishing communication with the BBLA, downloading data and returning to the deck all occupied less than two hours. ***This was the first use of this method to recover real data.***

Figure 2. Recovery of WHOI's depressor with CTD, USBL, optic modem and data-logger.

2. Successful deployment and recovery of CMRET's new lander, Figure 3, with University of Southern Mississippi's (USM's) sonar scanner for bubble detection. While it appeared that the scanner worked, the data-logger did not and no data were recovered. This system has been evaluated and is being modified for an April deployment.

Figure 3. CMRET's octagonal lander with sonar scanner and locator, USBL and acoustic releases.

Figure 4. CMRET's lander can be deployed and recovered using the Pelican's crane.

3. Successful use of the Noakes' Lander as a site evaluation tool. We used the lander (mass spectrometer not working, so no gas chemistry was available) to complete visual evaluations of three candidate sites for the Chimney Sampler Array (CSA)

redeployment on the Remotely Operated Vehicle-assisted recovery device (ROVARD). The downward-facing camera worked extremely well. We were able to identify bubbles in the water-column, to identify several different sea creatures, including the chemosynthetic *pogonophora* and to use the visual data to select a site.

4. Successful deployment of the ROVARD with one CSA.

Figure 5. CMRET's ROVARD lander with CSA is recovered using an acoustically released pop-up buoy which brings a cable to the surface for attachment to the ship's winch.

This cruise was followed immediately by a NRDA cruise to this site. We supplied the PI, Eric Cordes, with bottom information including locations of instruments and a high resolution multibeam basemap. This enabled the NRDA cruise to navigate with ease at our site, to supply us with additional imagery of benthic communities, and to verify correct orientation of the ROVARD.

An autonomous Underwater Vehicle (AUV) cruise to MC118 to test the newly installed polarity-preserving chirp system was made possible with CMRET participation and is summarized under Phase 4,Task 2.

MONITORING STATION SYSTEMS STATUS SUMMARY

Geophysical Sensor Systems/Geology

Geophysical studies as well as coring efforts have been used to define the baseline geology at the Observatory site. Multibeam swath bathymetry and chirp sonar systems on the C&C Hugin 3000 AUV have been used to define seafloor morphology and bottom reflectivity (see Figure 6) and shallow high resolution profiling. With detailed reprocessing of the data, extremely detailed images of the seafloor and ~60-70m profiles of the subseafloor have been made. These very high resolution images are placed in a regional context that we are now updating using the *Okeanos Explorer* multibeam data acquired late in 2011. In addition, a surface-source deep-receiver system or SSDR (single channel seismic profiling with resolution improved via source-signature processing), has been used to complete a 3x3km survey of the hydrate/carbonate mound at MC118 (officially named after the former MMRI/CMRET Director, Dr. Bob Woolsey, founder of the Consortium and of the Hydrates Monitoiring Station/ Seafloor Observatory). The resultant 109 profiles of very high resolution seismic data have undergone processing - including the application of Empirical Mode Decomposition (EMD) described by Battista et al. (2007) - to create a 3-D model of the mound. This dataset is capable of imaging features associated with gas hydrates – chimneys, fracture porosity, etc. – hundreds of meters below the seafloor. An industry data set, acquired by TGS-NOPEC has been evaluated by geophysicists and geologists in the Consortium in order to extend the range of baseline information from the MS/SFO site to the deeper subsurface and the source(es) of hydrocarbons and fracturing at depth. In addition, Consortium geophysicists have acquired Controlled-source Electro-Magnetic (CSEM) data adjusted for shallow hydrate targets and a Direct Current Resistivity data set to produce high resolution images beneath the mound. Although the CSEM data have not yet been processed and evaluated, they are expected to show distribution of hydrates and 3-D structures such as dipping faults to ~200m beneath the seafloor. Preliminary results of the resistivity data show likely hydrate concentrations associated with areas of faulting and fractures (conduits for migrating fluids) and suggest that these pathways for hydrocarbon migration open but subsequently fill with hydrate and become blocked to further fluid migration (Figure 7) and perhaps reopen or open elsewhere, forming seafloor features such as pockmarks and seafloor seeps and vents. Additional resistivity studies are planned that will improve the resolution of the initial efforts and may identify areas of greater/lesser hydrate concentrations.

Sensors designed and built for permanent installation at the Observatory include a vertical water-column array (VLA) of sensors to determine subbottom structure and materials and an orthogonal cross of horizontal line arrays (HLAs) of sensors. Advantages of the HLAs include utilization of surface noise produced by noise-generating ships of opportunity providing P-wave energy for the hydrophones of the vertical and horizontal arrays. Further, the composite vertical and horizontal arrays will be used in experimental work with natural ambient sound, such as ship noise or wind-driven wave noise, as a passive seismic energy source. The planned addition of accelerometers to the suite of seafloor sensors will enable passive monitoring via microseisms. These events are known to frequent the region, produced by ubiquitous salt movements as well as deeper, basement-related seismic events. They can be recorded and possibly related to various observed phenomena at the study site such as pore-fluid migration and large scale episodic fluid venting.

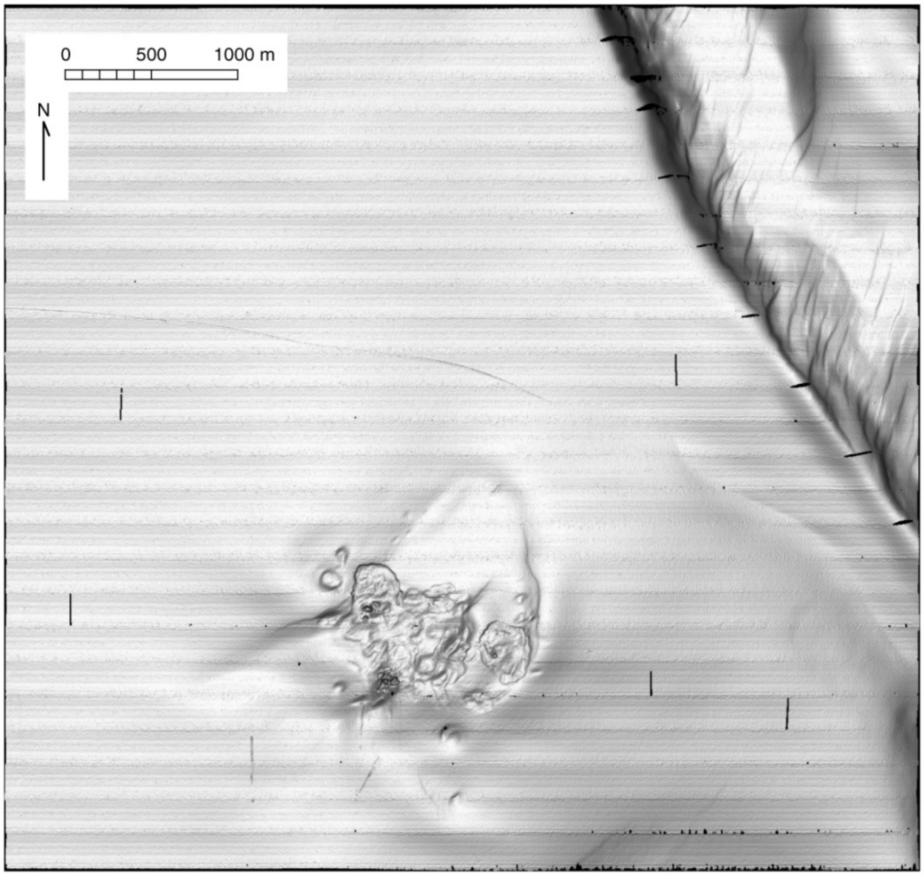

Figure 6. Multibeam image of Mississippi Canyon 118. Data acquired by C&C technologies and reprocessed by The University of Mississippi and University of Rome, La Sapienza.

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 4-component (4C) seafloor-based seismic sensors. In April, 2011, an Ocean Bottom Seismometer (OBS) experiment was conducted over a portion of Woolsey Mound to collect 4C data that will enable researchers to establish the shear features/characteristics of the shallow subsurface. Passive data were also collected via the OBSs and are being evaluated by the University of California-San Diego for their utility in monitoring the HSZ.

Additional 4C work will be performed when the HLAs are deployed. Software has already been written for this experiment. In addition, inversion of the seismic data with the resistivity data is anticipated as part of the University of Texas BEG effort (DOE).

Currently the completed water-column VLA, with the seabed HLA horizontal cross, is awaiting installation. The HLA's are complete and were successfully pressure-tested at Southwestern Research Institute in February, 2010, to 1000m water depth equivalents.

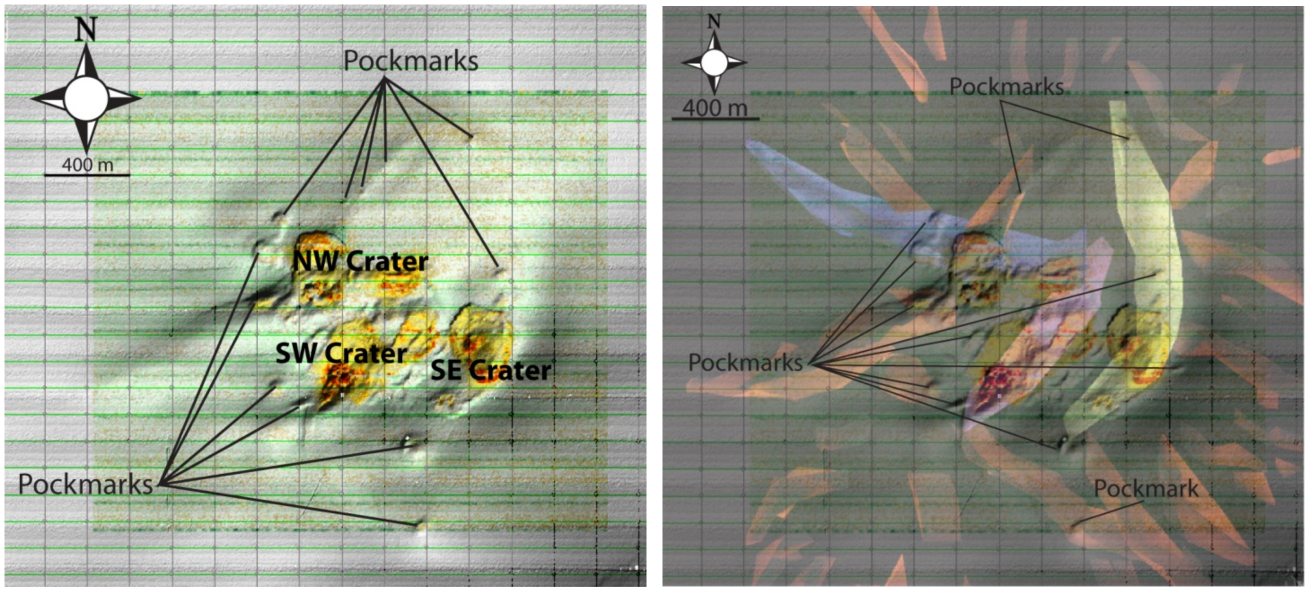

Figure 7. Woolsey Mound at MC118 has 3 distinct crater complexes. The image on the left shows bathymetry at the site. To the right, "master faults" – blue, violet, yellow – and shallower.radiating faults – orange – are plotted with this same bathymetry to illustrate surface expression of the fault system.

Additional geophysical studies are either complete, underway or in the planning stages. With access to the NIUST AUV, *Eagle Ray*, equipped with multibeam, additional bathymetry studies have been executed to evaluate the seafloor changes at the Observatory site, over time, including the evolution of chimneys, gas vents, sediment accumulations and changes in hydrate outcrops. This June 2009 survey was run simultaneously with Woods Hole Oceanographic Institution's (WHOI) Mass spectrometer, Tethys. During this survey, Tethys detected methane spikes in areas where the multibeam data indicated the possible presence of a crater that had not been evident in the 2005 survey. This critical find verifies the utility of these systems, particularly when used in concert. A new shallow-source/deep-receiver (SSDR) survey will serve the same purpose but will address changes in the subsurface, including the HSZ. Plans are advancing to mount a hydrophone on the *Eagle Ray* to eliminate cable strum by placing the receiver near the seafloor thereby improving the data as well as extending the range of usable data deeper into the subsurface by increasing the arrival time of the surface ghost. The Polarity Preserving/Discriminating Chirp sub-bottom profiler system has been installed in the Eagle Ray and a test cruise executed. We continue to work with Geoacoustics on problems in the software but initial results are promising. The goal of this technology is to enable researchers to more accurately discern reflectors related to near-bottom geologic features - including shallow gas horizons - to depths of approximately 50m. A particular benefit is its frequency compatibility with the AUV multibeam swath bathymetry mapping system, permitting simultaneous operation.

An additional industry data set acquired by Western Geophysical Company was purchased in 2010 and delivered in early 2011. Both USC and UM have copies of the data and are working together to unravel the complex deep geology of Woolsey Mound. This additional dataset will not only provide additional deep subsurface information (records are 12sec long), but will and add a time dimension to the deep regional structure. Amplitude variation with offset can be applied to this data set to discriminate between fluid and solid material in pore fluids, the latter providing evidence of hydrate. This survey, which includes 12 sec records, is expected to image the subseafloor from the seafloor to the salt. It also includes about 30% of the data into bordering blocks for full lateral coverage of the observatory block.

Construction of speed of sound probes to accompany CMRET's 10m coring capability is underway and will be used at targeted locations in an attempt to define a seismic signal for hydrate, something that has eluded hydrate workers to the present. Target locations have been identified based on the noise/scatter of signal noted in SSDR data collected from particular locations at MC118. CMRET is also constructing a site reconnaissance camera to inspect seafloor locations of interest prior to coring and/or deployment of landers and sensors on the seafloor.

Jumbo Piston Cores (JPCs) were collected by Consortium geologists and geochemists working with TDI Brooks, International aboard the R/V *Brooks McCall.* Five cores of roughly 12-15m length were collected from sites selected using a combination of geophysical surveys from the area and core histories. Sites of high resistivity readings were given priority as were sites where seafloor expression of gas expulsion and faulting are evident on multibeam images. Hydrates were recovered in the bottom 2 meters of the core from the site of highest resistivity readings (Figure 8). A newly acquired IR camera was used for the first time on this cruise and proved to be quite successful in predicting both high and low heat within unopened cores (Figure 9). This technique is being explored further and refined for use in future coring efforts as hydrate is known to dissociate rapidly upon recovery while temperature gradients may remain for longer periods.

The Consortium has submitted a Preproposal, followed by a full Proposal to the Integrated Ocean Drilling Project (IODP) requesting support for a series of boreholes to be drilled in support of this project when the appropriate vessel next tours the Gulf of Mexico. In addition, the MMRI/CMRET is involved in discussions with Fugro that could lead to the drilling of a borehole at MC118 for the benefit of the observatory project. Fugro has been involved in the hydrates observatory project since its inception and would like to provide this borehole at no-cost to the Consortium. However, ship charges will likely fall to the Consortium.

Figure 8. After 2 hours on deck, hydrate can still be observed in the bottom sections of JPC-001. The core contained hydrate layers, nodules, blades, grains and granules in extremely fine-grained host material.

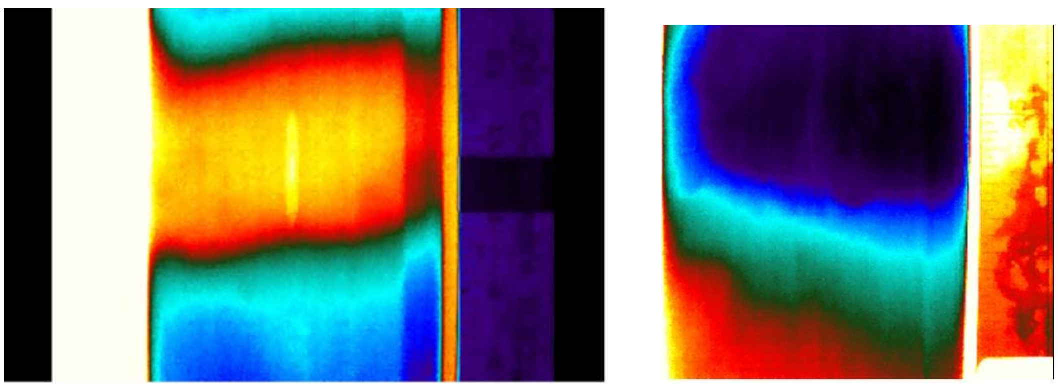

Figure 9. Images from the IR camera highlight areas of anomalous temperature. In the example at left, a void space in the unopened core shows as warmer (warmer color). In the example to the right, a hydrated section shows as cooler (cooler color).

Geochemical Sensor Systems

Experiments designed to assess water-column geochemistry, microbial communities and activities, hydrate host materials, bubble streams 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. Experimental analyses of MC118 microbial consortia (see Phase 2, Task 6, below) have shown the intriguing finding that *microbial cell wall material inhibits* *hydrate formation*, a necessary occurrence for the bacterial cell's survival, as it prevents hydrate formation-heats from being liberated directly onto cell surfaces. Microbes inhibit hydrate formation, thus enhancing their ability to survive the extreme conditions of the deep sea HSZ.

Evolution of geochemical sensor systems has helped define the baseline as well as the direction of geochemical research at MC118. Early in the history of the Observatory project, a 200m water-column oceanographic line array (OLA) was planned to monitor hydrocarbon pore-fluids venting from the surficial sediments in the vicinity of hydrate mounds and transiting the lower water column. As experience and an improved understanding of the hydrocarbon system and hydrography of the lower water column have emerged, a more comprehensive approach has been developed. The OLA (NETL/NOAA), has been modified to a 60m length and designed to monitor the benthic boundary layer, hence the designation Benthic Boundary Layer Array (BBLA). This array was deployed successfully in March of 2009 and recovered in June. Three months of water-column chemistry were recovered. This array was refitted to include a Contros methane sensor on the bottom node and redeployed at MC118 in September, 2010 and recovered in April, 2011. This data set has just begun to be evaluated but appears to include water-column indications of the Deepwater Horizon spill of April, 2010. Unfortunately, the Contros methane sensor failed after less than 24 hours at depth (1000m). Negotiations with Contros concerning repair/replacement of the sensor have not been productive and it appears they will return the damaged sensor without repair. As noted earlier, the BBLA was redeployed in June and the WHOI optic modem has been used successfully to transfer data remotely from the BBLA to the ship.

A small barrel-like, chimney sampler array (CSA), (NOAA/NIUST), outfitted with sensors that will collect chemical data related to hydrate formation/dissociation, was fabricated by STRC subcontractors and tested in shallow water. The prototype unit was deployed and tested at MC118 in September, 2006, using the Johnson SeaLink (JSL) manned submersible submarine. A modified and expanded version of this sensor system was deployed on the MMRI/CMRET-designed ROVARD at MC118 in September, 2010 (Figure 10), and was recovered in June, 2011. Initial inspection of the data reveals good data truncated after 3 weeks due to battery failure. This upgraded system has been redeployed (October) and is scheduled for an April recovery. Data from the first deployment appear to be very high resolution geochemical data.

The Noakes Lander with Automated Biological/Chemical Monitoring System (ABCMS) was used quite successfully in October to evaluate several sites under consideration for installment of the CSA. The Noakes system - which now includes a downward-looking camera - operated for 9 hours recovering visual data continuously and samples of water-column suspended material, on demand. Although the membrane induction mass spectrometer (MIMS) did not function, the electronics to and from it did. The membrane component of the MIMS failed and although several replacement membranes were fabricated onboard, none survived the rigors of emplacement into the MIMS.

The pore-fluid sampling array (PFA), was designed to sample and analyze pore-fluid chemistry of the shallow, near-seabed HSZ. The first PFA was completed in time for deployment during a May 2005 cruise using a 10m SFP in much the same way as the thermistor array (TA) was emplaced. The osmo-sampler retrievable section was recovered on the September 2006 JSL dive along with the TA data-logger. Smaller pore-fluid samplers were also deployed and expand the lateral coverage of pore-fluid geochemistry at the Observatory. Recovered water samples have since been processed yielding valuable data on the pore fluid chemistry representative of its location. The PFA design and its sampling success prompted the fabrication of a second PFA to expand the lateral coverage of the pore fluid investigation to additional areas of interest. A second unit was installed during the April 2008 cruise, penetrating a fracture zone within 3m of a 10m gravity core site which yielded significant hydrates (gravity corer and PFA precision guided by ultra-short base-line (USBL) navigation system). Smaller pore-fluid collecting devices or "peepers" were among the sensors deployed on the MMRI/CMRET-designed ROVARD that was recovered in June, 2011. Additional replacement osmoboxes as well as smaller pore-fluid sampling units - landers and peepers – will be deployed in the coming year. This device is also under consideration for adaptation to collect microbial growth information.

Figure 10. ROVARD with CSAs and peepers

Biological Experiments and Monitoring

The importance of microbial activity to the production and stability of hydrates has been acknowledged by Consortium researchers since the early discussions of the MS/SFO. The possibility of adding a microbial component to the station was discussed for several years prior to the addition of microbial researchers to the Observatory project via NIUST. Four projects were funded and provided ship time with the Consortium beginning in September 2006 with deployment of experiments on the sea-floor with the

JSL. Their work continues using the NOAA/NIUST specially designed Remotely Operated Vehicle (ROV), station service device (SSD), for deployment and recovery. The Consortium (via NIUST) has provided the microbial team with access to the site by making a portion of Consortium-requested ship time and ROV/SSD submersible time available for their use. Microbial collectors have been deployed and several sampling efforts (see Figure 9) have succeeded in beginning to elucidate the microbial activities at the observatory site. In this way, the MS/SFO becomes a three-way observatory providing geophysical, bio-geochemical, and microbial data from the sea-floor, eventually on a continuous, near real-time basis. This additional dimension has greatly expanded the utility of this multi-disciplinary facility and improved our ability to investigate and model the interrelated physical, chemical and biological processes at work at this active carbonate - hydrate mound complex, complete with dynamic hydrocarbon fluid venting.

Figure 11. The SSD recovering a push-core through bacterial mat from the seafloor at MC118, ~870m water depth.

In 2009, serious attention began to be given to the benthic macrofauna at MC118. Through collaborations with other researchers and the efforts of new student interns, we are beginning to unravel the history of the fauna on the seafloor, their ecology and history and how these factors reveal the venting history at MC118. Four submersible cruises to MC118 in 2010-11 have revealed much more diversity and complexity on the seafloor than previously known (see Figures 12 and 13). Additional cruises and projects, mostly carried out through affiliates of the CMRET, occurred through the end of 2011 with the CMRET providing maps, bathymetry, locations of seafloor instruments, hazards, etc. to researchers from a variety of institutions, participating in Deep Water Horizon recovery work at MC118.

Figure 12. Bacterial mats and clams form part of a chemosynthetic community on the seafloor at MC118.

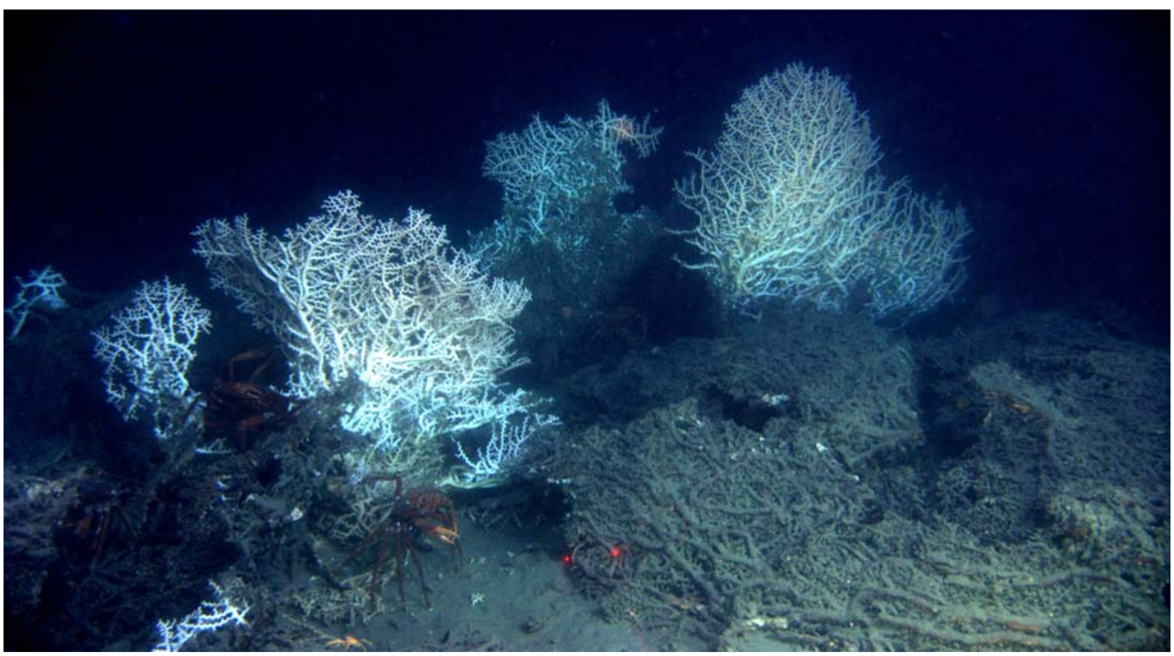

Figure 13. Deep Sea Corals at MC118. Reefs provide habitat, recruitment and nursery functions for a range of deep-water organisms including commercial fish species. Deep corals may provide windows into past environmental/ecological conditions (photo credit: Chuck Fisher, Chief Scientist Lophelia II cruise using the Jason II, October 2010 BOEMRE/NOAA supported).

Station Support Systems
Several Station Support Systems (SSS) have been and continue to be developed for the installation, operation, and maintenance of the station. These, with their funding sources are:

A. Integrated Data Power Unit (IDP), NOAA/NIUST; This unit will serve as the master station data logger and provide power *via* the battery system, It will also serve to convert the HLA ethernet signals to optical signals for fiber transmission via the Data Recovery System (DRS). The IDP is now complete and was installed at its intended location during the May–June, 2008 cruise. When, on the subsequent cruise to MC118 in fall of 2008, the crew failed to make contact with the IDP, the scientific staff agreed that the entire DRS system would have to be retrieved and evaluated. This was done on said cruise. The failure was evaluated by fabricators, Specialty Devices, Inc. (SDI) and corrections/repairs made. The entire system was redeployed April, 2010.

B. Absorption Glass Mat (AGM) battery system, MMS/BOEM, NOAA/NIUST; This system has been selected as the most appropriate power supply for the IDP, considering all factors pertinent to the power requirements of the station, cost and efficiency (minimal self-discharge). Droycon Bioconcepts (MMS-funded) conducted a study of the utility of a bio-battery system to provide power for the sea floor station. While the study demonstrated that this concept fell short of providing sufficient power to supply station needs, it indicated that it may well serve as a trickle charge system capable of extending the life of a conventional battery such as the AGM. Subsequently, a follow-up proposal was provided by Droycon for a full-scale test of a bio-trickle charge system for this application. It is anticipated that the AGM, fitted with the bio-trickle charge will reduce battery change-outs to once a year.

C. Data Recovery System (DRS) – MMS/BOEM; The station is designed for real time operation, to be hooked-up to a platform with mainland link *via* commercial fiber optic cable. Until such time that the hook-up can be made, data will be retrieved by periodic downloading of the IDP at approximate six-month intervals. Originally this was to be carried out by means of a buoy arrangement in the configuration of a capital letter "M" connected to the IDP by fiber-optic cable (reinforced with an ultrex high strength fiber) fitted with a wet-mateable communications link (WMCL). This arrangement had to be modified due to the discovery of the MC118 mound area by commercial long-line fishermen as a prime fishing ground. Concerns were that the upper mooring floats of the "M" would be at risk of entanglement by the long-lines. The new DRS arrangement allows the retrieval mooring to rest on the seabed until recalled to the surface via attached flotation after acoustic release of its sacrificial weight. On retrieval, the DRS system can be hooked-up on the surface *via* the WMCL and downloaded. On completion of the task, another weight is attached and the system and is lowered safely to the sea-floor, out of the reach of the long-line fishing operations. The DRS was successfully deployed and tested during the March, 2009 cruise and communications with it were successful during the June, 2009 cruise. Collection of "real" HLA data remains a task of the future.

D. Telemetry Buoy, NOAA/NIUST; The WMCL is also designed to accommodate a detachable telemetry system, the purpose of which is to provide a means of synchronizing (providing Time-0) the various dedicated seismic energy source pulses, both P and S-wave, with the appropriate receiving systems during a given dedicated-source seismic operation.

E. Station Service Device (SSD), NOAA/NIUST; The SSD is a specially designed ROV system for use on level-two-equipped, non-dynamically positioned vessels (available at a much lower day rate than a level one) for the purpose of deploying station sensors and support equipment. Battery change-out and general maintenance are also among the SSD tasks. The system differs from conventional ROVs in that, instead of being suspended in the usual manner, it works off a clump-weight/pressure compensated battery (its power supply), lowered to the sea-floor. A small, specially designed ROV is maneuvered from the clump-weight platform, powered by the battery and controlled *via* an umbilical, within a limited working radius (50m), but sufficient to carry out the required tasks of the station. Significant development of this system has taken place and its versatility continues to be apparent: From its first mission in 2007 - when it recovered microbial experiments from the seafloor - to its current capability of collecting targeted push cores, by virtue of its navigation capabilities and 3 cameras (Figure 11) the SSD continues to be adapted to Consortium researchers'needs. During the June 2009 cruise, over 30 hours of resistivity data were acquired using the SSD as the transport for the 1100m towed cable (the first time such a survey has ever been attempted with an ROV). In April, 2010, the SSD successfully carried equipment on the seafloor to the node that will accommodate the HLA data-loggers, deployed an array spool, collected push-cores and collected many hours of seafloor video images. In September 2010, the ROV worked in tandem with a new deployment platform called the ROVARD (ROV Assisted Recovery Device) to install geochemical chimney sampler arrays at specific, high value sites on the seafloor. We continue to upgrade the ROV and are currently increasing its depth rating by 50% and adding new camera, lights and optical multiplexers for improved imaging and reconnaissance capabilities.

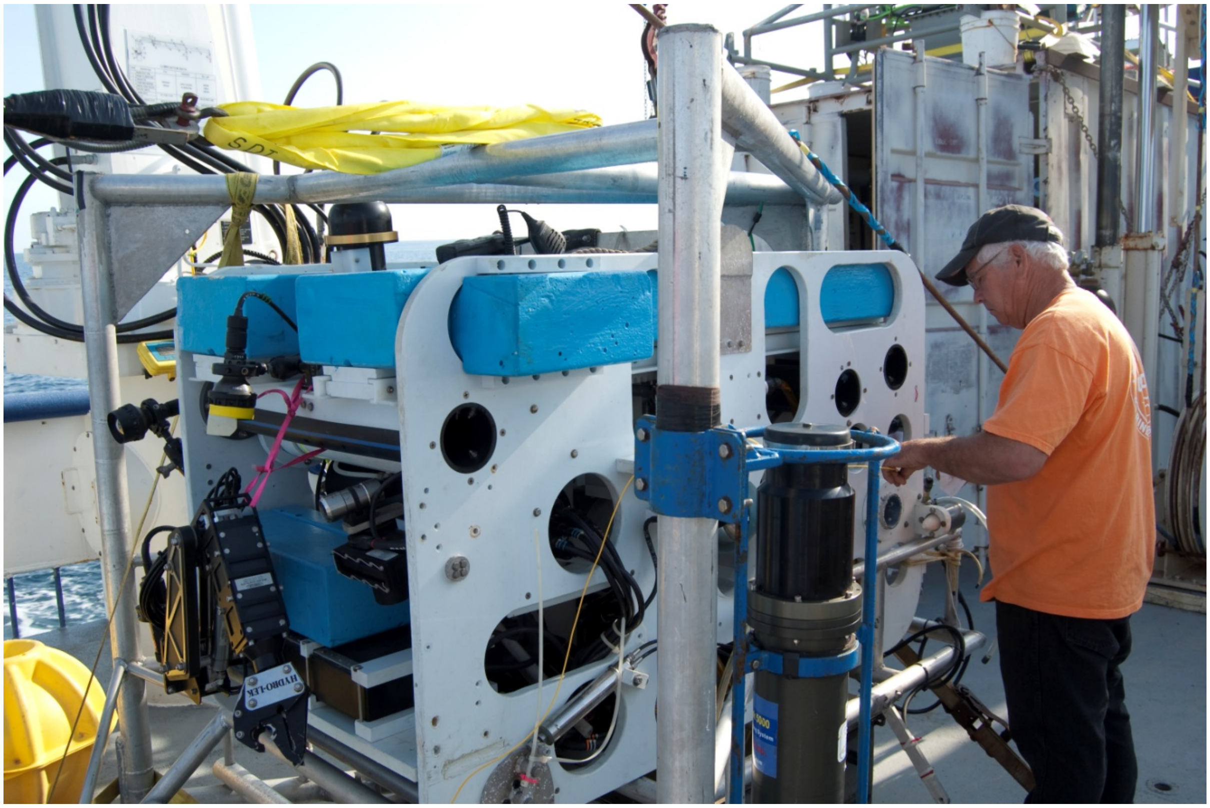

Figure 14. MMRI's electronics technician, Larry Overstreet, gives the SSD its final inspection prior to a dive.

F. Autonomous Underwater Vehicle (AUV), NOAA/NIUST: The AUV *"Eagle Ray",* acquired from ISE (International Submarine Engineering) and operated via a cooperative venture between NOAA, and NIUST, has completed sea trials of its basic operating, navigation and sea floor mapping systems and has conducted several seabed mapping projects. The ISE design is capable of operating to depths of 2200m and is equipped with a large instrument pay load capacity, making the vehicle ideal as a test platform for a variety of sensors. The MMRI division of NIUST, Seabed Technology and Research Center, STRC, is responsible for, among other things, developing new tools and sensors for the AUV, particularly systems applicable to the exploration of sea floor occurrences of gas hydrates and hydrocarbon seeps and vents. In late June, 2009, the *Eagle Ray* carried the Woods Hole Oceanographic Institute's (WHOI) mass spectrometer during its survey of the near-seabed (6m above seafloor) water column geochemistry at the MC118 test site. Also in progress is the adaptation of the CMRET, shallow-source/deep-receiver (SSDR) (MMS) high resolution seismic system (deep receiver component) for installation on the AUV which will greatly improve stability, near seafloor operation, data acquisition to subbottom depths of 500-700m, navigation accuracy, noise reduction and reduction of survey time by a factor of four. A polarity-preserving chirp system, has been designed, built and installed on the *Eagle Ray*. A test cruise was executed in July, 2011, data recovered and evaluated for performance of the software (Phase 4, Task 2.6). The MMRI-NIUST team continues to work with Geoacoustics to improve the system which is expected to go to MC118 in June, 2012.

G. Mola Mola AUV, NOAA/NIUST: This vehicle (Figure 15) will be used primarily as a visual survey tool. The *Mola Mola's* primary capability is to photograph, for mosaicing, imagery of the seafloor. Although some navigation issues remain to be resolved, many functions of the *Mola Mola* have been tested at-sea. A photomosaic of the site is a goal of the 2012 cruise season.

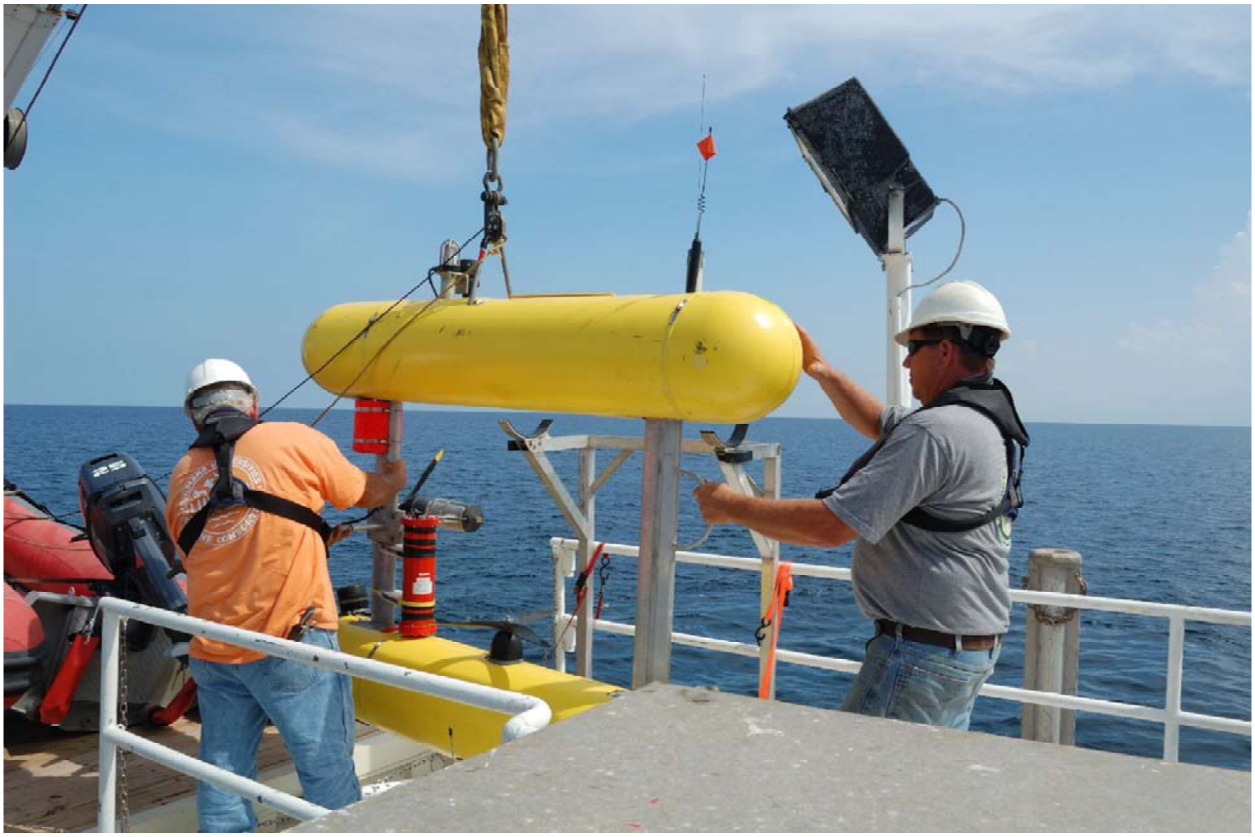

Figure 15. MMRI Electronics Technician, Larry Overstreet, and Research Systems Specialist, Brian Noakes (right), prepare the* Mola Mola *for deployment.

EXPERIMENTAL/ RESULTS AND DISCUSSION

PHASE 1 Tasks for FY 2006:

Task 1: Design and Construction of four Horizontal Line Arrays

This task is complete. Although the HLAs are still not deployed at the Observatory site, they are complete and ready for deployment, thus satisfying the obligation of SDI, the subcontractor. However, SDI has agreed to continue to work with MMRI toward the eventual goal of deployment of all arrays. The next effort is scheduled for July, 2012.

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, 3 and 4.

Task 4: Noise-Based Gas Hydrates Monitoring.

This task is complete.

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. Amplitude vs. offset (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.

University of South Carolina (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 included funds to purchase an additional, deeper, 3-D dataset from WesternGeco. Accomplishments of this phase are summarized in the Phase 3 sections.

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

4-C data were acquired by the MMRI and WHOI in April. WHOI has prepared the data files and delivered them to MMRI who has copied and made them available to the Bureau of Economic Geology for processing. There are some issues with the data strings being of inconsistent length. During the fall of 2011, MMRI sent a geophysicist to Austin to work with the BEG on this data set. We anticipate that the processing will take several months and have requested a no-cost extension of time – until June 30, 2012 - to perform the work. More recently, UT requested release from this subcontract, due to a lack of people at their Institution committed to completing the work. The University of Mississippi (UM) is working with UT to redirect the funds to UM and to have the work done by UM.

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 4 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 4 and progress is covered more fully in that section of this report.

TASK 6: Microbial techniques to extract carbon from stored hydrocarbon gases: Exploring Extent of Microbial Involvement in Seafloor Hydrate Formations/Decompositions and Establishing that Mechanism

This task is complete with the final report having been submitted in the previous reporting period. Funds remaining in this account were exhausted when the PI traveled to Edinburgh, UK to present results at the 7th International Conference on Gas Hydrates in July. In brief, these results include the MSU team's findings that indigenous microbes play an important part in the nucleation, accumulation, and dissociation of near-surface hydrates, that microbial techniques can be used to extract carbon from stored hydrocarbon gases—i.e., to assist in the production of the occluded hydrocarbon gases, and most recently, the intriguing finding that microbial cell wall material inhibits hydrate formation, a necessary occurrence for the bacterial cell's survival, as it prevents hydrate formation-heats from being liberated directly onto cell surfaces. ***They found the hydrate inhibitor to be peptidoglycan, a chemical common in microbial cell walls.*** Data were gathered showing this water-insoluble peptidoglycan polymeric compound, to be increasingly effective as an inhibitor - to hydrate formation - by increasing its surface area through cell lysing. A smaller, water-soluble, molecular component of the peptidoglycan polymer was tested and shown to retain hydrate-inhibiting properties. In tests comparing with a methanol standard, this water-soluble, glycan strand performed better in delaying gas hydrate formation (i.e., longer induction times) than similar amounts of methanol, the current industry standard used to inhibit hydrate formation in pipelines.

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 4 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.

Development of a Shallow Sediment Velocity Probe (SSVP) for use in the Gas Hydrates Research Consortium Sea Floor Observatory Program at MC118.

Introduction

A need for improved knowledge of sediment characteristics as part of the studies of the Gas Hydrates at the MC118 site prompted a desire to measure the velocity of these sediments. The successful installation of the Pore Fluid Array and Temperature Array with sensors installed to depths below the bottom of nearly 10 meters at MC118 opened the possibility of installing acoustic sensors on a similar probe as a method of measuring sediment velocity.

Background

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, is capable of driving and communicating with acoustic sensors, and can achieve a measurement accuracy sufficient to meet the needs of the studies at MC118. SDI has offered to include this development as part of an ongoing electronics package development aimed to provide rapid acoustic shallow water sediment measurement capability. The development has been slowed by other commitments to the overall program and resulted in the need to change electronics systems due to the rapid advancement of the electronic systems to be used.

Activities during this period

During the previous period the activities on this project included the software and instrumentation development. An A/D converter and hardware development system had been purchased and used in the development of the software. During software development we have found that both the hardware support and software support for the selected system is losing its user base due to the advent of a better system becoming available. As a result we have undertaken a change to the latest hardware system. Compatibility with our existing software is one of the factors in the selection process but it appears the final product will benefit from a completely new hardware system. A new development system will be selected and purchased shortly to allow us to complete the overall system development. On the hardware side, we are designing the housings for the hydrophones and preamplifier systems acquired during the last reporting period.

The bottom detection switch, battery power supply, electronics housing and probe design effort is continuing in this design phase.

Design Overview and Progress

The sediment probe will consist of a 10 meter long probe with imbedded hydrophones and a control head. The control head will include the controller/data logger, a bottom impact sensor, the battery power supply and the acoustic source. Mounted above the control head will be a USBL transponder to provide positioning information to the ship.

The operational plan includes, lowering the sediment probe to a depth of 30 to 50 meters above the sea floor, using the USBL system to navigate the sensor to the desire location, free falling the sediment probe into the sea floor, having the bottom insertion detected by the accelerometer sensor, leaving the probe in place for a suitable time to measure sediment velocity distribution along the probe length and having the ship winch pull the probe fee of the sea floor. The sediment probe can then be navigated to a new position and the process repeated without retrieving the probe to the surface.

Schedule
The present development plan should allow the sediment probe to be used on the spring cruise in 2012.

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 4.

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 4.

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

The University of South Carolina (Earth and Ocean Sciences) continued to participate in geophysical activities as part of the Gulf of Mexico-Hydrates Research Consortium. During the reporting period July through December 2011, we started to conduct a time-lapse analysis and comparison of two industry quality 3D seismic data volumes, from TGS Nopec and WesternGeco and continued the analysis on the jumbo piston cores collected in spring 2011.

This report summarizes our technical contributions as follows:

- Jumbo Piston Core Analysis
- Time-Lapse Seismic Analysis

We presented a poster at the American Geophysical Union (AGU) meeting in December, summarizing some of the work on rock physics model development.

Jumbo Piston Core Analysis

Five jumbo piston cores of ~15 meters in length collected in the vicinity of Woolsey Mound, MC-118 (Gulf of Mexico) (Figure 16) in January 2011 are studied by a geology team of five people from the University of Southern Mississippi and the University of South Carolina. The study uses stratigraphy, sedimentology, and structural geology principles.

Additional features like visible porosity, fluid content and smell are also reported. Specifically the following properties are used to describe and classify the cores:

I. Color: Physical property based on the sediments color. A soil color chart is used to identify them.

II. Mineral Composition: Refers to the mineralogic composition of the samples. The depositional environment is deep marine (continental slope). Water depths are neritic-to-bathial. Common mineralogies for this environment include: quartz, pyrite, feldspar, micas, carbonates, etc.

III. <u>Texture</u>: Texture refers to the size, shape and arrangement of grains that make up a sedimentary sample. Size of clasts or crystals is characterized by grain diameters; variation in grain size is called sorting and is a function of the mode of transport of materials and distance from the source. Particle size is the primary basis for classifying clastic sediments and sedimentary rocks regardless of clast mineralogy. The shape of grains - sphericity, roundness, angularity - is related to the distance and mode of transport from the source.

IV. <u>Bed contacts</u>: Type of contact, in terms of continuous sediment deposition, erosion or no deposition (erosional or depositional hiatuses).

V. <u>Fossil content</u>: Presence/absence and type of fossils, including shells, bones, or their replacements, and as traces of organisms including bioturbations, tracks, trails, and burrows.

VI. <u>Sedimentary structures</u>: Various sedimentary structures yield clues to the origin of the sample and its depositional environment.

VII. <u>Structural features</u>: Sediment deformation exclusively associated with tectonic stresses, - faults, fractures, cracks and folds - is reported.

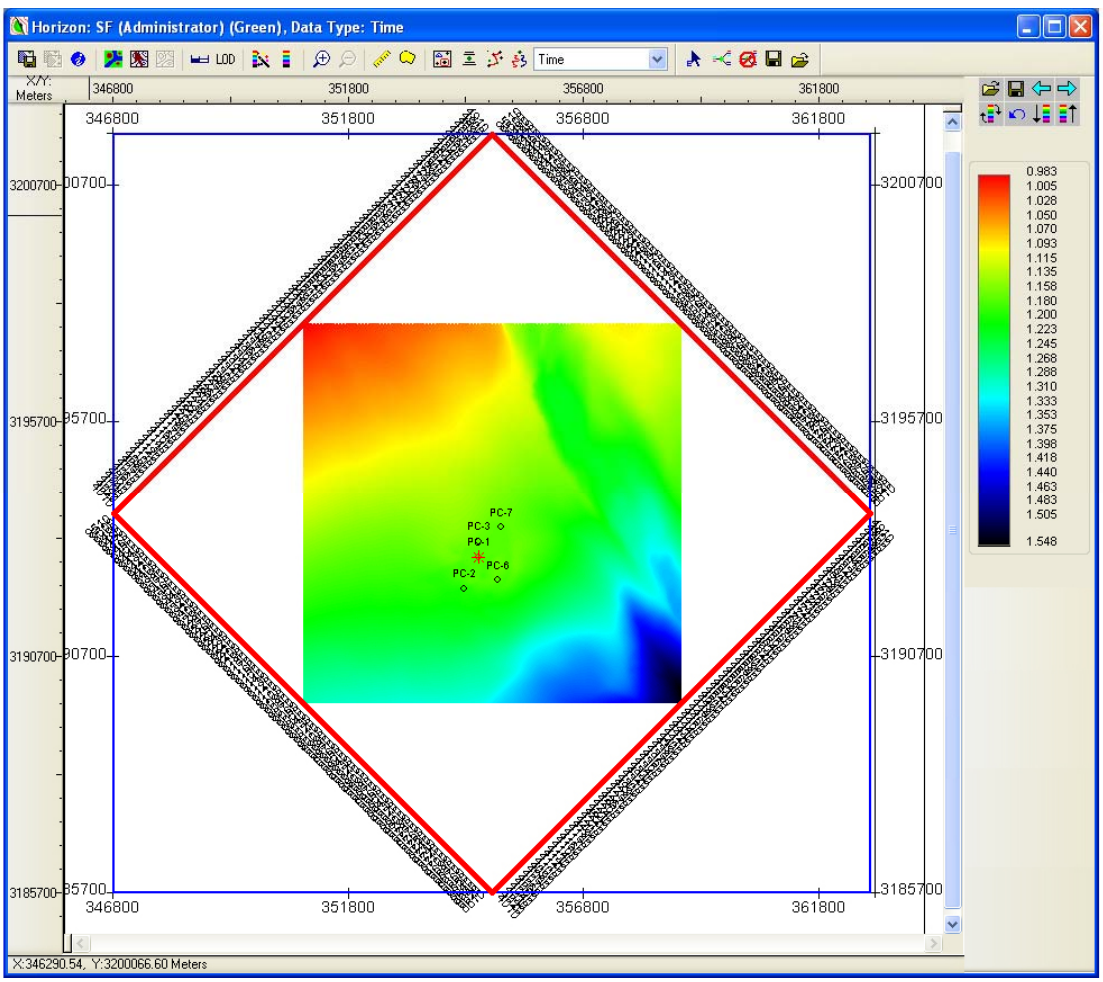

Figure 16. Sea floor structural map (in time) at MC-118 with piston core locations. Piston core (#1) with gas-hydrate recovery is shown in red.

RESULTS

- Fine-to-very fine grained sediments with large volume of pelagic/hemipelagic water-saturated clays (Figure 17).
- Minor presence of coarse-grained sediments like silt and fine-grained sands.
- Some signs of bioturbation.
- In some cores, strong H_2S and hydrocarbon smell are found.
- Minor presence of minerals such as quartz, mica and pyrite and organic material.
- Presence of cracks and visible porosity in some cores.
- Most individual lithofacies are present in all cores.

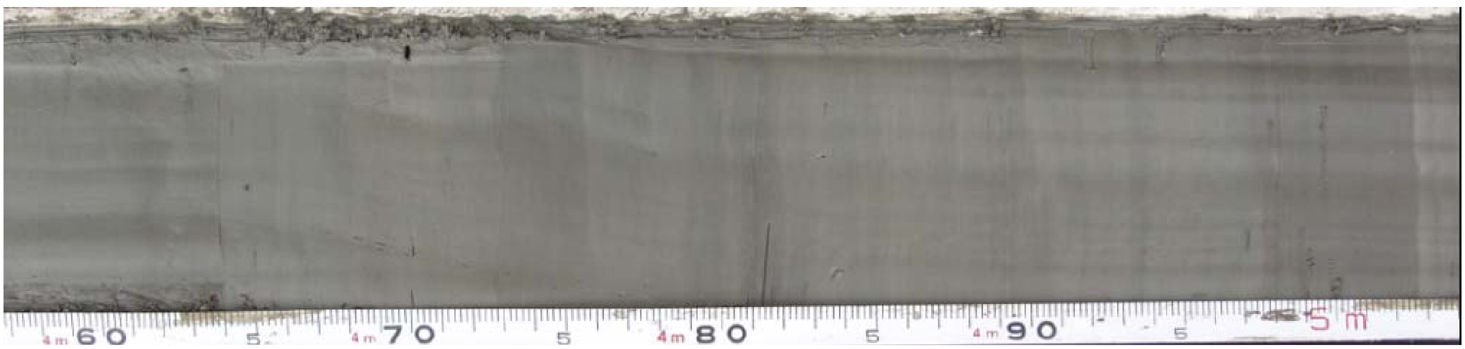

Figure 17. Section of core # 6.

ACTIVITIES PLAN

1. Facies classification: based on lithofacies (done).
2. Electronic data base assembling (done).
3. Facies association-correlation.
4. Depositional environment interpretation or facies modeling: based on facies association.
5. Absolute age determination: Biostratigraphic study (subject to funds).
6. Sequence stratigraphic analysis: Depositional systems and chronostatratigraphic analysis. Core+electrical logs+biostratigraphic data integration. Depositional cycles calibration with glacioeustatic sea level chart (subject to activity # 5).
7. Sedimentation rate estimations (subject to activity # 5).
8. Oxygen isotope analysis (subject to funds).

Time-Lapse Seismic Analysis

Time-lapse seismic monitoring, also known as 4D seismic analysis, is widely used in the oil-industry for reservoir depletion monitoring (Tura et al., 2005), as well as in CO_2 sequestration monitoring activities (Chadwick et al., 2005). Except for few documented cases (Riedel, 2007; Bangs et al., 2011), there is a paucity of literature for 4D seismic analyses in *cold seep* areas, due to their extremely dynamic nature and hardly predictable behaviors through time. It mainly consists of comparing two or multiple seismic data sets acquired in the same area through time, preferably having similar acquisition/processing parameters, with the aim to detect changes in sub-surface anomalies that likely reflect variations in pore spaces saturation (i.e. oil, gas, CO_2, and maybe gas hydrate).

At this time, time-lapse seismic analysis is still in the early stage. The analysis is being carried out using Hampson Russell CGGVeritas software, but in the future, a special module included in Kingdom Suite SMT software may be necessary as well (i.e. Rock Solid Attributes).
The data used for this purpose are: 3D standard seismic data acquired by TGS in 1999-2000; 3D standard seismic data acquired by Western Geco in 2002-2003. The main purpose is to determine whether or not significant/detectable changes in hydrocarbon anomalies within the GHSZ have occurred in a short time frame, for instance 2-2.5 years.

When it comes to performing 4D analyses and comparing two seismic datasets, preferably they should have similar geometry and acquisition/processing parameters. Ideally, prior to any interpretations those conditions have to be met; otherwise, interpretations may be merely speculative.

Although the Western Geco and TGS data belong to the same typology of standard 3D data, which means they were acquired and processed with standard and similar techniques, some processing steps were needed in order to have the two data sets comparable. The first step in doing 4D seismic consisted in setting a data set (usually the older) as reference, and the newer or the newest as monitor. In our case, TGS data were chosen as reference and Western Geco data as monitor.

The processing sequence applied consisted in:

- re-sampling Western Geco data (according to TGS data sample rate);
- 3D geometry re-binning of the Western Geco (according to TGS data geometry);
- cross correlation time-shift or static shift (according to TGS data timing of events);
- gain normalization (according to TGS data gain).

Two processing steps, *phase matching* and *shaping filter*, are still in the experimental stage on Western Geco data in order to be fully compared to TGS data, thus avoiding eventual artifacts. However, preliminary results from the time-lapse seismic monitoring are encouraging, showing that some sub-surface anomalies (i.e. hydrocarbon anomalies) are different on the two data sets.

Figure 18 shows two snapshots of the Sleeping Dragon, located near the SW Crater Complex. It is one of the largest seafloor gas hydrate outcrops documented in the Gulf of Mexico (pictures were taken 4 years apart).

Figure 18. The Sleeping Dragon at Woolsey Mound, one of the largest seafloor gas hydrate outcrops in the Gulf of Mexico (gas hydrates are light-brown color; carbonates are grey). The picture on the left was taken in 2006, whereas the one on the right was shot in 2010. Note the significant change (increasing) in size of the carbonate/hydrate body, suggesting ongoing hydrocarbon flux (photos courtesy of MMRI, University of Mississippi).

Although the pictures seem to be taken from a different angle, there’s no doubt about the change in size, suggesting an active hydrocarbon flux through time from the underlying reservoirs, which has been feeding the seafloor gas hydrates more or less continuously. Can these changes, observable on the seafloor, be correlated with changes in the sub-surface? Even though the pictures were taken in different times with respect to the seismic data (2006 and 2010 for the pictures versus 1999 and 2002 for the two seismic datasets), the Sleeping Dragon is an extremely dynamic area with active vents, therefore a detailed 4D seismic analysis would be worthwhile anyway. For this purpose, we made a comparison between TGS and Western Geco data in the same area where the Sleeping Dragon lies on the seafloor. The results can be seen in figures 19 and 20. The comparison was made essentially through a Cross-Correlation function. Figure 19 shows the results of the Cross-Correlation between Western Geco and TGS data starting from the seafloor down to a shallow portion of the subsurface, where changes would be expected but not relevant; as a matter of fact, here the mean correlation is 88%. Since the correlation in areas off-mound, which can be considered more quiescent with respect to the mound, the mean correlation between the two data sets is about 92%, we could infer that no drastic changes occurred in the near-seafloor of the Sleeping Dragon from 1999 through 2002. On the other hand, figure 20 shows the results of the Cross-Correlation between the two data sets, related to one of the shallow amplitude anomalies previously interpreted as free gas at the base of the GHSZ (Macelloni et al., 2012 – in review). Here, dramatic changes could be expected based on the time-variant model suggested by Macelloni et al.. Sure enough, in this case the mean correlation between Western Geco and TGS is 78%, which is about 15% less than the off-mound areas considered as quiet, and there are also several areas where the correlation is lower than 30%. ***This may suggest a variation through time for the hydrocarbon saturation at the base and/or within the GHSZ.***

Another comparison between the two data sets was made, again related to an area of *Woolsey Mound* sub-surface where shallow amplitude anomalies at the base of the

GHSZ were interpreted as free gas. The area is located away from the Sleeping Dragon and it includes the location where the core, JPC-1 was taken from the seabed during the Jumbo Piston Coring cruise in January 2011 (the only core where gas hydrates were recovered and sampled). This time, the comparison was made through the seismic attribute “instantaneous amplitude” (Taner, 2001). Essentially, high amplitude values indicate potential gas accumulations in the subsurface (Figure 21). Although the data look similar, overall, the comparison between Western Geco and TGS data shows a remarkable difference in amplitude anomalies toward east from the JPC-1 location (Figure 21). If we assume that the amplitude anomalies present on TGS data were reflecting hydrocarbon accumulation beneath the GHSZ, the lack of such anomalies on Western Geco data may indicate that an upwards hydrocarbon migration occurred during the period 1999-2002 (area within the black circle in Fig. 21). This suggests that significant changes in *Woolsey Mound*’s sub-surface anomalies may have occurred in a time frame of just more than two years, thus confirming the very dynamic nature of the mound.

Since a *phase matching* and a *shaping filter design* need to be addressed yet, in absence of a full processing sequence all preliminary assumptions inferred from 4D seismic analyses have to be considered speculative, and the above interpretations should be treated cautiously. However, because the instantaneous amplitude attribute is independent from the phase, changes seen in the instantaneous amplitude showed in Figure 21 could be considered fairly reliable.

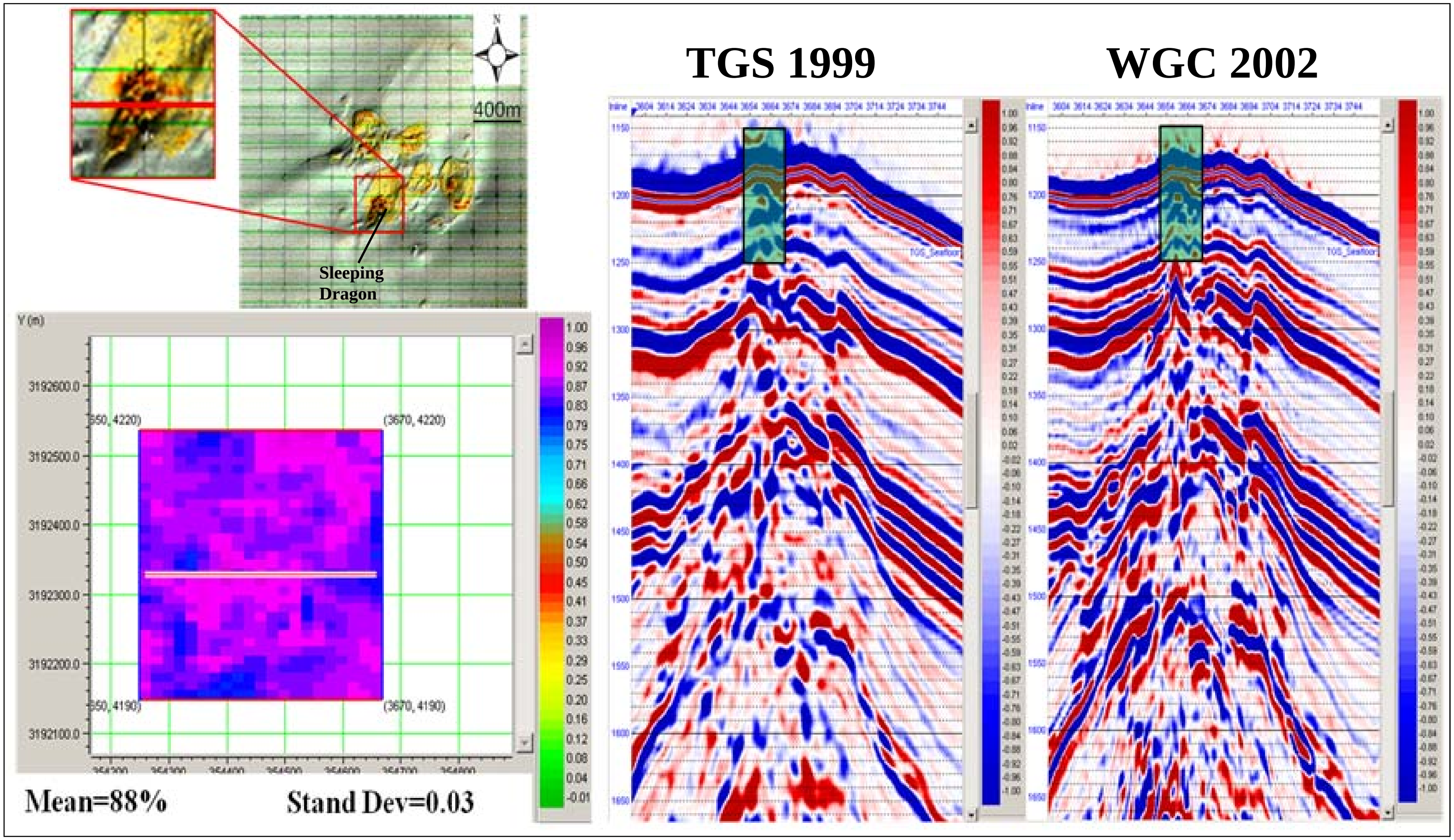

Figure 19. Example of 4D seismic analysis using TGS data, acquired in 1999 and Western Geco data, acquired in 2002 (see text for details). The comparison is made essentially through a cross-correlation function. On the upper left corner, the back-scatter bathymetry surface of *Woolsey Mound* and a close-up of the area investigated (red box). On the right, two coinciding E-W oriented profiles of TGS and Western Geco data; the green shaded box shows the "near seafloor" time window chosen for the comparison and its lateral extent is the same as that of the red box. On the lower left corner, the cross-correlation plot related to the area in the red box and the time window of the green shadowed box. The mean cross-correlation value between the two data sets is 0.88 (or 88%), suggesting that no drastic changes occurred between 1999 and 2002.

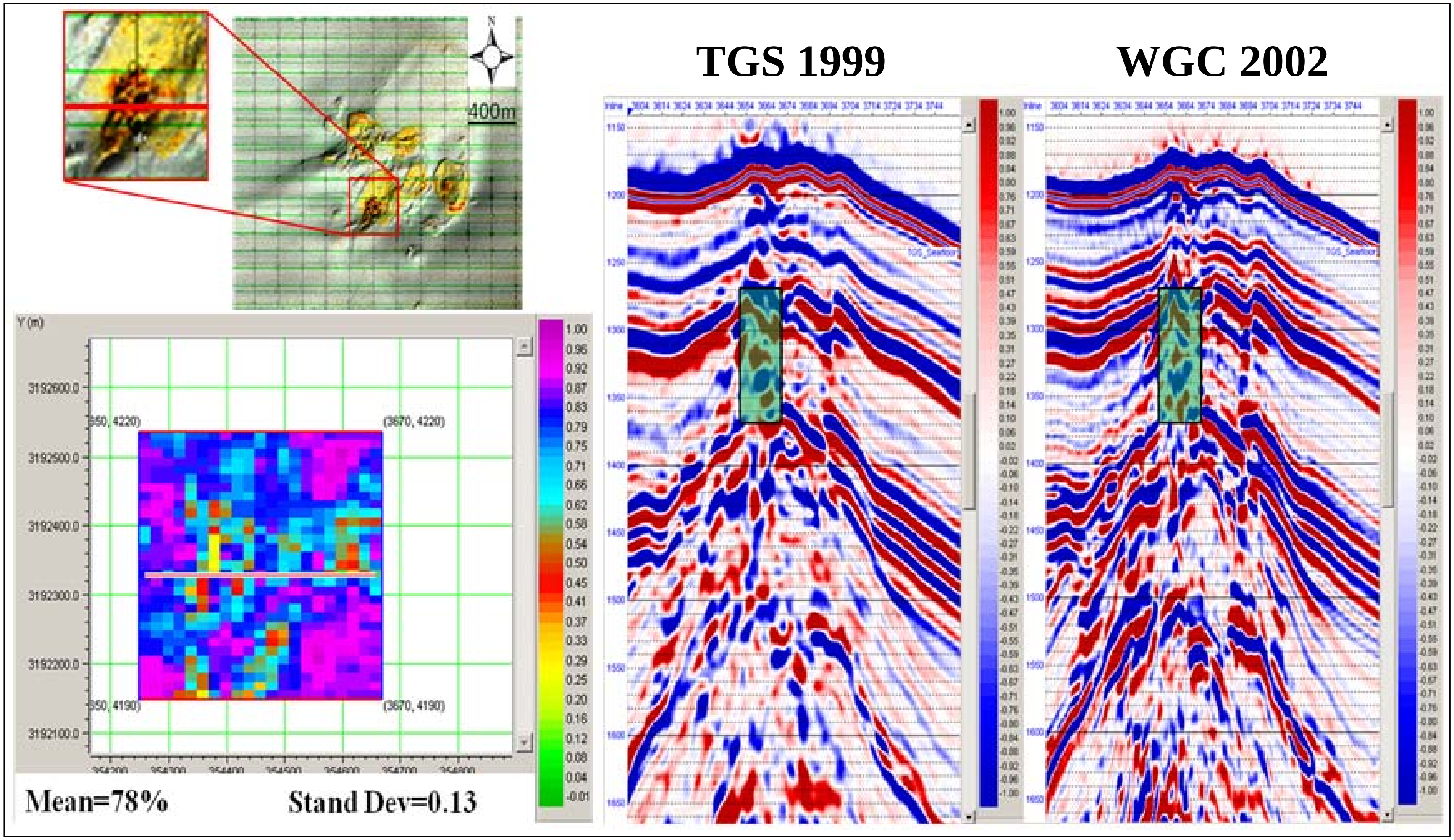

Figure 20. Another Example of 4D seismic analysis using TGS data, acquired in 1999 and Western Geco data, acquired in 2002 (see text for details). Here the area chosen for the correlation is the same as in fig.19, but the time window used is deeper (from 1270 ms through 1370 ms) and includes one of the shallow amplitude anomalies previously interpreted as free gas at the base of the GHSZ. In this case, changes would have been expected based on the model suggested Macelloni et al.. As a matter of fact, the mean cross-correlation value between the two datasets is 0.78 (or 78%), with several areas where the correlation is lower than 30%, suggesting that significant changes in hydrocarbon anomalies may have occurred between 1999 and 2002.

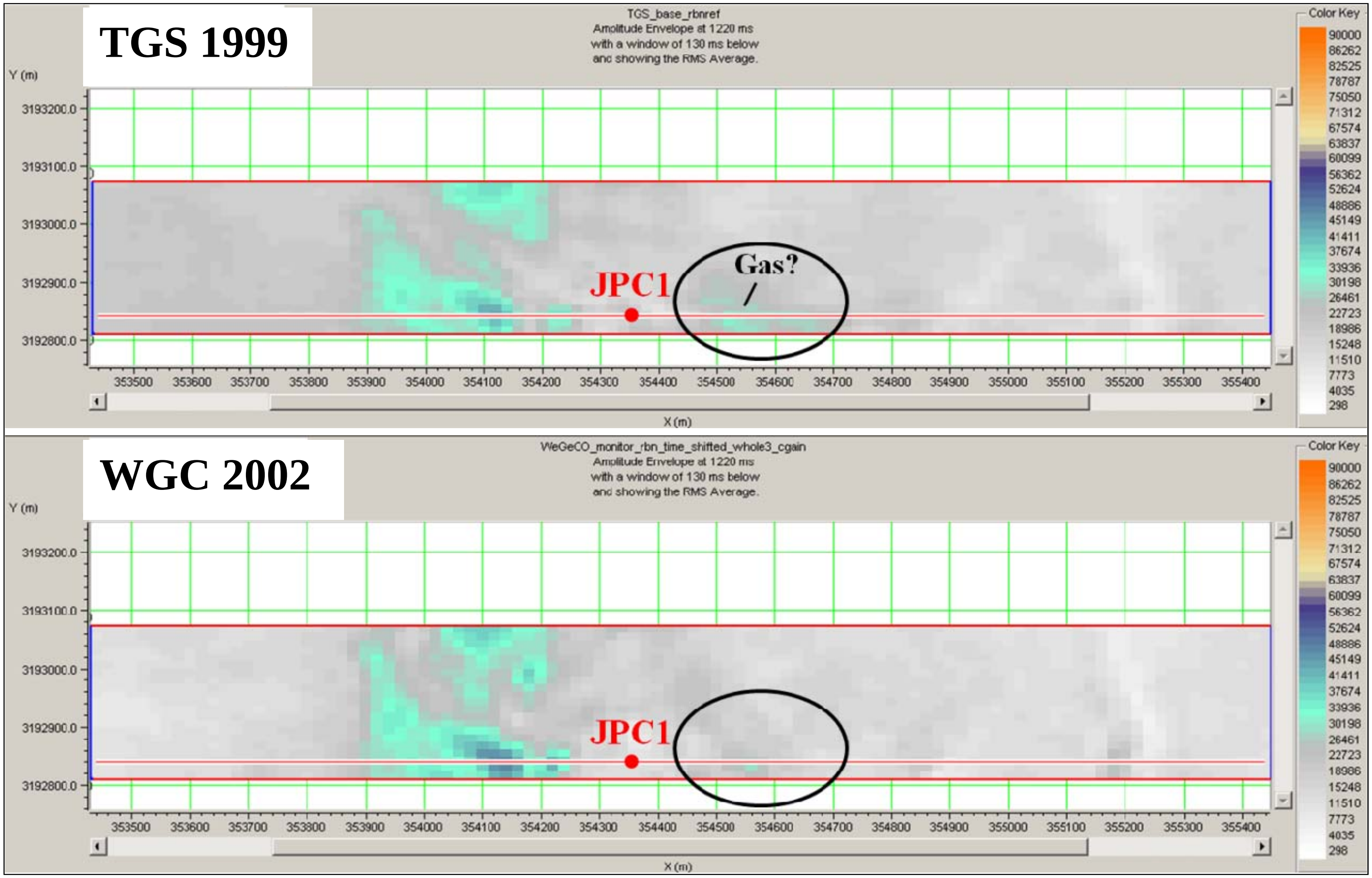

Figure 21. Instantaneous amplitude (or *amplitude envelope*) slices extrapolated from TGS (top) and Western Geco (bottom) data. The red circle denotes JPC1 location. The amplitude values are the RMS amplitude calculated from 1220 msec through 1350 msec b.s.f., thus including areas where shallow amplitude anomalies previously interpreted as free gas at the base of the GHSZ. Since here higher amplitude values (cyan and blue) are interpreted as free gas, the lack of such anomalies on Western Geco data may indicate an upwards hydrocarbon migration occurred during the period 1999-2002.

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

4-C data were acquired by the MMRI and WHOI in April, 2011. WHOI has prepared the data files and delivered them to MMRI who has copied and made them available to the Bureau of Economic Geology for processing. There are some issues with the data strings being of inconsistent length. MMRI sent a geophysicist to Austin to work with the BEG on this dataset. We anticipate that the processing will take several months and have requested a no-cost extension of time – until June 30, 2012 - to perform the work. This subcontract is being rewritten to return the funds from the University of Texas to the University of Mississippi who will perform the processing of the 4-C data with UT in an advising capacity.

Anticipated Results: Through the combination of activities defined here and those identified in Phase 2, Task 3 results will include: Images of the near-seafloor geology at the Observatory site, MC118, that reveal the internal architecture of the deep-water hydrate system at MC118 and which, when combined with reservoir monitoring techniques, can be used to establish structure and internal sequences. Impedance profiles will be extended from the seafloor to below the base of hydrate stability and provide density information.

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 4 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 4 and progress is covered in that section of this report.

TASK 6: Microbial techniques to extract carbon from stored hydrocarbon gases: Exploring Extent of Microbial Involvement in Seafloor Hydrate Formations/Decompositions and Establishing that Mechanism

This task is complete with the final report having been submitted in the previous reporting period. Funds remaining in this account were exhausted when the PI traveled to Edinburgh, UK to present results at the 7th International Conference on Gas Hydrates in July. In brief, these results include the MSU team's findings that indigenous microbes play an important part in the nucleation, accumulation, and dissociation of near-surface hydrates, that microbial techniques can be used to extract carbon from stored hydrocarbon gases—i.e., to assist in the production of the occluded hydrocarbon gases, and most recently, the intriguing finding that microbial cell wall material inhibits hydrate formation, a necessary occurrence for the bacterial cell's survival, as it prevents hydrate formation-heats from being liberated directly onto cell surfaces. They found the hydrate inhibitor to be peptidoglycan, a chemical common in microbial cell walls. Data were gathered showing this water-insoluble peptidoglycan polymeric compound, to be increasingly effective as an inhibitor - to hydrate formation - by increasing its surface area through cell lysing. A smaller, water-soluble, molecular component of the peptidoglycan polymer was tested and shown to retain hydrate-inhibiting properties. In tests comparing with a methanol standard, this water-soluble, glycan strand performed better in delaying gas hydrate formation (i.e., longer induction times) than similar amounts of methanol, the current industry standard used to inhibit hydrate formation in pipelines.

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 4 and progress is reported in that area of this report.

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. This responsibility is completed for FY09 with the completion and acceptance of this year-end report to DOE, 42877R18. A compilation of administrative duties and responsibilities is presented in Phase 4, Task 7.

Task 9. Project Summary Updates:

These appear as Task 8 in Phase 4.

PHASE 4 Tasks FOR FY2010

TASK 1: Program Management Plan

This task is complete.

Task 2: Integration of Multiple Methods of Geological and Geophysical investigations to advance Shallow Subsurface Characterization at MC118, site of the Gulf of Mexico Hydrates Research Consortium's Seafloor Observatory

The focus of this task is to collect, assemble, integrate, and interpret multiple geo-datasets that have been/will be collected to investigate the characteristics of the hydrocarbon system at the site of the Seafloor Observatory being installed by the Gulf of Mexico Hydrates Research Consortium at MC118. There are six subtasks associated with this task order. Progress on each is as follows:

Subtask 2.1. Recipient shall contract heat-flow data collection surveys across the hydrate mound area at MC118. In late December, TDI Brooks notified us that they would be able to fit us onto a cruise to Mississippi Canyon and Vioska Knoll scheduled to depart Freeport Texas in mid-January. Although the schedule has slipped and the cruise has not yet departed, we are on alert and will send 2-4 people to advise/select probe locations as per the consensus of the Consortium members who have expressed their needs and opinions regarding the sites from which heat flow will be most beneficial.

Subtask 2.2. Recipient shall contract to have giant piston cores collected from areas of interest at the Observatory site. This subtask was completed and a report of activities made during the previous reporting period.

Subtask 2.3. Recipient shall process and interpret the polarity-preserving chirp data collected with the AUV-borne system, to define the shallow geometry of the fluids/gas pipe system and integrate these results with the geological (core analyses) and geophysical data.

The new Polarity Preserving Chirp (PPC) sub-bottom profiling system was successfully integrated into the *Eagle Ray* AUV and the first sea trial was executed in July, 2011. The cruise departed Cocodrie, LA aboard the R/V *Pelican* bound for Woolsey Mound seafloor observatory site in Mississippi Canyon Block 118. Upon arrival at the site, fresh to brackish water gyres were encountered which presented significant ballasting issues with the AUV. A deep water dive at MC118 was therefore not possible. Fresh water gyres are not uncommon at MC118 but they are generally thin enough layers as not to pose a problem. The record discharges from the Mississippi River in 2011, however, created larger than normal gyres.

An alternative site was selected at a poorly mapped area of suspected gas expulsion features in Ewing Banks block 873. High-resolution bathymetric mapping of the site with the AUV confirmed the presence of gas expulsion features including mud volcanoes and pockmarks, making for an ideal test-site for the new PPC system on the *Eagle Ray* AUV. The primary goals were to evaluate the integration of software, communication links, and the potential for interference (noise) with other systems on the AUV. The first transect with the chirp system was conducted with the multibeam sonar turned off to eliminate that system – and any potential for acoustic interference between these two sonar systems - from the operational software of the AUV. The dive was completed successfully and three more transects were completed with the multibeam sonar turned on and fully operational.

The PPC system worked well and passed many of the tests prescribed in its specs including "friendly" operations with the AUV software. The PPC system did not interfere with the normal operations of the AUV and there was no apparent interference with the multibeam system. Sub-bottom profiles were acquired from all four transects adding the third dimension to the bathymetric map. Faults, fractures and gas expulsion features are clearly seen on the profiles. These early results are somewhat limited by the many noise bands over-printing the data. The source of the noise bands is the acoustic modem used to communicate with the AUV;, because the system was new, the operators stayed in constant contact with the vehicle. Now that the system has been proven, interrogations - and therefore noise - can be limited to the end of track.

Figure 22. A profile (location on bathymetry at lower right) of shallow sub-bottom sediments recovered with the new PPChirp system. Although frequent interrogations of the AUV caused excessive noise (vertical features), much detail is visible in the profile, including signal polarity.

Developmental problems continue with the system and we are working with the vendor to resolve these. Currently the system will not take set-up commands consistently. Adjustment to the source signal (gain, frequency sweep, etc) and sampling rates are not adjustable to the standards set out in the specifications nor to our basic operational parameters. There is also much concern about the anti-aliasing filter applied to the recorded data and we are pursuing this with the vendor as well.

In summary, with this new system, we can now obtain high-resolution sub-bottom profiles that are co-registered with the bathymetry. We have the preservation of the polarity which is one of the basic tools used to begin to estimate the physical properties of the sediments. The system also allows us full access to the raw data so we can start to develop new processing techniques. One of the first tasks is to define the anti-aliasing filter inherent in the system, needed to obtain a calibrated source signature. To achieve this we will need to have a receiver in the far field (most likely on the seafloor). With this information, we can begin to build our own match filters that record the acoustic signal more precisely with a goal toward improving the resolution and achieve greater accuracy in interpreting the acoustic response of sub-bottom sediments.

Subtask 2.4 The recipient shall perform sedimentological, lithological, paleontological and geophysical analyses of the newly recovered cores (Phase 4, subtask 2.2) and shall integrate the results with previous core studies. The University of Southern Mississippi core-logging team has opened, photographed and described the cores from the JPC cruise. Laboratory analyses are partly complete and should be finished by the spring of 2012. Analyses include grain-size analyses, mineralogical analyses, microfossil analyses and lithologic analyses as well as electric log analyses at Stennis Space Center’s office of NAVOCEANO.

Subtask 2.5 Recipient shall collect solid outcropping gas hydrates and/or authigenic carbonate/hydrates samples at the MC118 Observatory site using the existing pressure-chamber sampler in conjunction with the STRC ROV. The construction of the small pressure vessels is complete and they have been fitted to the Station Service Device (SSD) Remotely Operated Vehicle (ROV). The CMRET/SDI team has scheduled an SSD cruise that includes attempting to collect hydrate samples, July 2012.

Subtask 2.6. The recipient shall refurbish 4C nodes, donated by CGG Veritas for deployment and use in shear experiments as defined in Phase 2 task 3, and Phase 3 task 3.

This subtask was rewritten and rebudgeted from 3 years of DOE awards to the CMRET. It now reads:

Phase 3, Task 3: Near seafloor geology at MC118 using converted shear-waves from 4C seafloor sensor data (Subcontractor: John Collins, Woods Hole Oceanographic Institution)

This task is complete. The data have been delivered to CMRET in both SEED and SEGY formats and CMRET has, after inspecting the data, copied and delivered a set to UT-Austin (Hardage) for 4-C analyses and to enable them to fulfill the FY08 subcontract. In addition a copy of the data was delivered to UCSD (Gerstoft) for analysis of ambient noise in the data. A full report of cruise activities is available at the MMRI website: http://mmri.olemiss.edu/Home/Publications/Cruise.aspx

As noted earlier, UT's responsibilities have been largely transferred to the University of Mississippi. Progress on this subtask is discussed further under Phase 3, Task 3.

TASK 3: 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.* (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.,* 2008). 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. Venting activity has 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 (*Sassen*, 2006). 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 was 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 had to be spread over a couple of years. The work was 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.

In preparation for the extension of the approach to treat multidimensional problems, SAIC 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, it is now possible to carry out preliminary multidimensional studies and we are in a better position to proceed toward the final goal of a multidimensional, multi-component modeling capability. A description of STAR/HYDCH4 was provided in a previous letter report (July 2010).

The work during Year 3 (2010-2011) mainly consisted of developing a 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) for incorporation into STAR and/or THROBS simulators. The progress made till the end of June 2011 was described in a previous letter report (July 2011).

Work performed during the report period
Contract Matters
SAIC subcontract for Year 3 with the University of Mississippi was finalized towards the end of September 2010. A no-cost extension till the end of June 2012 was granted in the fall of 2011.

A paper based on the work performed under the contract (Garg and Pritchett, 2911) was presented by Sabodh Garg at the 7th International Conference on Gas Hydrates (ICGH 2011), July 17-21, Edinburgh, Scotland, United Kingdom. A copy of the paper is appended to this report.

Dr. Sabodh Garg attended the Gulf of Mexico Hydrates Research Consortium Meeting held on November 8, 2011 in Jackson, Mississippi, and presented an update of the work performed by SAIC.

Technical Progress
During the current report period (July 1, 2011 to December 31, 2011), work was continued on debugging and testing the new equation-of-state package (HYDGAS). The contract funds are nearly exhausted (around 97% of the total), and the remaining amount is insufficient to complete this effort. We are trying to identify additional resources that may become available for this work. If we are successful in obtaining additional support, we will complete the HYDGAS package, and perform preliminary calculations to characterize the effect of a gaseous mixture on hydrate formation at the Hydrate Mound. In any event, a final report will be prepared by the end of the current project period (June 2012).

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

Integrating geochemical and geophysical studies to characterize the sulfate methane transition zone of a complex carbonate hydrate mound in Northern Gulf of Mexico

Rachel Wilson, Leonardo Macelloni, Laura Lapham, Antonello Simonetti, Charlotte Brunner, James Knapp, Carol Lutken, Camelia Knapp, Ken Sleeper, Marco D'Emidio, and Jeffrey Chanton

ABSTRACT
Five locations were sampled for sediment geochemistry across a salt-dominated dome complex using 20m long piston-assisted cores. Coring locations were chosen based on their relative position to three large fault conduits transecting the dome. Gas hydrate was retrieved from a core immediately adjacent to the northernmost fault. Isotopic evidence and low C_1/C_2+C_3 in gas captured from the evolving hydrate were consistent with a thermogenic gas source for the recovered hydrate. Isotopic evidence suggests that biogenic sources dominate the remaining sites cored. Isotopic depletion was significantly correlated with the estimated depth of the sulfate-methane transition zone

suggesting that the supply of isotopically-enriched (possibly thermogenic) methane varies across the complex and is greatest near the blue fault.

INTRODUCTION

Mississippi Canyon lease block 118 (MC-118) is located in the Gulf of Mexico along the Louisiana continental shelf Figure 23A). Large outcropping methane hydrates have been observed at this site over a period of at least 7 years and the presence of methane hydrates buried within the sediment is inferred from resistivity data and the serendipitous coring of hydrate during geological coring surveys. A distinctive feature of this site is Woolsey Mound, a large salt-diapir associated hydrate/carbonate mound-complex (McGee et al. 2009) in the southern end of the lease block. Seismic profiling of the site has revealed an extensive fault system radiating from a salt diapir located approximately 600m below the surface (McGee et al. 2009; Knapp et al. 2010). It has been hypothesized that the faults act as channels for deep thermogenic source reservoirs to connect with the surface (McGee et al. 2009). Further, the presence of higher molecular weight hydrocarbons (C_1 – C_4) and the enriched isotopic values ($\delta^{13}C$ = -47‰) of the methane from hydrates sampled at this site support a deep thermogenic hydrocarbon source (Sassen et al. 2006). In this study we use geochemical profiles from cores to better understand the role of faults as conduits for fluid flow to understand the potential for hydrate accumulation across the mound complex. The objectives of this study were to groundtruth the geophysical data and to understand the chemical and physical environment, all of which play a key role in both the physical and biological processes observed at this site.

Hydrates have been implicated as both a mechanism to “store” methane, preventing or slowing release to the atmosphere, and as a potential dynamic source of methane poised to rapidly release a large quantity of methane if the factors governing the hydrate stability are perturbed (Kvenvolden, 1993). Unfortunately, those factors are still poorly understood, especially the geochemical parameters necessary to maintain hydrate stability. Characterizing the chemical environment at hydrate-bearing sites will help us to further understand the parameters controlling hydrate stability and assess the potential for dynamic methane release.

MATERIALS AND METHODS

Study Site

Underlying Woolsey Mound, are at least three principal faults associated with the rising salt diapir (Knapp et al. 2010) although a three-dimensional representation illustrates the complexity of the shallow sediment system (Simonetti et al. 2011; Figure 23B). The principal faults will be referenced by color throughout the following discussion (Figure 1B). The yellow fault delineates the southeast crater, the blue fault delineates the northwest crater, and the purple fault delineates the southwest crater. Geochemical activity and faunal diversity vary across the mound (Lapham et al. 2008; Lutken et al. 2011) correlated with morphological and sedimentological features (Macelloni et al. 2010) and are thus likely tied to the hydrocarbon-rich fluid supplied by these faults via enhanced chemosynthetic production (Sassen et al. 2004).

Core Location Rationale

JPC-001 and JPC-003

JPC-001 is located in close proximity to the blue fault which is associated with high microbial activity (Lapham et al. 2008) and extensive bacterial mats (Lutken et al. 2011). Macelloni et al. (2010) based on high frequency backscatter in acoustic data infer the presence of disseminated hydrate associated with this fault, suggesting a very strong conduit of hydrocarbon-rich fluid flow to the shallow sediments. JPC-001 was targeted to provide insights on the mechanisms governing the upward flux of fluids, formation\dissociation of hydrate, and exchange in the methane\sulfate reduction zone. JPC-003, located off the blue fault, was chosen to serve as a background control site for sediments and pore fluids that are removed from the fault influence.

JPC-002

JPC-002 coring site was chosen based on its proximity to the purple fault in an area where chirp data suggests compressed sedimentary stratigraphy indicating possible sediment slumping and/or uplift. Faunal diversity is comparatively low in this area (Lutken et al. 2011); however, the absence of acoustic anomalies suggests that this site is relatively quiescent with little fluid migration.

JPC-006

JPC-006 was targeted to groundtruth acoustic blanking most likely due to the presence of free gas (Sager et al. 1999 and references therein) associated with the purple master fault. The anomaly at this site is constrained below 10-12m, thus this site was of particular interest during this coring cruise in order to obtain further information not readily available by conventional gravity core operations (for example in Lapham et al. 2008). Further, this area is associated with a particularly high faunal diversity perhaps supported by increased hydrocarbon fluid flow.

JPC-007

JPC-007 was collected near a pockmark associated with the yellow fault. This fault appears to transect a shallow gas accumulation before intersecting the sediment water-interface (Simonetti et al. 2011). Analysis of core lithology (Brunner, C., elsewhere) confirmed that the sediments in the collected cores were composed entirely of clayey silts, with none of the sand layers that typically host gas accumulation or hydrate formation and revealed that sediments in all cores deeper than 1-2m were deposited rapidly by dilute turbidity currents with elevated organic matter content relative to typical bathyal sediments. It is suggested that this fault is an intermittent conduit for gas transit to the seafloor, and that at times the growth of hydrate may temporarily decrease fluid flow resulting in episodic venting at the seafloor (Simonetti et al. 2011, L. Macelloni, unpublished). JPC-007 was collected to gain insight into the fluid-flow regime associated with the yellow fault.

Sampling Protocol

Five coring locations were chosen based on the presence of acoustic anomalies in the seismic data (Map 1; Table 1). Piston--assisted gravity cores (TDI Brooks International) were used at each of the five sites to collect sediment samples. These cores are capable of collecting up to 20m of sediment under perfect conditions. Once on deck, the core was capped, and the crew cut the core into 3-foot sections capping at each cut before the core lengths were brought into the lab for sampling. Cores were sampled for porewater at the top of each 3-foot interval. Additional samples were taken at closer intervals within the first 1m of JPC-007 and JPC-003. The core sections were re-capped and returned to shore for lithologic analysis.

For porewater samples, sediment (3mL) was removed using a modified syringe, placed into a 20mL serum vial and immediately capped. Degassed, de-ionized water (3mL) was added to each vial, the contents were shaken to create a slurry and then frozen, inverted for methane analysis. Rhizons (Seeberg-Elverfeldt et al. 2005), fitted with syringes, were used to extract porewater from sediments. Extracted porewater was then subdivided for separate treatment prior to chemical analyses. 500uL of the sample was stored in an o-ring sealed microcentrifuge tube, acidified with 50uL 10% nitric acid for sulfate and chloride analysis. 2mL of the remaining sample, destined for dissolved inorganic carbon (DIC) concentration and $\delta^{13}C_{DIC}$ analysis, were then injected into a pre-evacuated, stoppered, 10mL serum vial and frozen. A small (~1mL) sediment sample was placed into a pre-tared, covered petri dish and frozen for porosity analysis. All chemical analyses were completed onshore after the completion of the sampling cruise at Florida State University.

Hydrates were recovered in core JPC01. Various means were attempted to collect this hydrate. Pieces of hydrate were placed in canning jars and water was added. The jars were sealed with Teflon tape and brass rings before being frozen upside down to trap the evolving gas. Four subsamples of the hydrate “disk” were taken and each subsample was placed into a 20mL serum vial and capped. An open syringe was inserted into the septum of each vial, the evolving hydrate was allowed to passively fill the syringes which were purged twice before being filled a third time and then closed with a 3-way valve. The contents of the syringes were then injected into separate, evacuated, stoppered serum vials for hydrocarbon and stable isotope analysis. All hydrate gas samples were analyzed for methane and $\delta^{13}C$ using the same procedure as sediment samples.

Chemical Analysis of Samples

Dissolved methane concentrations were measured on a Shimadzu GC-2014 Gas Chromatograph following headspace equilibration (as per Lapham et al. 2008). Sulfate and chloride concentrations were obtained on a Dionex Ion Chromatograph (Sunnyvale, California) following the methods of Lapham et al. (2008).

DIC concentrations and carbon isotope ratios of both methane and DIC samples were analyzed using a Delta Mat Finnigan Isotope Ratio Mass Spectrometer coupled to a Hewlett-Packard 5890 GC. Stable carbon isotope ratios are reported in standard δ-notation: $\delta^{13}C = (R_{sample}/R_{standard} - 1)*1000$, where $R = {}^{13}C/{}^{12}C$. $\delta^{13}C_{DIC}$ were obtained following acidification of the samples with 43% nitric acid.

RESULTS

Upon bringing JPC-001 onto deck, gas expansion inside the core resulted in several meters of sediment extruding from the top of the core liner that was either captured in buckets or lost on deck. As the core was cut, we found many large (on the order of meters) gas voids, making exact depths difficult to determine. We estimate depths in this core based on the difference between the total penetration depth of the core and the 3-foot core liner section number. Blades and grains of hydrate were noted beginning about 2m from the bottom of the core. There was also a solid disk (2cm thick) of hydrate filling the entire diameter of the core suggesting that the core liner had penetrated a hydrate layer, essentially coring the hydrate.

Methane

The methane concentrations in cores JPC-002, JPC-003, JPC-006, and JPC-007 were uniformly low at depths shallower than 780 cm below the seafloor (cmbsf) (Figure 24). Methane concentrations in JPC-006 increased to a maximum of 3mM at 823cmbsf. This is above predicted saturation at atmospheric pressure (1.2mM), thus, taking into consideration possible degassing during ascent/sampling, this represents a minimum concentration for this depth. Methane concentrations in JPC-002 reached a maximum of 600μM at 1113cmbsf. Methane in cores JPC-003 and JPC-007 reached maximum concentrations of 720μM and 1.3mM respectively at the bottom of the sampled core. JPC-001 (where the hydrate was found) had higher methane concentrations over shallower core depths than the other cores. Methane concentrations were approximately 10mM by approximately 400cmbsf and then decreased to a constant 1.3mM from 1000cmbsf to 1740cmbsf. The concentration in the core then increased dramatically to 12mM at the base of the core where hydrate was abundant. Again, because of likely degassing these concentrations represent minimum values for the core. Stable carbon isotope ratios were depleted in cores JPC-002, JPC-003, JPC-006, and JPC-007 (-67‰ to -94‰). JPC-001 methane was enriched relative to all other sites (-45‰). Systematic differences among the different collection schemes for the hydrate were not observed. All hydrate collected were combined to give an average $\delta^{13}C$ = -40.4‰ ± 0.7‰ (n = 10).

Dissolved Inorganic Carbon

Dissolved inorganic carbon (DIC) concentrations generally increased from the sediment-water interface with depth in the core up to the depth where methane concentrations began to increase, at which depth DIC concentrations declined somewhat in most cores, with the exception of JPC-001 (Figure 24). With the exception of JPC-001, $\delta^{13}C_{DIC}$ approached 0‰ near the sediment/water interface and became systematically depleted with depth in the core to the approximate DIC concentration maximum. Below this point, $\delta^{13}C_{DIC}$ became progressively enriched with depth. Although the shallowest depths of JPC-001 were lost, the general trend in this core is an increase in both DIC concentration and $\delta^{13}C_{DIC}$ enrichment. The $\delta^{13}C_{DIC}$ approaches +40‰ in positive δ-value!

Sulfate

Sulfate depletion depths varied across the sites. Sulfate was found deepest in cores JPC-003 and JPC-007 where the sulfate depletion depth was ~12m. Sulfate was found to about 11m in JPC-002. Sulfate depletion depth in JPC-006 was around 6m. Nearly all the sulfate was depleted in JPC-001 by ~3m (Figure 25). These depths correspond well with the increase in methane concentrations as well as the inflection in $\delta^{13}C_{DIC}$ values in the cores, thus defining the SMT at each of these coring locations. The rates of sulfate depletion were estimated from the slopes of the concentration with depth curves at each location with the exception of JPC-001 where no shallow sediment was recovered. Sulfate depletion rates were estimated in each of the cores from the slope of the sulfate vs. depth curves as per Lapham et al. (2008). The sulfate depletion rates for cores JPC-002, 003, and 007 were 0.03 mM cm^{-1}, 0.02 mM cm^{-1}, and 0.02 mM cm^{-1} respectively. The sulfate depletion rate over all data points in JPC-006 was 0.04 mM cm^{-1}, but the sulfate depletion rate over the linear range of decrease in the ~4 to 8m depth range for this core was 0.08 mM cm^{-1}(Figure 25).

DISCUSSION

The deepest depths to which we measured sulfate concentrations and the gradient in sulfate concentrations with depth varied in cores collected across the mound. In all except core JPC-001, the methane concentrations increase at depths greater than the minimum sulfate depth of the respective core. The sulfate-methane transition zone (SMT) is a characteristic feature of methane-bearing anoxic sediments, where methane and sulfate coexist (Iversen and Jørgensen 1985) below which, bacterially-mediated sulfate reduction has exhausted the supply of sulfate. Above this zone, diffusion and sulfate reduction rates control sulfate concentrations in sediment porewaters as nearly all of the upwardly advecting methane is oxidized within the SMT (Iversen and Jørgensen 1985; Joye et al. 2004; Pohlman et al. 2011). Thus variations in the depth of the SMT can indicate variability in the supply of substrates for SR (i.e. methane and other hydrocarbons). The depth of the SMT (Figure 24) and the sulfate gradient, varied across the mound. Further, the sulfate depletion depth was correlated with methane isotope values (Figure 26) suggesting that sulfate reduction is substrate limited and advecting fluid near faults can act to stimulate microbial activity in areas supplied by actively venting deep reservoir methane. Cores JPC-002, JPC-003, and JPC-007 all have similar trends in geochemical profiles, while JPC-006 and JPC-001 have very dissimilar geochemistry and will be discussed in detail separately. In cores JPC-002, JPC-003, and JPC-007 sulfate, methane, and $\delta^{13}C_{DIC}$ profiles (Figures 25 and 26) are consistent with microbial anaerobic oxidation of methane (AOM) coupled to sulfate reduction (SR). The concentrations of DIC in all of the cores are lower than expected given the amount of sulfate depletion observed, suggesting that either DIC degassed during sampling, or DIC was removed by a non-fractionating mechanism such as carbonate precipitation (Chanton et al. 1993). No carbonates were observed in any of the cores indicating that low DIC values are most likely due to sample degassing (C. Brunner, personal communication). The average sulfate depletion rates, estimated from the slopes of the sulfate vs. depth profiles, in cores JPC-002, JPC-003, and JPC-007 of 0.02 mM cm^{-1} is similar to what Lapham et al. (2008) found in their “moderate” microbial activity cores suggesting that methane advecting towards the sediment-water interface is simultaneously generated by and fueling microbial processes at these sites.

JPC-006

JPC-006 was chosen as a coring site due to its proximity to the purple fault that

radiates from the salt dome to the surface. Sulfate concentrations in JPC-006 are similar to the expected seawater value (28mM) up to a depth of >3m (Figure 25), below which the sulfate is rapidly consumed and fully depleted by a depth of approximately 7m. The sulfate minimum coincides with the lowest methane concentrations in the cores and relatively high DIC concentrations. Cumulatively, these three lines of evidence suggest AOM-coupled sulfate reduction is occurring in these sediments and that the sulfate-methane transition zone (SMT) occurs at a depth of ~7m.
Expected diffusion profiles at steady-state should be linear from the surface to the depletion depth (Figure 25), thus we conclude that conditions at this site are not at steady-state. Similar non-linear sulfate profiles have been observed in the Gulf of Mexico at other salt-dominated features (Pohlman et al. 2008). In that study, chloride concentrations were used as a conservative tracer to estimate the effects of physical processes vs. biogeochemical removal of sulfate. Although the chloride concentrations in core JPC-006 do trend, generally, upwards with depth (Figure 25), the extreme values are not very different from those expected in seawater (536-560mM). Claypool et al. (2006) find evidence of organoclastic sulfate reduction in non-linear sulfate profiles which cannot be ruled out in our samples. The sulfate profile from core JPC-006 could be explained by bioturbation-caused mixing of the shallower sediment layers increasing the supply of sulfate by incorporating seawater sulfate into the sediments. However, organisms capable of bioturbating sediment to ~4m depth have never been observed at this site. Alternatively, the observed sulfate profile (Figure 25), may be explained by a recent intrusion of methane into these sediments. Previous microbial activity may have been low in the absence of excess methane and sulfate concentrations may have been established at ~28mM to depths >3m. Recent fault activity could have provided a new conduit for methane flow into this section. The result would be that sulfate is quickly consumed as this new methane source is oxidized. The observed sulfate profile is consistent with a relatively recent intrusion date of the methane as the theoretical diffusion profile for sulfate has not yet been established. The DIC concentration profile in this core also deviates from the predicted diffusion line (Figure 24). This suggests either 1) the DIC is being consumed by subsurface processes or 2) production of DIC at depth has increased recently and is not yet at steady-state with respect to diffusion. Methane isotopes are generally enriched at depth and reach the most depleted values at the base of the SMT (Figure 24). Additionally, DIC isotopes are slightly more enriched at the SMT than what would be expected from AOM production (□ = 1.05). Cumulatively, the isotopic results suggest that methanogenesis, producing isotopically light methane from DIC, is occurring coincidentally with AOM at the base of the SMT (Whiticar and Faber 1986; Pohlman et al. 2008; discussed in Holler et al. 2009). Thus, we suggest that a recent intrusion of thermogenic methane, perhaps enhanced by tectonic activity, is mixing with a biogenic methane pool at this site. The intermediate isotopic values of the methane (-67‰), neither characteristically thermogenic or definitively biogenic, indicate that the relative size of the two pools are similar and that the recent intrusion of fluid flow is not large enough to fully dominate the methane signal at this site.

Core JPC-001

Hydrate was recovered in the deeper sections of JPC-001 (Figure 23) including bladetype and a large piece of hydrate filling the entire diameter of the core liner. The high ethane and propane content of the evolved gas, as well as the enriched isotope values of the methane ($\delta^{13}C$ = -40.4‰ ±0.7‰) support a thermogenic origin for the hydrate source gas at this site (Sassen 2006). Methane concentrations in this core were highest in the deepest section, and were also the most isotopically enriched (Figure 24). It should be noted that these concentrations reflect minimum values as samples likely degassed losing methane during ascent. The very top section of this core was lost due to gas expansion and expulsion of sediments during recovery. Although we do not have the uppermost sediment from JPC-001 to compare sulfate depletion rates to other coring sites, qualitatively we show that nearly all of the available sulfur in this core has been reduced by 3m depth (Figure 25) suggesting high methane supply at this site. The DIC values are hugely enriched relative to all other coring locations and relative to the methane isotope values. The □ between methane and DIC approaches 1.09 in the deepest portions of the core. The gas contains a high proportion of propane and other higher molecular weight hydrocarbons, consistent with a thermogenic origin. Oxidation of propane and butane are expected to contribute enriched DIC because of their relative $\delta^{13}C$ and because they are associated with lower $□_{DIC\text{-}hydrocarbon}$ values (1.0057 and 1.0016 respectively; Kniemeyer et al. 2007). Thus, the enriched DIC values in this core may reflect inputs of propane and butane oxidation in addition to AOM. As discussed above, methanogenesis can influence the DIC pool simultaneously with AOM under certain conditions (Whiticar and Faber 1986; discussed in Holler et al. 2009). The $□_{DIC\text{-}methane}$ value associated with methane production is around 1.08 (Chasar et al. 2000), however, given the high concentrations of DIC (Figure 24) and enriched methane isotope values observed, it’s unlikely that methane production is contributing significantly to the enriched DIC isotope values observed in this core unless CO_2 is also being carried upwards.

Variation in SMT depth across sites

The depth of the SMT was inversely correlated with the stable carbon isotope composition of the methane gas in the sediment porewater (Figure 26). The correlation between $\delta^{13}C_{methane}$ and depth of the SMT implies that microbial oxidation rates are higher in zones with greater contributions of methane from deep reservoir sources. If this trend were simply the result of high rates of methanogenesis at depth in cores JPC-001 and JPC-006 and the methane was being oxidized as the fluid advected towards the surface, then we would expect the methane below the SMT to be depleted at depth and become more enriched in shallower sediments as it gets oxidized on its way to the surface. However the trend in core JPC-006 is for the $\delta^{13}C_{methane}$ values to become increasingly enriched with depth. This would suggest a deep thermogenic source of methane mixing with MOG products at shallower depths (e.g. Lapham et al. 2008). Although the $\delta^{13}C_{methane}$ in core JPC-006 is not definitively thermogenic (-66.8‰), the ratios of methane to ethane (C_1/C_2; Table 1) in the samples are ~ two orders of magnitude lower than biogenic ratios observed at other sites (e.g. Martens et al. 1991) lending further support to a thermogenic methane source contributing to the total methane pool sampled in this core. In general we conclude that the thermogenic methane supply is greatest at the blue fault. While thermogenic methane is likely to the shallow sediment methane pool associated with the purple site, the rate of supply appears to be much lower. Finally we could detect no indications of thermogenic methane supply at the yellow fault site.

CONCLUSIONS

Six locations were cored across a salt-dominated dome complex (Figure 23). Geochemical profiles indicate methane sources (biogenic, thermogenic, and mixed) supplied to the shallow sediments varied across these locations. Results of the core collected near the yellow fault were very similar to those found for the ‘background’ core collected (JPC-003), we found no evidence of thermogenic methane contributing to the shallow sediment profiles. At the purple fault we do find weak evidence of thermogenic methane contributions, although it appears to be mixing with biogenically-sourced methane at this site. The location near the blue fault had the strongest contributions of thermogenic methane, as inferred from $\delta^{13}C$ and sulfate information. Thus, while moderate methane sourcing to the shallow sediments may be accomplished via the purple fault, the blue fault appears to be the most active conduit for hydrocarbon-rich fluid to the shallow sediments measured at this time.

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Core Number	Geophysical Justification	Sulfate depletion depth (m)	sulfate depletion rate (mM/cm)	avg C_1/C_2	avg. $\delta^{13}C_{methane}$ (‰)
JPC-001	acoustic blanking; “blue” fault; high resistivity anomaly	3m	NA	50	-45.8
JPC-002	compressed stratigraphy; constraining the “purple” fault	11m	0.03	1100	-67.5
JPC-003	constraining the “blue” fault	12m	0.02	3100	-93.9

JPC-006	acoustic blanking; near the "purple" fault	6m	0.04^{*}-0.08^{+}	120	-62.7
JPC-007	pockmark; surface expression of "yellow" fault; high frequency scatter	12m	0.02	830	-78.6

Table 1. Composite chemistry for Jumbo Piston Cores recovered from Woolsey Mound, January, 2011.

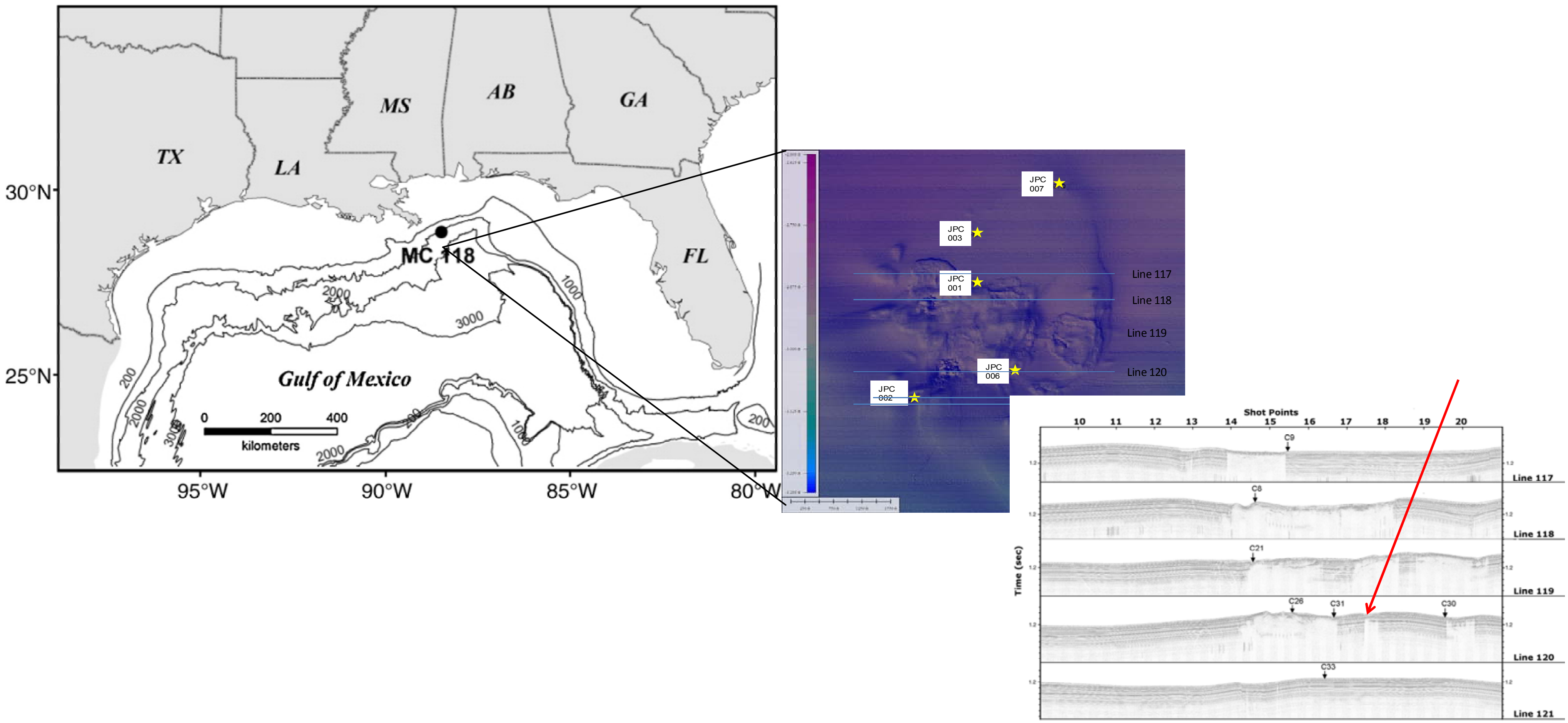


Figure 23A. Location of MC-118 Study Site within the Gulf of Mexico (from Lapham et al. 2010), Bathymetric Map of Study Sites, and sites (Macelloni and D'Emidio) located on chirp profiles (Jim Knapp and Antonello Simonetti).

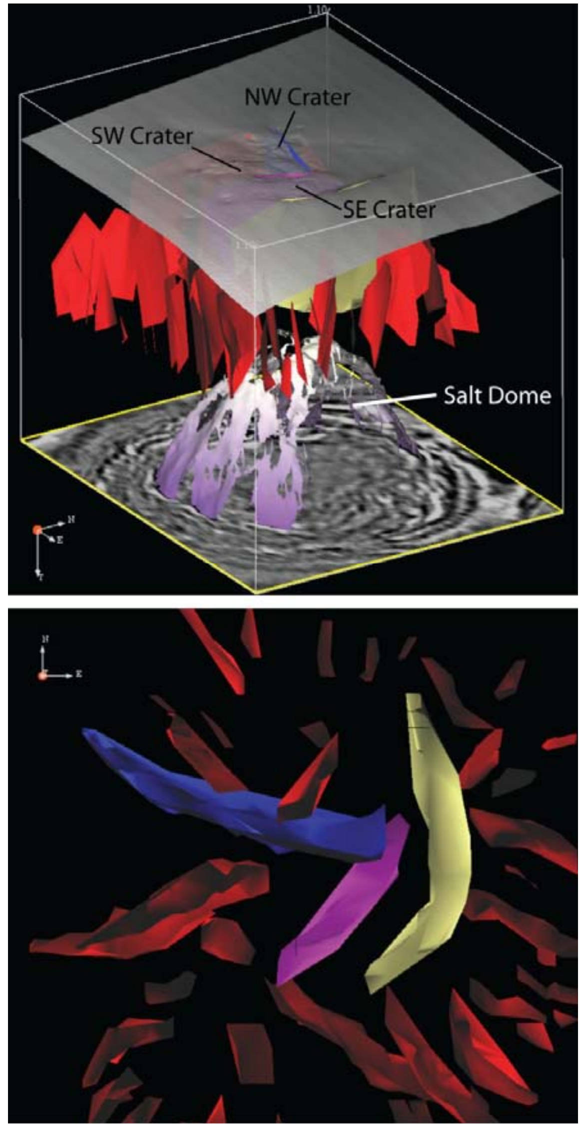
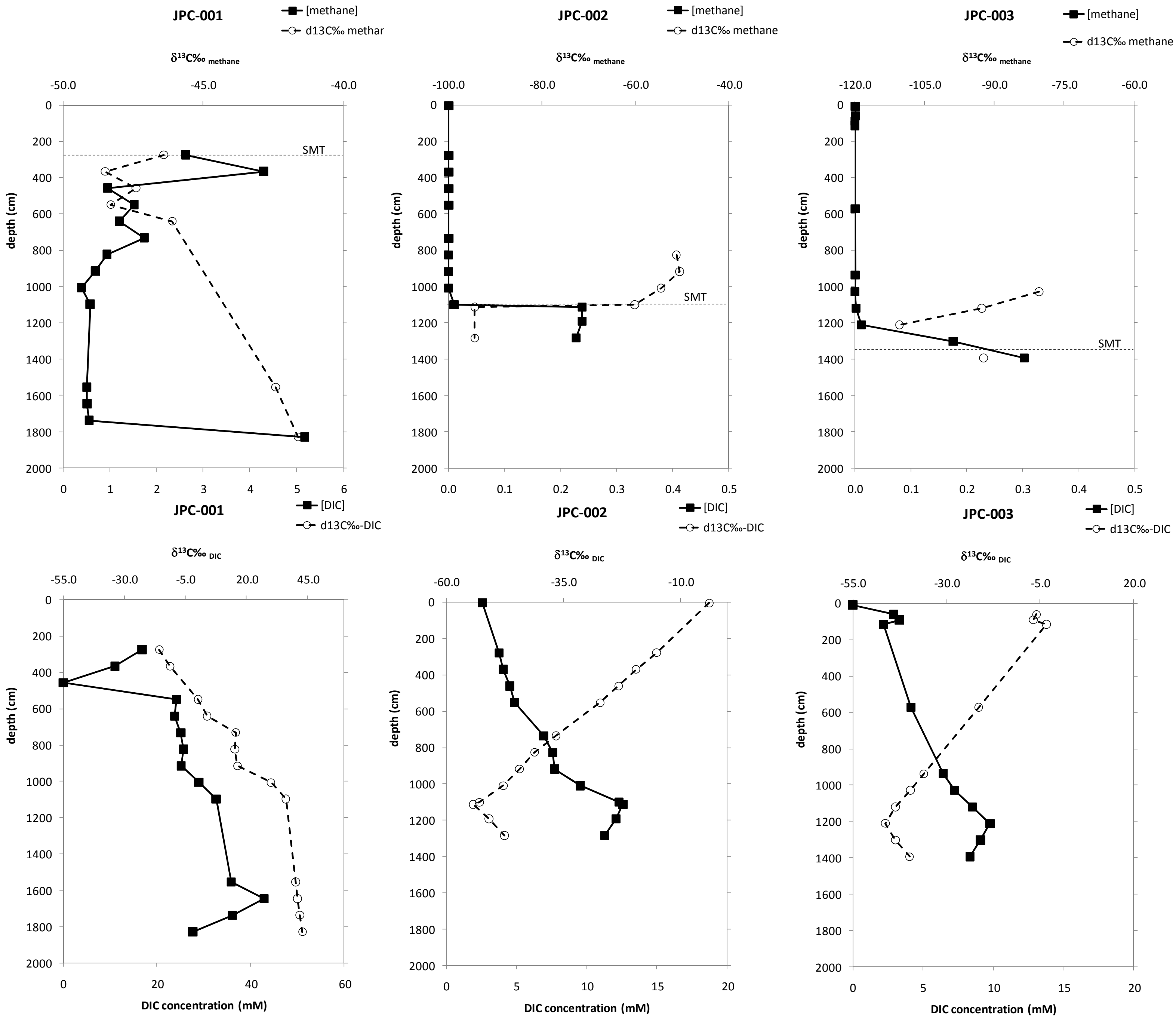


Figure 23B: Three dimensional model of the Woolsey Mound fault complex (Simonetti et al., 2011).


JPC-001
[methane]
d13C‰ methar
δ13C‰ methane
-50.0
-45.0
-40.0
SMT
depth (cm)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
0
1
2
3
4
5
6
JPC-002
[methane]
d13C‰ methane
δ13C‰ methane
-100.0
-80.0
-60.0
-40.0
SMT
0.0
0.1
0.2
0.3
0.4
0.5
JPC-003
[methane]
d13C‰ methane
δ13C‰ methane
-120.0
-105.0
-90.0
-75.0
-60.0
SMT
0.0
0.1
0.2
0.3
0.4
0.5
JPC-001
[DIC]
d13C‰-DIC
δ13C‰ DIC
-55.0
-30.0
-5.0
20.0
45.0
0
20
40
60
DIC concentration (mM)
JPC-002
[DIC]
d13C‰-DIC
δ13C‰ DIC
-60.0
-35.0
-10.0
0
5
10
15
20
DIC concentration (mM)
JPC-003
[DIC]
d13C‰-DIC
δ13C‰ DIC
-55.0
-30.0
-5.0
20.0
0
5
10
15
20
DIC concentration (mM)

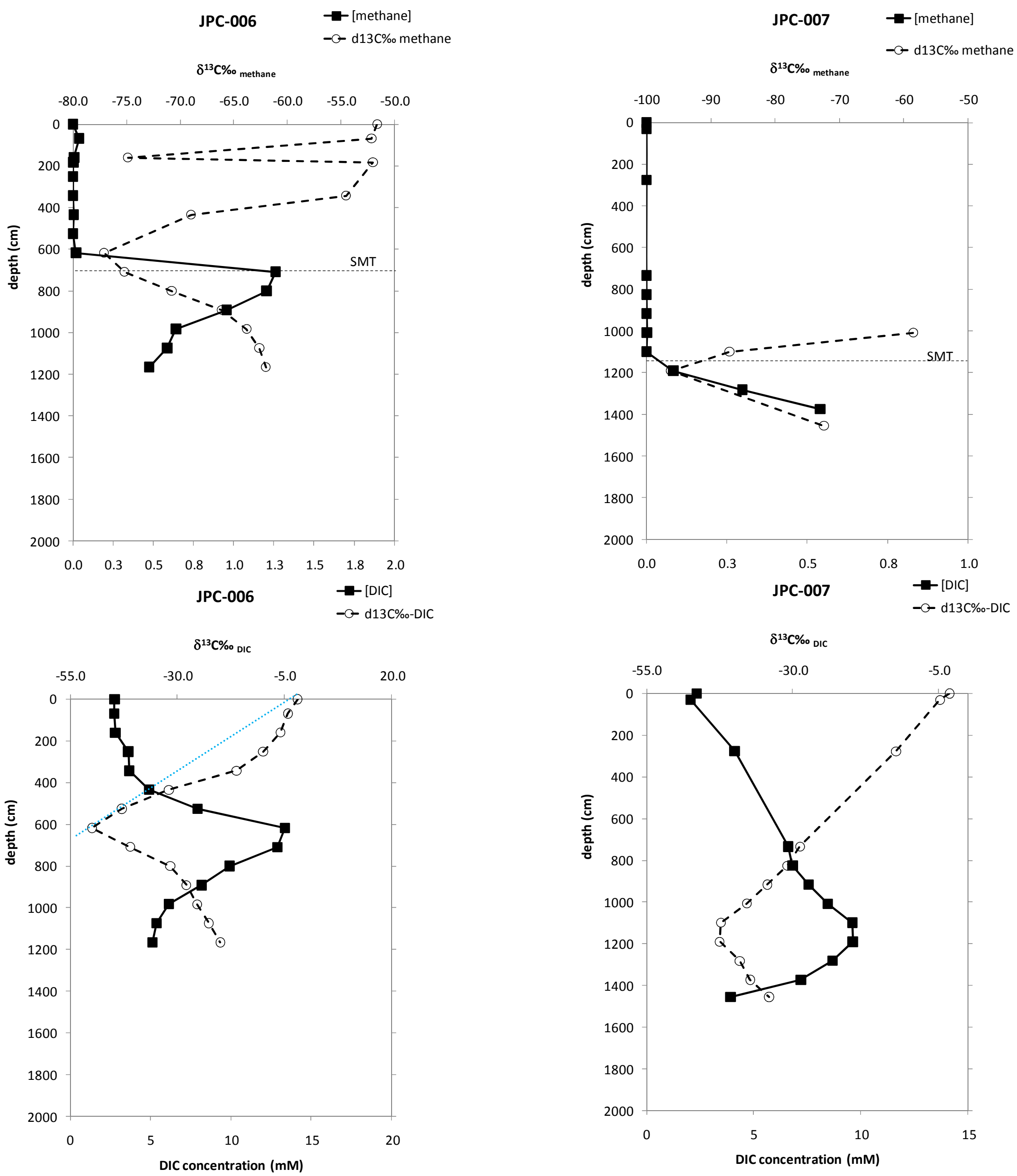
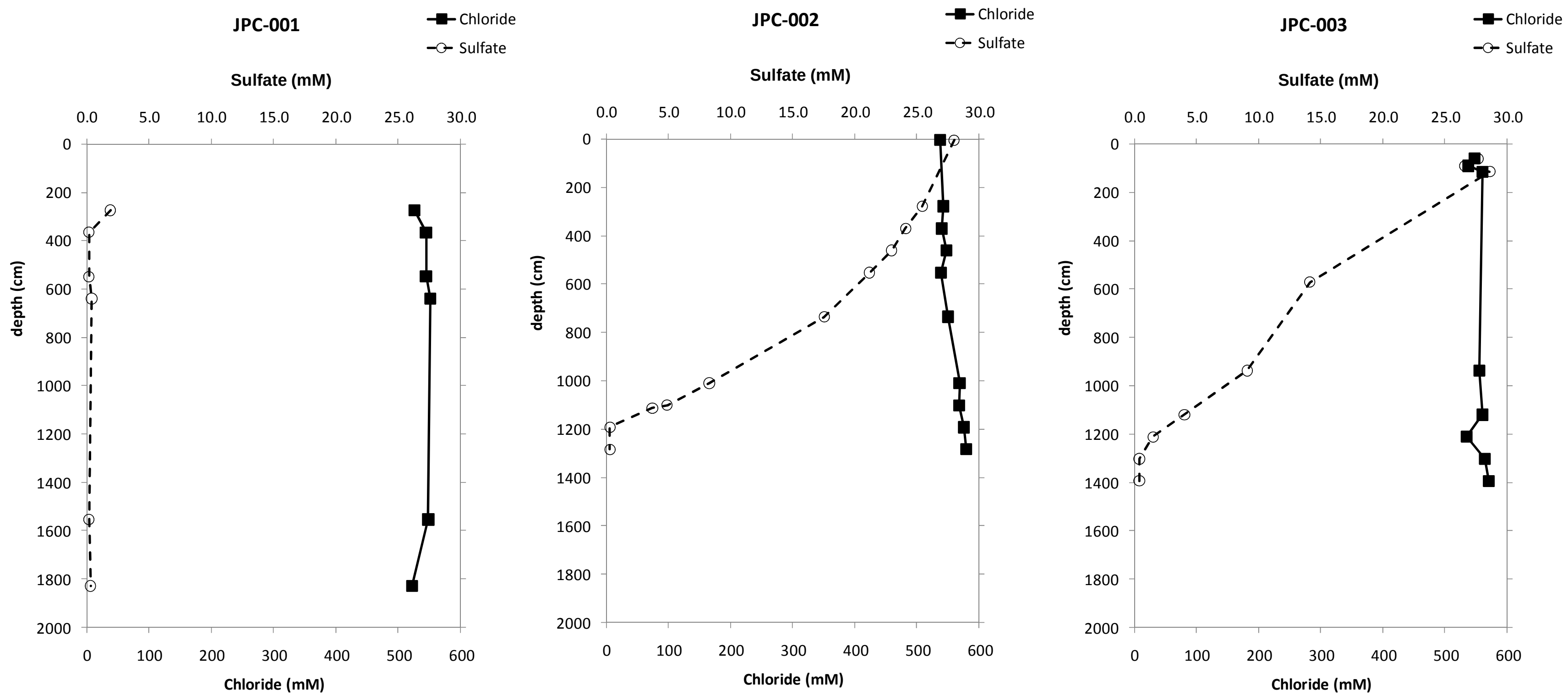


Figure 24: Methane, $\delta^{13}C_{methane}$ and DIC $\delta^{13}C_{DIC}$ profiles at each coring location. The blue dotted line in JPC-006 DIC profile indicates the predicted diffusion line at steady-state.


JPC-001
Chloride
Sulfate
Sulfate (mM)
depth (cm)
Chloride (mM)
JPC-002
Chloride
Sulfate
Sulfate (mM)
depth (cm)
Chloride (mM)
JPC-003
Chloride
Sulfate
Sulfate (mM)
depth (cm)
Chloride (mM)

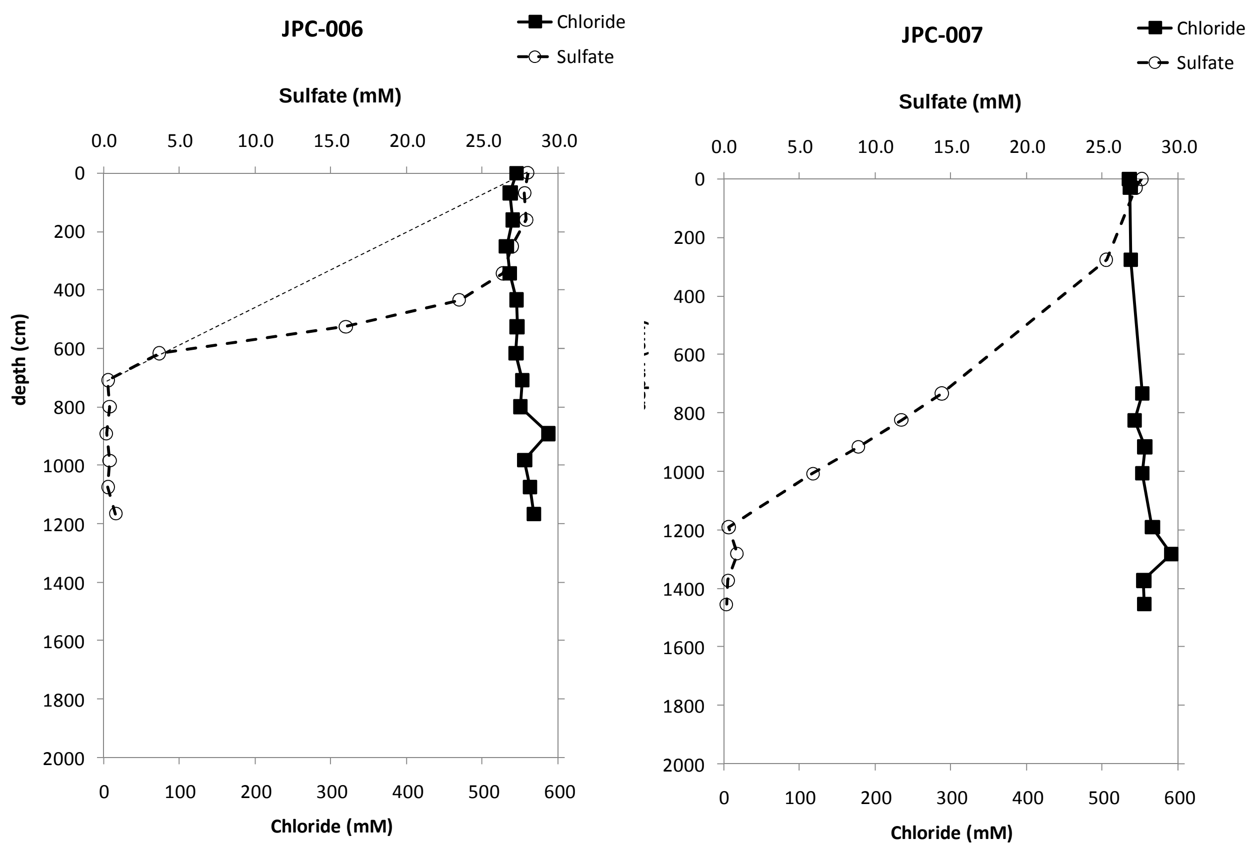


Figure 25: Chloride and Sulfate concentrations with depth in each of the JPC cores. The dotted line in JPC06 sulfate profile indicates the predicted steady-statfusion line.

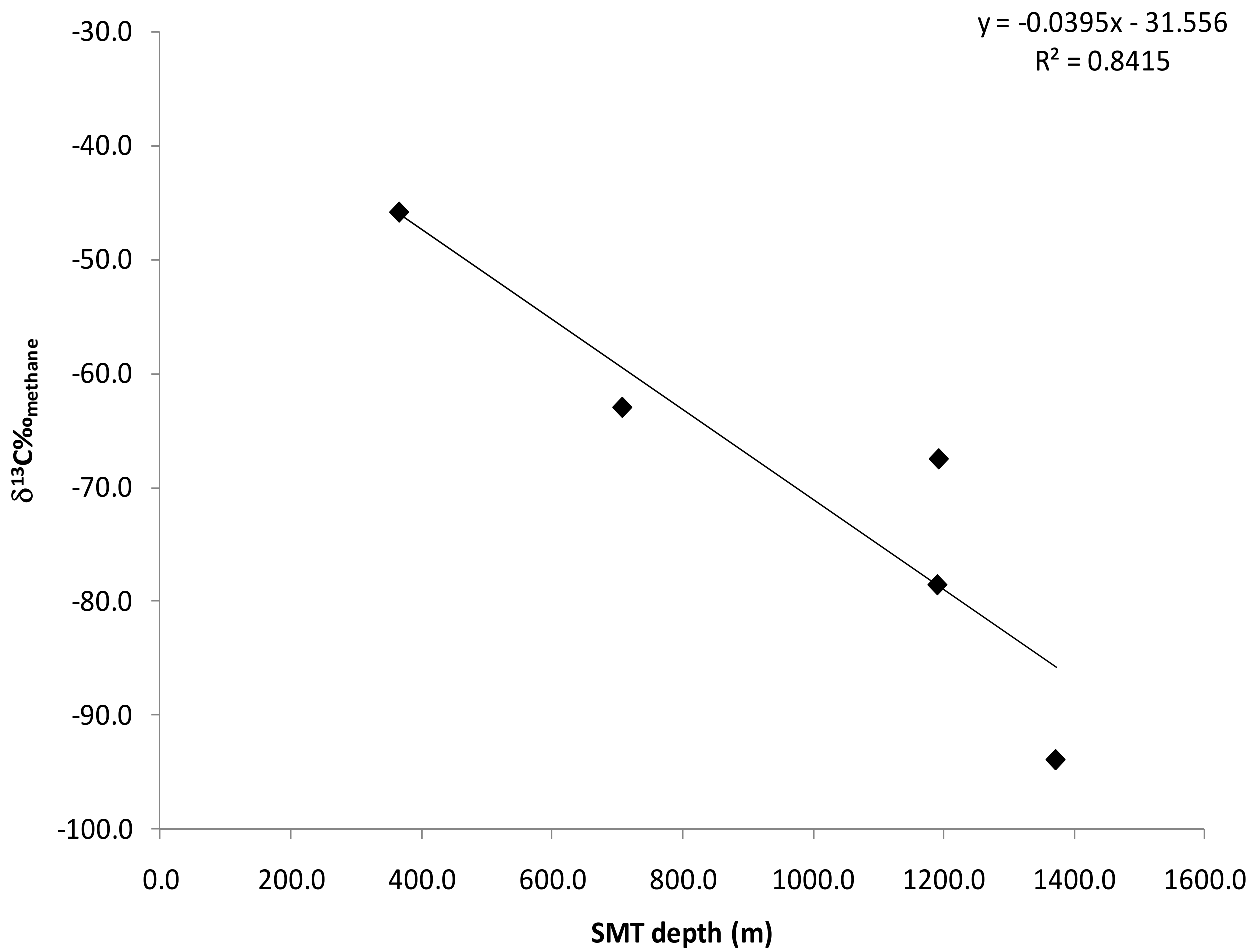


Figure 26. Correlation of SMT depth with isotope values across all sites

1. Publications
    a. Lapham, LL, RM Wilson, and JP Chanton. (2012) Pressurized laboratory experiments show no stable carbon isotope fractionation of methane during gas hydrate dissolution and dissociation. In *Rapid Communications in Mass Spectrometry* **26**: 32-36.
2. Meetings
    a. Wilson participated in the 7th International Conference on Gas Hydrates in Edinburgh, Scotland on July 17-21, 2011 and reported results of long-term continuous monitoring of sediment geochemistry using the pore-fluid array collection instrument.

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

A contract has been established 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 2010 through August 2011, respectively. A no-cost extension has been granted to extend the working time through July, 2012. General schematics were drawn for the Lander components which included the underwater mass spectrometer and multi filtration system. The Lander and surface vessel are linked by the same fiber optic cable as the SSD ROV. The electronics interfacing the fiber optic cable and Lander instrumentation have been installed in a pressure housing and have undergone extensive laboratory testing.

Individual filter assemblies, or packs have been constructed (Figure 27) to be utilized 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.

Figure 27. Filter assembly mounted on distilled water pumping station.

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.

The Lander frame was constructed of stainless steel and is configured to house the filter rack (containing up to 30 individual filter packs); membrane introduction mass spectrometer (MIMS) and lithium battery pack; and Lander battery packs (Figure 28). The Lander has also been equipped with a color video camera that can send live video through the fiber optic interface to the surface vessel. The camera (with LED light ring) is positioned downward to view the seafloor and the additional lighting is angled to avoid backscatter from suspended solids. The camera and lights can be turned on/off as needed to avoid unnecessary drain on the Lander's batteries. The MIMS is mounted with multiple hinge clamps that can readily fasten the MIMS housing and battery pack in position. The MIMS interfaces with the Lander's electronics package where the RS-232 communication is converted to the fiber optic cable mounted on the R/V *Pelican*.

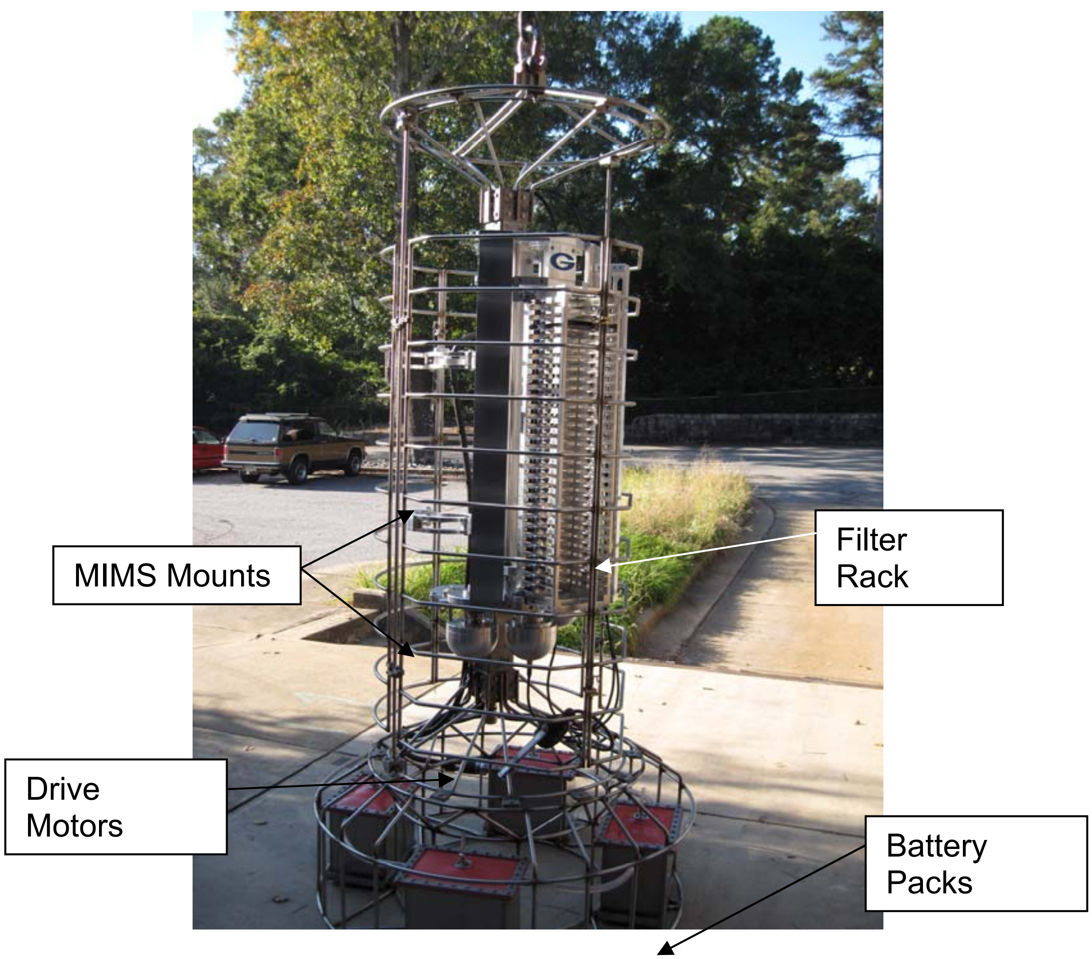


Figure 28. Lander assembly.

The Lander was scheduled for the October cruise to test the mechanical systems and fiber optic communication. The Lander had been pressure tested in February 2011, but had not been previously tested in the marine environment. The Lander was transported to Cocodrie, LA on October 12, 2011 and loaded onto the LUMCON R/V *Pelican* the following day. The *Pelican* departed the LUMCON facility around 9:00 pm October 13 and headed for the MC118 research area.

After several projects were deployed, the Lander was staged on the stern for pre-deployment preparations. The membrane introduction mass spectrometer (MIMS), installed inside the Lander frame was experiencing problems with a vacuum leak, so could not stream data during the deployment. Even though the MIMS could not be in full operational mode, it was decided to mount it on the Lander to test communication during deployment. After the fiber optic cable splice was completed linking the Lander to shipboard computers, it was ready for deployment. The Lander was launched from the *Pelican's* stern at midnight, October 15 ready for testing (Figure 29). Floats were attached to the fiber optic cable to keep it buoyant during times when the Lander touched down on the seafloor (Figure 29).

Figure 29. Lander deployment (left) and floats attached to fiber optic cable (right).

Test filter samples were collected near the surface to ensure that the system was functioning after deployment. Since this was the first saltwater deployment for the Lander, care was taken to check the system for potential structural leaks which might cause system failure. Computer commands were sent to the Lander and four filters were collected. The pump was run for 15 minutes per filter which pumped an estimated 4 liters of water. The Lander was then lowered to 200 m and 400 m depth with four more filters per depth collected. The same procedure of 15 minutes pumping was conducted at both depths. The Lander was then lowered to 600 m depth. At this point, the pump did not appear to respond to surface commands giving concerns of a potential leakage. The Lander was returned to the surface and back on deck by 5:00 am. After removal of the pump housing, no water had been detected, but the pump's magnetic drive had been moved slightly by the housing flexing while under pressure. The drive was repositioned and the pump housing replaced. All systems were tested on deck and proved functional.

The Lander was redeployed by 6:00 am and lowered back to 600 m. The pump was tested and proved to be working properly. The Lander was then lowered to 800 meters with the pump still functioning properly. At this time, it was decided to lower the Lander to the seafloor to test filter collection while running video and lights. All communications with the Lander proved successful with the video, light, and pump responding as requested. Even though the MIMS was not producing water sample analysis, communication with the MIMS was successful throughout the deployment. During deployment, various pump speeds were tested which led to a successful maximum increase of water flow to one half liter per minute.

While deployed directly above the seafloor, the Lander visited 3 sites at MC118 (28° 51.4089'N/88° 29.5088'W; 28° 51.4214'N/88° 29.5894'W; and 28° 51.1877'N/88° 29.2056'W). The seafloor was viewed at each station with limited video saved on the computer hard drive. The longest video file saved was approximately 30 minutes and required 25 megabyte space on the hard drive. With a terabyte of storage space, considerable video can be collected with the Lander. The video gave sufficient detail that allowed the identification of shells, fish, starfish, and worms on the seafloor (Figure 30). Holes in the seafloor were noted as signs of biological activity or potential gas seepage. While the video was in operation, the filter pump was also employed effectively allowing the Lander to collect filter samples while viewing the seafloor.

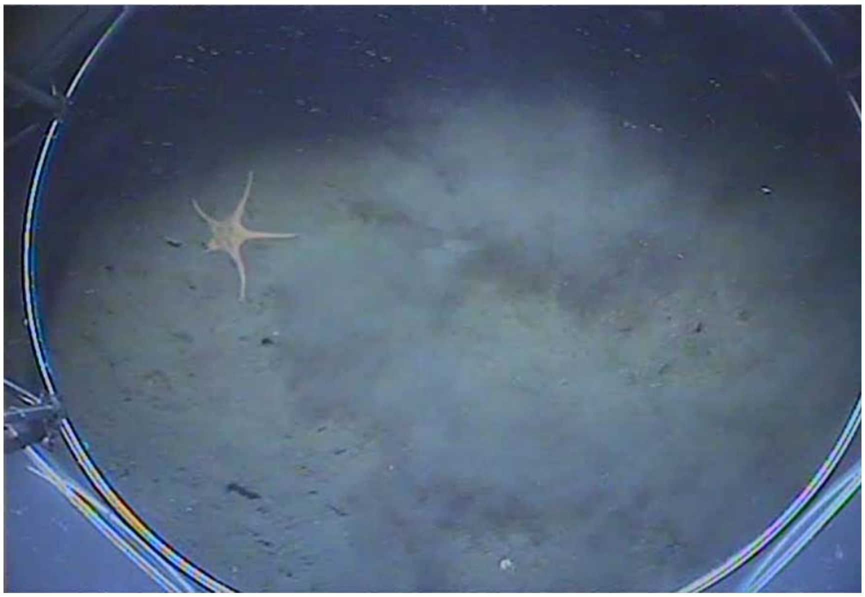


Figure 30. Example of video collected during the Lander deployment.

After approximately 9 hours of use, the Lander was back on deck by 10:00 am. Except as noted, all systems continued to function properly during the deployment.

As a result of the deployment, several Lander functions were identified needing attention. First, it appeared that the connection between the water pump and the filter cartridge may have been leaking allowing the water to be pulled from outside the filter instead of flowing through the filter. Several of the filter samples will undergo microbial analyses to determine if the filtration was successful or not. The cause of this leakage, most likely due to improper cam alignment or the sealing face, will be determined and corrected before the next deployment. The Lander software, although functional is not user friendly at this time. Efforts will be made to refine the software allowing more streamlined use of the Lander controls. Finally, an additional light needs to be added to the downward facing video camera to eliminate a shadow effect shown during the video

Continued Research on MIMS

SRI has continued efforts to investigate methods to improve detection limits for methane using the MIMS by implementing a cold trap system between the membrane inlet and the ion source of the mass spectrometer. The major component of the cold trap is a Model K508 Stirling cooler assembly from RICOR Cryogenic & Vacuum Systems, and the overall design is based on one devised by scientists at the Alfred Wegener Institute in Germany. Their prior work has shown that a temperature of -90 degrees C is sufficient to trap water vapor to improve their methane detection limit by over an order of magnitude (private communication). We plan to test the SRI cooler system in early 2012 to evaluate the improvement in methane detection limits for the SRI MIMS systems.

The design for a new smaller and lower power MIMS instrument has been completed, all of the major internal components (e.g., mass analyzer, high vacuum pump, roughing pump, and water sampling pump) have been assembled, and preliminary tests have been performed. Figure 31 is an engineering model of the new MIMS underwater system with components mounted inside the pressure housing (without electrical wiring and fluidic plumbing). The new custom power distribution board has been constructed and tested with the MIMS components. The microcontroller board and a custom peripheral board to control MIMS operation and data collection have been designed and all components ordered. The microcontroller board construction and testing is almost completed. Construction of the peripheral board and final assembly and testing of all components is expected to be completed in the next three months.

Planned Efforts

During Spring 2012, funding permitting, the Lander will be outfitted with 12 Niskin bottles for bulk water collection. Operational software will be written for the Lander systems allowing more user friendly operation. The pump to filter connection will be reengineered to provide a more secure connection. The new MIMS will be bench tested and readied for installation into the Lander. It is anticipated that the Lander upgrades and new MIMS will be field tested at MC 118 during the September 2012 *Pelican* cruise. At this time, the system will be evaluated at depth to determine functionality and determine any future hardware/software modifications.

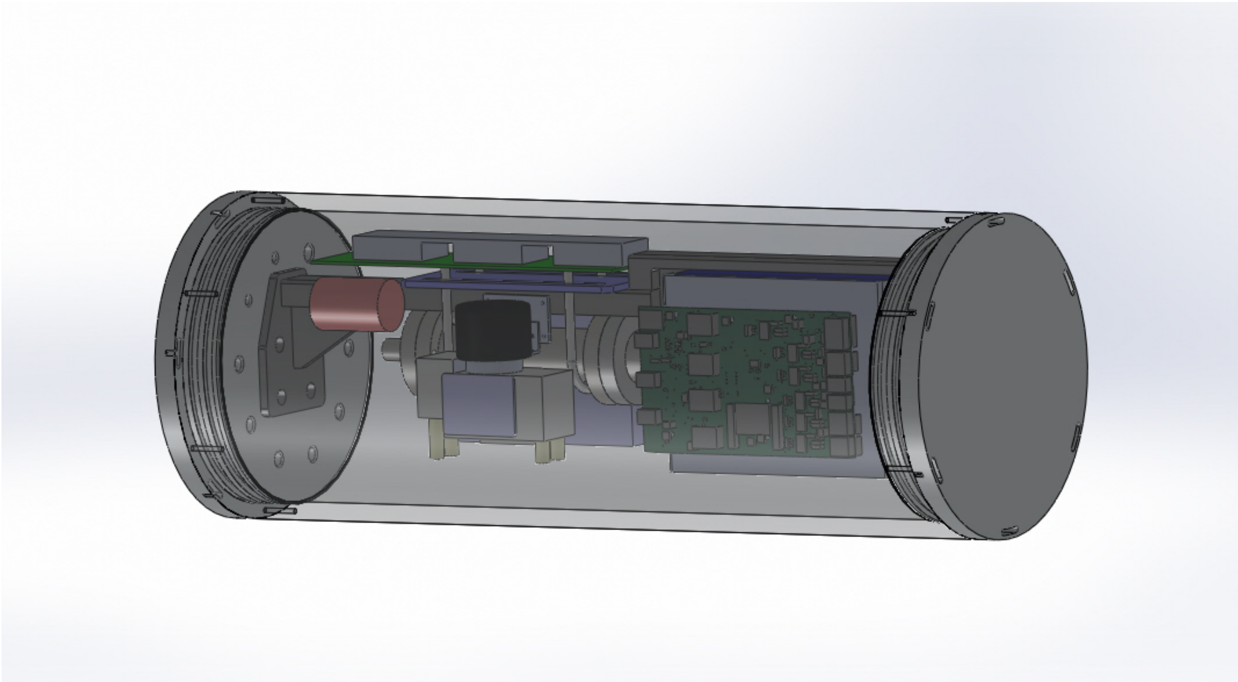


Figure 31. 3-D schematic of new MIMS system with components mounted in pressure housing. Electrical and fluidic connections are not shown.

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

EFFORT SUMMARY:

In 2011, Dr. Leifer did not officially work on the hydrate consortium project, although he made significant progress on several research aspects that directly support consortium objectives and the overall direction of his hydrate consortium research.

A powerful Reson 7125 AUV was acquired, through a non-academic funding source that is true 256 beams, has far higher spatial and temporal resolution and also dynamic range than the Imagenex Delta T. A large aluminum lander was constructed to support the 7125 and new more powerful rotator, as well as deep sea power and light batteries to support its far greater power draw. The Consortium Imagenex Delta T now is configured to collect continuous data in horizontal fan mode while the Reson 7125 rotates in vertical fan mode. In addition, previous deployment problems arose from electrical issues for the large number of wires inside the electronics bottle. All signals and power are now routed with a custom built printed circuit board by SCRIPPS, which also includes short circuit and over voltage protection. Several spare boards also were acquired. In addition to a small diameter underwater housing, large (12” diameter) by 18” long, modular housings (up to 4 are available for connection, were acquired with large (8”) windows to allow fluorometric measurements through the window. A field test of the lander system, is planned for mid February.

Also available for future research is a Picarro greenhouse gas sensor that can measure methane to 0.1 ppb at 10 Hz, and could pick up very subtle methane atmospheric enhancements. Furthermore, significant improvements in gas chromatographic detection of very low levels of n-alkanes larger than ethane, specifically C2-C10 alkanes, alkenes, and BTEX at concentrations of 10-30 parts per trillion. These improvements were achieved through switching to better columns and dramatic improvements in power noise filtering through a regenerative power supply, UPS. This latter system should enable high quality measurements even aboard the R/V *Pelican*. With these sensitivities, natural gas source fingerprinting becomes feasible.

As part of the 2010 Pelican research cruise, which suffered from weather issues, data was collected during the drive from the departure port, Cocodrie, LA, to California. Driving was chosen because of the ability to maintain watch on the sensitive gas chromatography instrument, the potential for collecting in transit data, and costs comparable to transport and lodging versus shipping and flying. During the return trip, atmospheric methane concentrations were recorded once per forty seconds, approximately. These showed significantly elevated methane associated with fossil fuel industrial activities. A manuscript is close to submission to Atmospheric Environments.

Progress also was made in analyzing the data from the HYFLUX experiment, whose funding ended a few years ago and presented at the fall AGU 2011 meeting. These data were of ROV collected water samples while following a bubble plume from MC118 on the downcurrent side of the plume. The bubbles were followed from the seabed to the mixed layer. Analysis clearly showed that higher n-alkanes were being transported from the deep sea to shallow water. Moreover, the changes in composition showed strong changes at the boundary of the hydrate Type 1 and hydrate Type II depths, suggesting that hydrate processes were critically important to enabling deep sea methane to reach shallower waters.

Task 7: 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:

- Technical semiannual progress report 42877R20 covering progress of DOE-funded projects as well as additional Consortium accomplishments for the time period January 1 – June 30, 2011, was completed and submitted to DOE during this reporting period. Regular monthly reports documenting progress of subcontractors and the Consortium in general have been less formal, taking the form of email and telephone updates.
- The Gulf of Mexico Hydrates Research Consortium held a fall meeting in Jackson, Mississippi in November. Proceedings of this and previous Consortium

meetings are posted on our website at: http://mmri.olemiss.edu/Home/Publications/Conference.aspx.

- Short summaries of several Consortium projects are now listed and described on the MMRI website at http://mmri.olemiss.edu/Home/projects/marine.aspx
- CMRET/STRC has developed habitat maps for MC118 based on multiple video, coring, and acoustic surveys of the site. The map identifies areas in need of additional surveys and provides a base line for future habitat evaluations.
- Additional funding possibilities through GRI-2 are being pursued through efforts at the CMRET and through CMRET cooperations with other Institutions affiliated with the Consortium.
- Consortium scientists planned, contracted for and executed a research cruise aboard the R/V *Pelican*, October 13-16. Objectives that were met were: 1. Deploy the optic modem, establish contact with the BBLA and download 3 months' worth of data, 2. Using the Noakes Lander, survey potential sites for the second long-term (several months) deployment of the CSA geochemical array via the ROVARD, 3. Deploy the ROVARD with CSA aboard., 4. Deploy and recover calibration mooring outfitted with USM double sonar scanner at a potential seep site for bubble volume measurements. Although this last objective was met only in part, the difficulty was discovered by the time the cruise returned to port and the system is likely to be deployed on the April, 2012 coring cruise.
- The duplicate WesternGeco dataset acquired by CMRET has been evaluated and has already led to the discovery of multiple characteristics not previously identified in any dataset from MC118. Beginning data analyses have contributed to the Consortium effort and some of these are represented in presentations and publications.
- Jumbo Piston cores have been logged on the Geotek logger at Stennis Space Center through a subcontract initiated by the CMRET especially for this effort.
- Noise data from the April 2-9 cruise to collect 4C data have undergone preliminary analyses by the University of San Diego, Scripps Oceanographic Institution team. Although noise is a problem, they think they can remove it and get some useful data from this effort. In addition, they will be able to evaluate the prospects for future noise data utility and improving the way we may collect noise data. A proposal to use drilling noise as a source is being designed.
- 4-C data collected on via the OBS units have been delivered to UT-Austin in SEGY and SEED formats. UT will perform the data-processing and interpretation via the software developed by them for this purpose under Phase 2 of this Cooperative Agreement. A CMRET geophysicist spent 2 months at UT-Austin assisting in this effort that will take several additional months' concerted effort to complete.
- In April 2011, NRL and C&C Technology tested the upgraded version of NRL AUVs Remus 2500 and Remus 6000 over Woolsey Mound. Scientists from MMRI-CMRET-STRC took part in the cruise. Remus AUVs accomplished 5 dives over the site, collecting ultra-high resolution side scan sonar and video images over specific targets selected by MMRI scientists. In particular the Southwest Crater has been intensively investigated; near bottom images have been collected over the sleeping dragon outcrop, sonar data of a frequency

range never collected before have been recovered. These data have been reprocessed and show detail greater than that of any data we have had access to previous to this time. We can see our larger instruments on the side-scan sonar data!

- Michela Ingrassia and Martina Pierdomenico, Visiting Scholars at the CMRET/STRC from July, 2010 through May, 2011 both graduated from the Department of Marine Sciences, University of Rome with highest honors for the work they did while at the University of Mississippi, working with Consortium geoscientists at the University of Mississippi at the Pennsylvania State University and at the NOAA Northeast Fisheries Science Center, New Jersey.
- Leonardo Macelloni and Marco D'Emidio were instrumental in the success of the 2011 Hudson Canyon photo survey using NIUST's AUV *Mola Mola*.
- SAIC has coded the equation-of-state (HYDGAS) module. It is a relatively large code (over 15,000 lines; see appendix A). that is presently being debugged and tested. The HYDGAS package is designed for use with the STAR and/or THROBS simulators. Given the pressure, internal energy, and gas composition, the HYDGAS module will provide mass/volume fractions of hydrate, gas and liquid phases together with other thermodynamic data (e.g. mole composition of gases in the hydrate, liquid and gas phases, temperature, etc.).
- Several Consortium members presented their work at the 7th International Congress on Gas Hydrates in Edinburgh in July. These are listed in the Appendix of new publications and presentations.
- The presentation, *Biogeophysical Classification of Seafloor Seeps at a Carbonate-Hydrate Mound, Northern Gulf of Mexico*, by Carol Lutken and Michela Ingrassia received the AAPG Award of Excellence, "TopTen" Poster Presentation at the AAPG International Convention and Exhibition in Milan, Italy, October 21-25.
- Several Consortium presentations were made at the Annual Meeting of the American Geophysical Union in San Francisco, December, 4-9, 2011. They appear in the Appendix of New Publications and Presentations.

Task 8. Project Summary Updates:

Periodic website updates are the responsibility of the CMRET together with DOE. Publications are added to the Consortium list as they appear or as notification is received and a revised list of recent publications accompanies this report.

The Consortium website continues to be expanded and updated though there is much information still awaiting posting. Unfortunately, funding challenges have necessitated shifting personnel from this important task to other more pressing duties. It is a goal of the CMRET to get many of the older reports, logs and other data posted. Geological and geophysical pages for the website, including core locations and descriptions, cruise reports, meeting presentations, online geophysical data collected by the CMRET, reports of meetings and many maps derived from Consortium effort.

We are now in the process of adding meeting reports, posters, systems summaries and cruise reports to this site.

CONCLUSIONS

This report covers the accomplishments of the six-month period from July 1 through December 31, 2011, 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: one cruise to test, deploy and recover instruments has been made; we have assisted in the NOAA Hudson Canyon cruise. AUV acquired photo data as well as lander photodata and additional chemical data have been acquired. Jumbo Piston cores have been logged and partially analyzed validating a capability to integrate multiple datasets to predict hydrate in the shallow subsurface with greater accuracy than any known single method can provide. Innovative data processing techniques and approaches are being 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. HLA configuration and deployment challenges continue and we continue to develop new deployment and recovery approaches and techniques to overcome them. A preliminary hydrate 3-gas model is approaching completion and use of real data. Poster and oral presentations have been made at national and international meetings. Manuscripts have been submitted to peer-reviewed journals and additional papers and presentations have resulted from Consortium research efforts. Progress in AUV tasks and in deployment methods has been made; a polarity-preserving chirp system has been installed on and test data collected using the NIUST AUV, Eagle Ray. Every effort has been – and will continue to be – made to maximize Consortium members' access to and benefit from the cruises scheduled for 2012 though without additional resources these will be curtailed. New funding sources continue to be sought. 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. Funding through GRI-II announcement is being sought.

ACRONYMS AND ABBREVIATIONS

3-D	3-dimensional
4-D	4-dimensional
4-C	four component
ABCMS	Automated Biological Chemical Monitoring System
AGM	Absorption Glass Mat (battery)
AOM	anaerobic oxidation of organic matter
AUV	autonomous underwater vehicle
AVO	amplitude vs. offset
BBLA	Benthic Boundary Layer Array
BEG	Bureau of Economic Geology (University of Texas)
BOEM	Bureau of Ocean Energy Management
BSR	bottom-simulating reflector
C&C	Chance and Chance
C_1/C_2+C_3	ratio of methane to ethane plus butane

CGGVeritas	Compagnie Générale de Géophysique (CGG) and Veritas
CMRET	Center for Marine Resources and Environmental Technology
CMSHYD	stand-alone computer program; Sloan's statistical thermodynamic approach
CSA	Chimney Sampler Array
CSEM	Controlled-source Electro-Magnetic
CTD	Conductivity, Temperature, Depth
$\delta^{13}C$	ratio of stable isotopes 13C:12C
DIC	dissolved inorganic carbon
DOC	Department of Commerce
DOE	Department of Energy
DOI	Department of the Interior
DRS	Data Recovery System
EGL	Exploration Geophysics Laboratory
EMD	Empirical Mode Decomposition
EOS	equation-of-state
FY	Fiscal Year
GI	Gas injection
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
IODP	Integrated Ocean Drilling Program
IR	Infrared
ISE	International Submarine Engineering
JPC	Jumbo Piston Core/Coring
JSL	Johnson SeaLink
LWD	logging while drilling
LUMCON	Louisiana Marine Consortium
MC	Mississippi Canyon
MeOH	Methanol
MIMS	membrane introduction mass spectrometer
MMRI	Mississippi Mineral Resources Institute
MMS	Minerals Management Service
uM	micromolar
MOG	
MPa	Mega-pascal
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
NRDA	Natural Resource Damage Assessment
NRL	Navy Research Laboratory
NURP	National Undersea Research Program

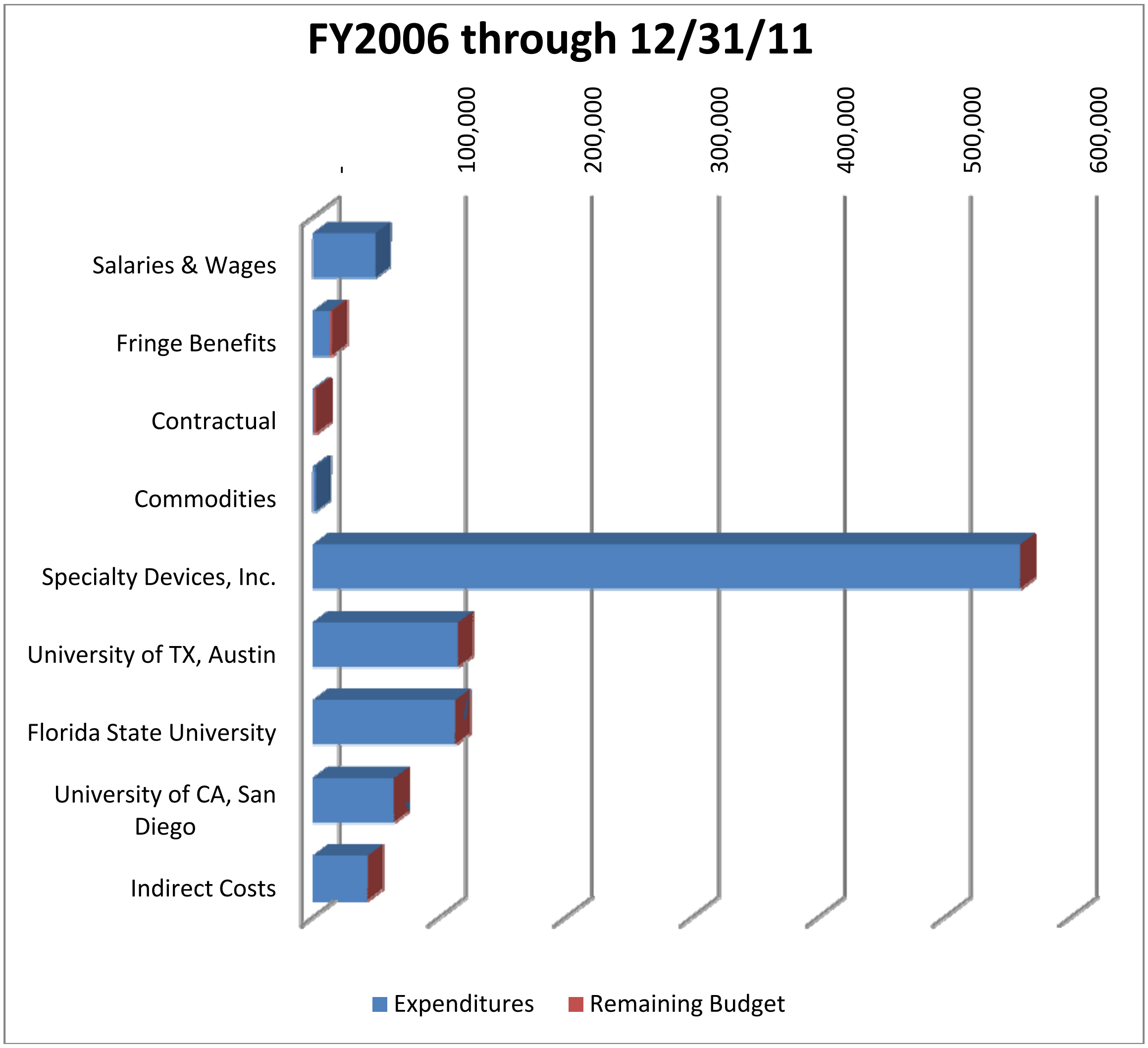
OBS	ocean bottom seismometer
OER	Ocean Exploration and Research
OLA	Oceanographic Line Array
P-wave	compressional wave/pressure wave
PFA (=PCA)	pore-fluid array
P-P	P-wave mode (P wave down and P wave up)
PPC	polarity-preserving chip subbottom profiling system
P-SV	converted-shear mode (P-wave to SV-shear wave conversion)
PVT	pressure-volume-temperature
ROV	remotely operated vehicle
ROVARD	ROV Assisted Recovery Device
R/V	Research Vessel
SAIC	Science Applications International Corporation
SDI	Specialty Devices, Inc.
SFO	Sea Floor Observatory
SFP	Sea Floor Probe
SMT	sulfate-methane transition zone
SR	sulfate reduction
SRI	SRI, International
SSD	Station Service Device
SS/DR	Surface-Source Deep Receiver
SSS	Station Support Systems
STAR	SAIC’s multidimensional simulator
STAR/HYDCH4	constitutive description
STRC	Seabed Technology Research Center
TA	thermistor array
TGS-NOPEC	geophysical data (2-D, 3-D) acquisition company
THROBS	SAIC’s hydrate simulator
UCSB	University of California, Santa Barbara
UCSD	University of California, San Diego
UGA	University of Georgia
UMS	underwater mass spectrometer
USBL	ultra-short baseline navigation system
USC	University of South Carolina
USGS	United States Geological Survey
UT	University of Texas
UVTC	Underwater Vehicle Technology Center
VLA	vertical line array
WesternGeco	Western Geophysical Company
WHOI	Woods Hole Oceanographic Institution
WMCL	wet-mateable communications link
NRDA	Natural Resource Damage Assessment
NRL	Navy Research Laboratory
NURP	National Undersea Research Program

OBS ocean bottom seismometer
OER Ocean Exploration and Research

OLA	Oceanographic Line Array
OSV	Offshore Supply Vessel
P-wave	compressional wave/pressure wave
PFA (=PCA)	pore-fluid array
PVT	pressure-volume-temperature
ROV	remotely operated vehicle
ROVARD	ROV Assisted Recovery Device
R/V	Research Vessel
SAIC	Science Applications International Corporation
SDI	Specialty Devices, Inc.
SFO	Sea Floor Observatory
SFP	Sea Floor Probe
SR	sulfate reduction
SRI	SRI, International
SSD	Station Service Device
SS/DR	Surface-Source Deep Receiver
SSS	Station Support Systems
SSVP	Shallow Sediment Velocity Probe
STAR	SAIC's multidimensional simulator
STAR/HYDCH4	constitutive description
STRC	Seabed Technology Research Center
TA	thermistor array
TGS-NOPEC	geophysical data (2-D, 3-D) acquisition company
THROBS	SAIC's hydrate simulator
UCSB	University of California, Santa Barbara
UCSD	University of California, San Diego
UGA	University of Georgia
UM	The University of Mississippi
UMS	underwater mass spectrometer
USBL	ultra-short baseline navigation system
USC	University of South Carolina
USGS	United States Geological Survey
USM	The University of Southern Mississippi
UT	University of Texas
UVTC	Underwater Vehicle Technology Center
VLA	vertical line array
WesternGeco	Western Geophysical Company
WHOI	Woods Hole Oceanographic Institution
WMCL	wet-mateable communications link

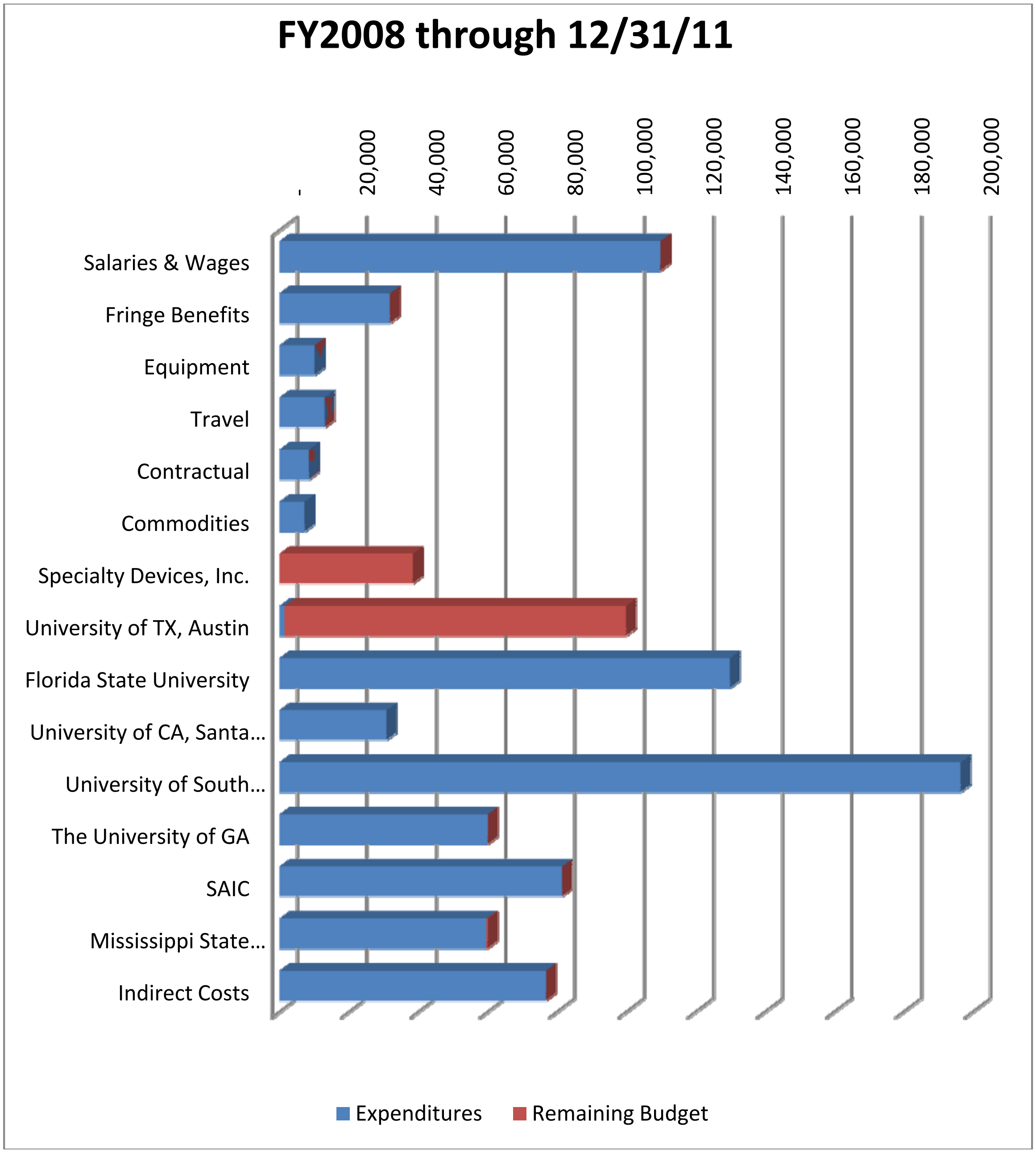
COST STATUS

As can be seen in the figures and tables that follow, Phase 1 (FY06) funds are essentially spent. Funds remaining in Phases 2 and 3 (FY08 and FY09) are primarily the 4C experiment and the speed of sound probe. The 4C experiment should move quickly now that the data have been acquired. The probe is being reevaluated but should be tested this year. We hope to conduct the coring work that will test this system in April. Phase 4 (FY10) is progressing reasonably though some projects will remain unfinished without some additional funds.



Mississippi Mineral Resources Institute
DOE DE-FC26-06NT42877
Funding Status as of 12/31/11

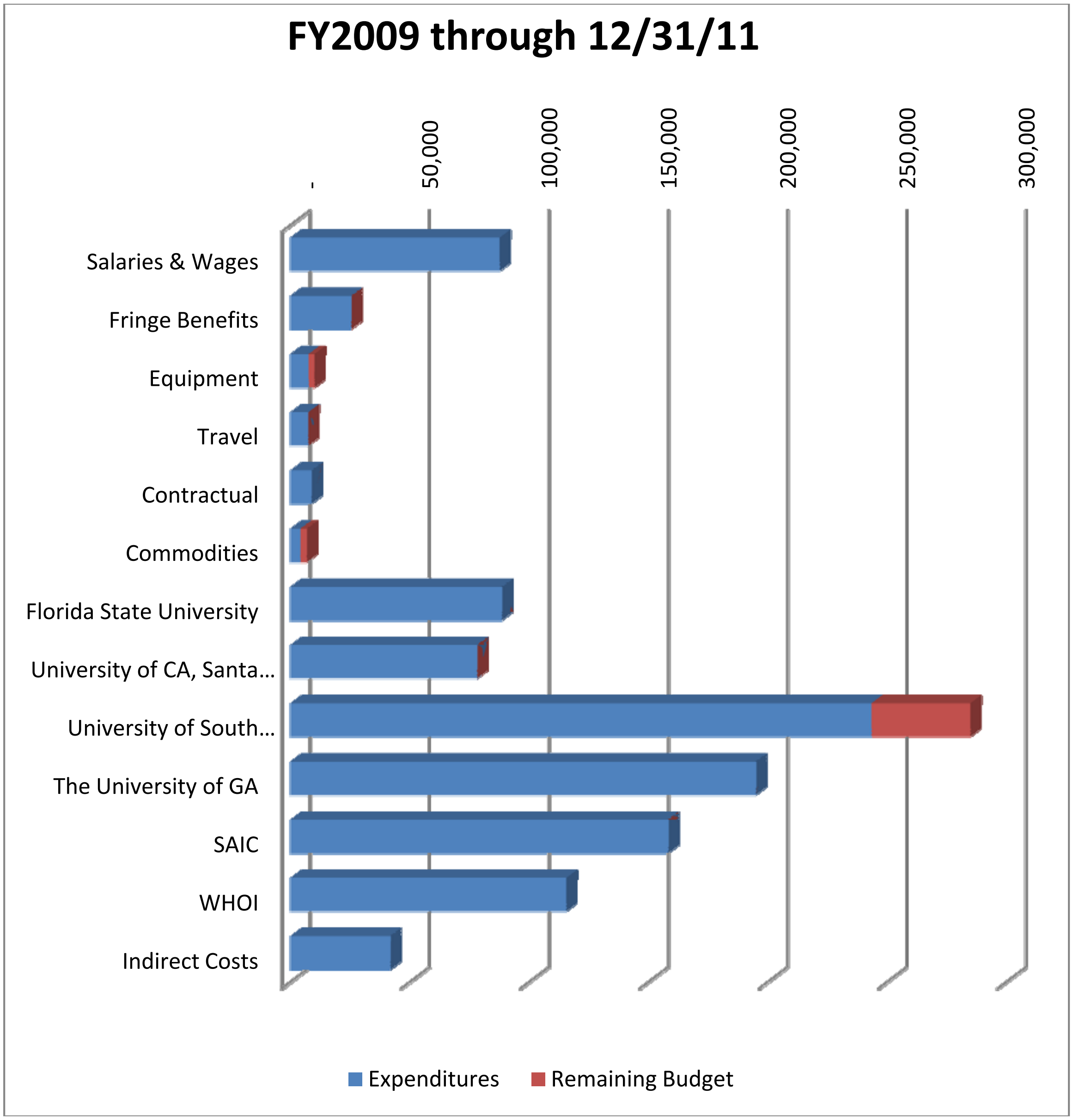
FY2006	Expenditures	Remaining Budget
Salaries & Wages	49,309	(229)
Fringe Benefits	13,471	1,646
Contractual	1,026	1,474
Commodities	2,176	(2,176)
Specialty Devices, Inc.	559,912	-
University of TX, Austin	114,979	21
Florida State University	112,520	-
University of CA, San Diego	64,113	-
Indirect Costs	43,155	187
Total	960,661	923



FY2008 through 12/31/11
-
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, Santa…
University of South…
The University of GA
SAIC
Mississippi State…
Indirect Costs
Expenditures
Remaining Budget

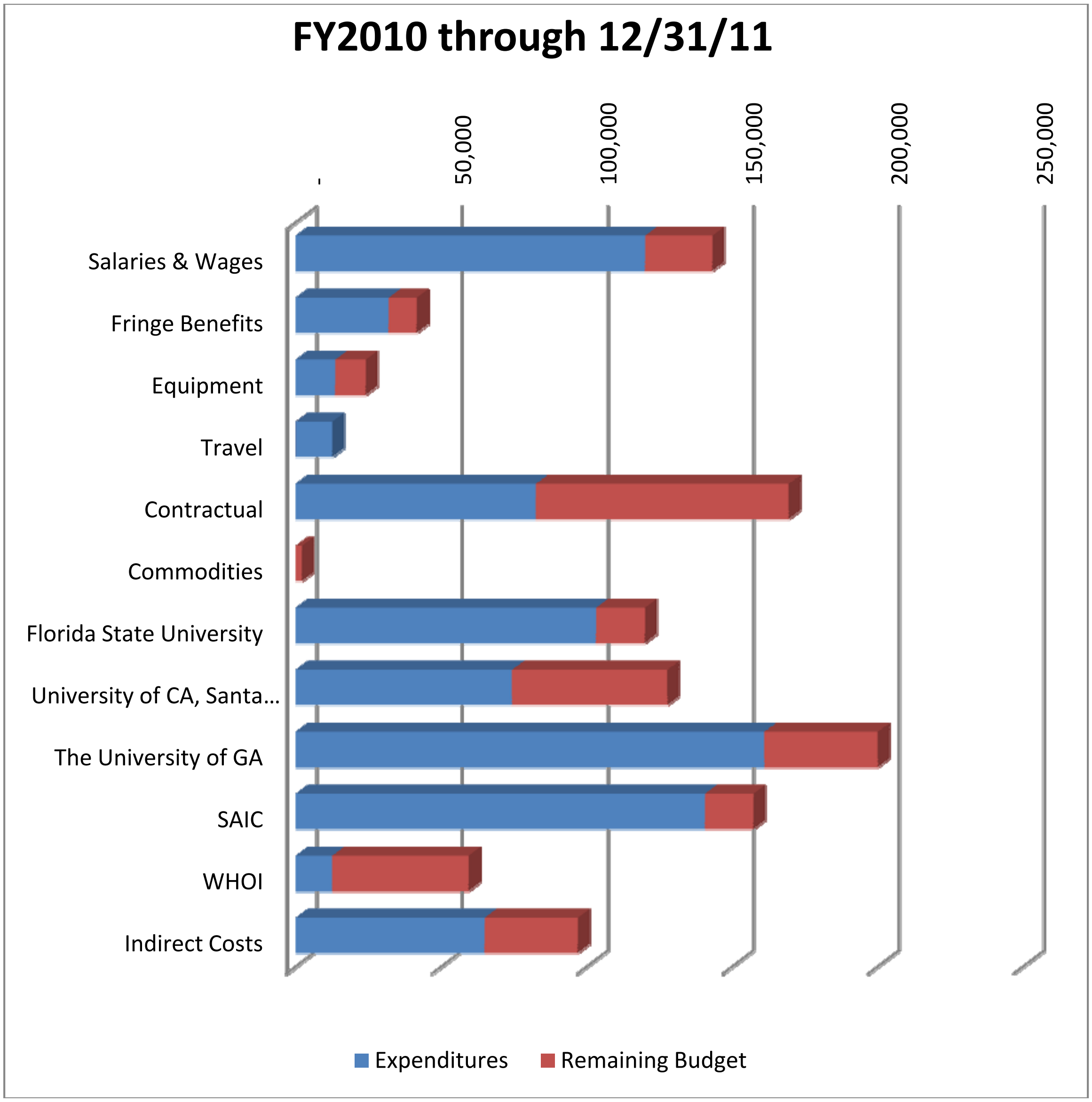
Mississippi Mineral Resources Institute
DOE DE-FC26-06NT42877
Funding Status as of
12/31/11

FY2008	Expenditures	Remaining Budget
Salaries & Wages	109,809	-
Fringe Benefits	31,845	-
Equipment	10,000	-
Travel	13,000	-
Contractual	8,500	-
Commodities	7,215	-
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	59,539	463
Indirect Costs	76,796	-
Total	817,046	137,354


FY2009 through 12/31/11
-
50,000
100,000
150,000
200,000
250,000
300,000
Salaries & Wages
Fringe Benefits
Equipment
Travel
Contractual
Commodities
Florida State University
University of CA, Santa...
University of South...
The University of GA
SAIC
WHOI
Indirect Costs
Expenditures
Remaining Budget

Mississippi Mineral Resources Institute
DOE DE-FC26-06NT42877
Funding Status as of
12/31/11

FY2009	Expenditures	Remaining Budget
Salaries & Wages	87,602	-
Fringe Benefits	25,405	-
Equipment	7,546	2,454
Travel	7,400	-
Contractual	8,717	-
Commodities	4,075	2,693
Florida State University	88,508	-
University of CA, Santa Barbara	78,118	-
University of South Carolina	243,449	41,451
The University of GA	195,029	-
SAIC	158,252	-
WHOI	115,550	-
Indirect Costs	41,775	-
Total	1,061,426	46,598


FY2010 through 12/31/11
-
50,000
100,000
150,000
200,000
250,000
Salaries & Wages
Fringe Benefits
Equipment
Travel
Contractual
Commodities
Florida State University
University of CA, Santa...
The University of GA
SAIC
WHOI
Indirect Costs
Expenditures
Remaining Budget

Mississippi Mineral Resources Institute
DOE DE-FC26-06NT42877
Funding Status as of
12/31/11

FY2010	Expenditures	Remaining Budget
Salaries & Wages	120,050	23,101
Fringe Benefits	31,883	9,631
Equipment	13,544	10,456
Travel	12,478	(78)
Contractual	82,583	86,917
Commodities	-	2,108
Florida State University	103,200	16,781
University of CA, Santa Barbara	74,346	53,397
The University of GA	161,116	39,005
SAIC	140,606	16,653
WHOI	12,548	46,780
Indirect Costs	64,893	32,002
Total	817,247	336,753

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 continuing to be expanded and refined. 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. However, expansion of the site characterization, including a time element, is moving forward forward with the analysis of additional industry standard data from WesternGeco. An additional multibeam survey and a side-scan survey of extremely high resolution, obtained in May, have been reprocessed for integration into the CMRET's characterization. Several partial photo surveys have been conducted at MC118 and we have received a portion of these datasets. Jumbo Piston Coring analyses is nearly complete and a report will be submitted when the core data are complete. constraining the shallow data.Chemical surveying has added valuable information to the site baseline characterization. The polarity-preserving chirp system has been installed on the NIUST AUV , tested at-sea and should go to MC118 in June, 2012. CMRET/STRC continue to work with the manufacturer, Geoacoustics, to debug the acquisition software. The photo-AUV, Mola Mola is scheduled to survey MC118 in June, 2012.

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

Data were recovered from BBLA by means of the optic modem. This is the first ever recovery of real data with this technology, a milestone in itself for the scientific community. The ROVARD with a single CSA onboard was deployed in October. Additional attempts to recover instruments – primarily the PFA-2 - are scheduled for July, 2012.

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.* Deployment cruises for this task failed to get the job done. We have scheduled a March meeting to reevaluate this approach. We need to get something on the seafloor and the current thinking is that the long arrays can be converted to a series of shorter arrays that include hydrophones as well as a seismometer and accelerometer.

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. However, time-series geochemical data from the BBLA and CSA are now being processed and evaluated. Heat-flow, pore-fluid and JPC data will be will soon be available to modeling efforts.

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. The multibeam and mass spectrometer surveys are complete. We have received a complementary update in the multibeam from the Navy C&C along with very high resolution side-scan sonar data from MC118. We will use our 2005 survey to calibrate a new AUV they are testing for the Navy. 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 dataset has been collected and delivered to subcontractors for analyses. UM has participated in the data evaluation and will become the major data processing and evaluation team as the UT team is no longer entirely available for this work.

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 now being incorporated into the final model. Unfortunately, funds are exhausted so this project remains incomplete though SIC researchers are seeking additional funds to enable them to complete it.

New Milestones – and status - from FY10 Program Management Plan

Milestone 5: Collect and evaluate giant piston cores from the MC118 Sea Floor Observatory. This Phase 4 milestone is tied to Task 2 and is estimated to be complete in June, 2011. This task is essentially complete. The cores have been collected and initial inspection completed. Cores have been logged (opened, logged and photographed at Stennis as personnel find time to accomplish this task on the ~75m of recovered core.

Milestone 6: Collect heat-flow data from MC118. This Phase 4 milestone is tied to tasks 2 and 3 and is estimated to be complete by March, 2012. This task depends on TDI's schedule. We are scheduled to go out early in 2012.

Milestone 7: Collect and evaluate additional gravity cores to complete sedimentation model, support geochemical and geophysical (structural) characterization of MC118. This Phase 4 milestone is tied to Tasks 2, 3 and 4 and is estimated to be complete by April, 2012. This task has slid as the April cruise had to be cancelled in light of certification issues with the vessel. We have rescheduled to coordinate coring with speed of sound probe testing.

Milestone 8: Integrate geophysical datasets with geochemical and biological data. This Phase 4 milestone is tied to tasks 2 and 3 and is partly complete but ongoing. This task is in progress and results thus far have contributed significantly to numerous evaluations of MC118, most significantly the selection of sites for both the JPC and heat-flow cruises as well as our gravity coring cruise. An updated habitat map, tentatively tied to the shallow high resolution seismic and acoustic data was presented at the 2011 International AAPG in Milan and was awarded a "top ten" poster status for the entire meeting. We intend to continue this novel approach to seep evaluation.

Milestone 9: Purchase and learn to operate an Infrared camera for the purpose of distinguishing hydrates in unopened cores. This Phase 4 milestone is tied to tasks 2 and is estimated to be complete by April, 2011. This camera has been received and used on the JPC cruise. Initial results were very promising and work is ongoing to improve the carriage and scale display. The goal is to use it on our April coring cruise to identify which cores and sections are likeliest to contain hydrates and/or exhibit gas expansion.

Milestone 10: Collect and analyze hydrate and "slime"(= protective ? biofilm) at hydrate outcrops in an effort to explain the existence and persistence of hydrate in seawater undersaturated for methane. This Phase 4 milestone is tied to tasks 2 and 4 and is estimated to be complete by September, 2011. Pressure chambers have been built with this goal in mind but they have not yet been fitted to the SSD. By our July, 2012 cruise, these should be on the SSD.

Milestone 11: Recover additional pore-fluid time-series via additional instrument (PFAs, osmolander, peepers) deployments and recoveries. This Phase 4 milestone is tied to task 4 and is estimated to be complete by October, 2011. We have deployed several systems of pore-fluid collection. Peepers were collected via the ROVARD. Analyses counterindicate this collection technique as the collection bags leaked. An intermediate-sized PFA (1.5m probe length) has been designed to fit onto the ROVARD. Actual deployment will be by means of a spring released arm that will be activated after the lander reaches the seafloor.

Milestone 12: Deploy the ABCMS lander in upgraded configuration including video, lights reduced-size mass spectrometer, and altimeter. This Phase 4 milestone is tied to task 5 and is estimated to be complete by October, 2011. This lander system was deployed very successfully, 9 hours of deployment time logged, many with video, The video camera worked extremely well and samples were collected successfully though analyses in the lab indicate collection rate may have been too rapid. Unfortunately, the MIMS mass spectrometer did not return chemical data. An improved model is under construction for the next outing with this assembly.

ACCOMPLISHMENTS

Major accomplishments of this reporting period include:

Advances in mapping capabilities including fine-scale mapping of shallow deposits.

Using the Noakes Lander to survey potential sites for lander/instrument deployment

Deploy and recover new calibration mooring outfitted with USM double sonar scanner

Beginning data analyses of the WesternGeco dataset

Jumbo Piston cores have been logged on the Geotek logger at Stennis Space Center

Noise data from the April OBS cruise have undergone preliminary analyses

4-C data analyses is moving forward at the UM

Michela Ingrassia and Martina Pierdomenico, Visiting Scholars at the CMRET/STRC both graduated from the Department of Marine Sciences, University of Rome with highest honors; they also forged valuable new cooperative relationships with Penn State University and NOAA Northeast Fisheries Science Center, NJ.

Leonardo Macelloni and Marco D’Emidio were instrumental in the success of the 2011 Hudson Canyon photo survey using NIUST’s AUV *Mola Mola*.

Consortium members have made many presentations at national and International meetings. The presentation, *Biogeophysical Classification of Seafloor Seeps at a Carbonate-Hydrate Mound, Northern Gulf of Mexico*, by Carol Lutken and Michela Ingrassia received the AAPG Award of Excellence, “TopTen” Poster Presentation at the AAPG International Convention and Exhibition in Milan, Italy, October 21-25.

First ever recovery of 3 months real field data remotely via optic modem
ROVARD redeployed successfully – proven instrument recovery capability
Recovery of geochemical data and sediment samples from the near-seabed and shallow seabed – BBLA and CSA and ROVARD
Processing of High-Definition side-scan sonar data from MC118

PROBLEMS/DELAYS

The majority of delays in the program derive from failure of researchers to have projects ready for at-sea tests, challenges presented by working at 900m water depth and/or shortage of funds. The single cruise we conducted this reporting period, though extremely successful was cut short in order to save days for deployments and tests of sea-worthy instruments and systems, rather than spend additional time and funds at-sea with proven projects (Noakes lander, CMRET's new lander, Optic Modem). This was a major factor in the cancellation of our August cruise – the mass spectrometer was diverted to oil spill recovery work by Continental Shelf Associates and so unavailable for our scheduled survey. We have requested 3 Pelican cruises for 2012 but are facing additional personnel challenges at CMRET with two of our four shop guys gone (1 retired; 1 at another job) We have hired one replacement who is working out very well, but are still feeling very shorthanded, having lost 40 years of experience at-sea between these two employees. We have one new student this fall but have had two graduate and move on.

Having cancelled two cruises in 2011 caused a tremendous back-up in our funded projects to go to sea but we are attempting to be equitable as well as reasonable in allocating our limited resources. The ROVARD was designed, built and employed in an effort to alleviate some of the back-log.It is likely that we will have to figure a way to charge sea-time to the many projects that traditionally depend upon Consortium funds and expertise to provide them access to time and facilities and personnel at sea. The deployment of the HLAs has been an ongoing challenge that is being reevaluated as we learn more about how we can satisfy active and passive noise requirements.

Weather dictates cruise scheduling and successes. Although three cruises have been scheduled for 2012, weather conditions cannot ever be predicted and we face similar delays in the future.

Electronics at depth will always be challenging. The SDI/CMRET team continues to work 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. Processing and interpreting Western Geco data.
2. 4C data- passive data evaluated
3. JPCs logged and mostly described
4. Additional modeling, including additional seismic, acoustic and faunal data.
5. Cruise accomplishments and deployments: Noakes' lander as a site evaluation tool, ROVARD, optic modem proven as an alternative to physical data collection.

6. Progress Report from January – June, 2011
7. Publications and presentations at national meetings.

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