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

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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.

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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 SDDR data by acquisition of targeted cores and velocity profiles at MC118 Hydrate Mound.

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TASK 6: Quantification of Seep Emissions by Multibeam Sonar 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.

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

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 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 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. 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 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.

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. Most recently, geophysicists and geologists at the University of South Carolina and the University of Mississippi established that the observatory site lies directly over a rising salt dome, that "master faults" extend from the salt body to the seafloor, 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.

Several cruises have been conducted by and participated in by Consortium members this reporting period. In January, we participated in the R/V *Brooks McCall* cruise that collected five Jumbo Piston cores from MC118 (Phase 3, Task 2; Phase 4 Tasks 2 and 4). Notable accomplishments of this cruise include verification of hydrate in the shallow subsurface at sites where we predicted it should be and successful first use of the Infrared (IR) camera to identify hydrate and gas in unopened cores (Phase 4 Task 2). Our participation in a March NRDA cruise aboard the HOS OSV *Sweetwater*, provided us with more access and imagery of the coral communities at MC118. This collaboration continues as oil spill recovery work continues at and near MC118. An April cruise was aboard the M/V *Bunny Bordelon* designed and executed to recover Ocean Bottom Seismometer data from Woolsey Mound. This dataset has been transferred to subcontractors at University of Texas-Austin for 4-component 4C analysis and at University of California-San Diego for ambient noise analysis (Phase 1, Task 4; Phase 2, Task 3; Phase 4, Task 2). This cruise also included the successful recovery of the Benthic Boundary Layer Array (BBLA). Consortium participants proved to be key to the successes of a C&C Technologies facilitated Navy cruise to test two new Autonomous Underwater Vehicles (AUVs). Wanting to test the vehicles against a site with established (C&C) bathymetry, C&C recommended MC118. As a result, we have new multibeam and very high resolution side-scan sonar surveys as well as some photo imagery from our site. In June, we conducted a cruise to MC118 aboard the R/V *Pelican* that resulted in some successful work with the Station Service Device (SSD) Remotely Operated Vehicle (ROV) as well as recovery of the ROV-Assisted Recovery Device (ROVARD) and associated instruments and redeployment of the BBLA. A notable achievement of this cruise was the remote recovery of data from the BBLA using an optic modem on a lander. This method enables data recovery without risk of collision, entanglement, etc. of instruments or recovery to the sea surface. Unfortunately, damage to the SSD resulted in its failure and repairs will be time-consuming enough that the August cruise has been cancelled. An October cruise to return the SSD to service is scheduled. At this time, we hope to deploy a horizontal array and conduct additional resistivity surveying.

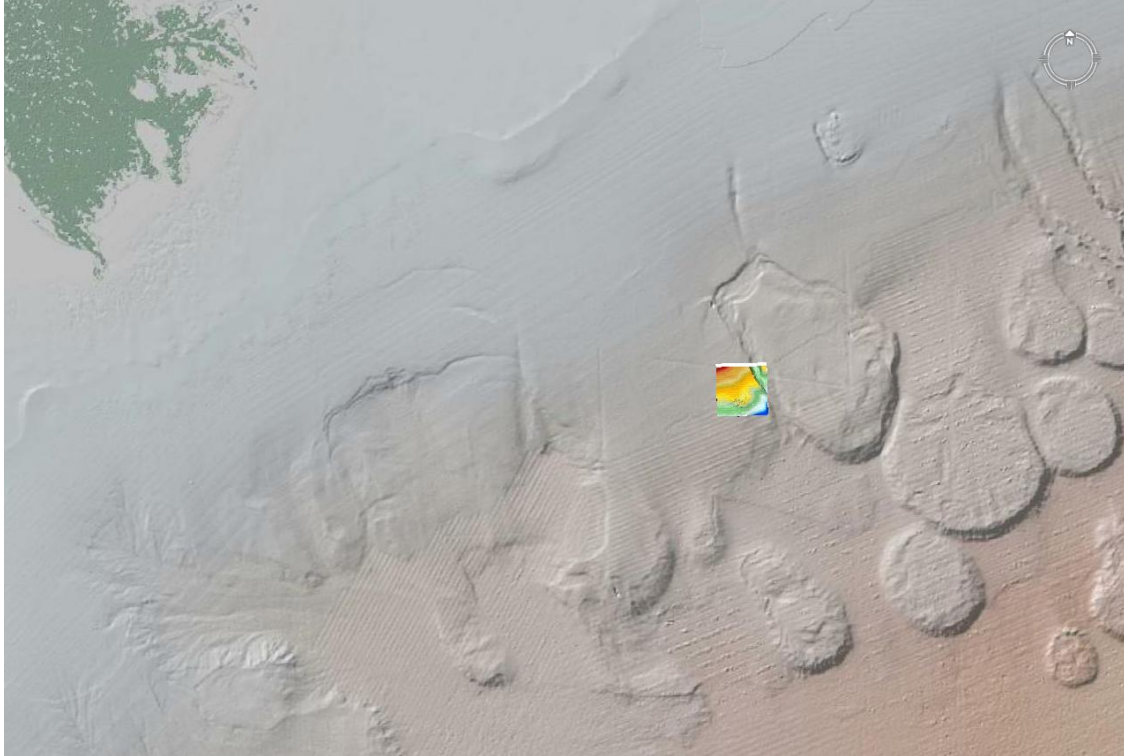


Figure 1. MC118 is located ~30 miles off the toe of birdsfoot delta in the edge of a massive slump.

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 (autonomous underwater vehicle) have been used to define seafloor morphology and bottom reflectivity (see Figure 2) 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. In addition, a surface-source deep-receiver system or SSSDR (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 Monitoring 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 data set is capable of imaging features associated with gas hydrates – chimneys, fracture porosity, etc. – hundreds of meters below the seafloor. Portions of an industry data set, acquired by TGS-NOPEC have 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 3) 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.

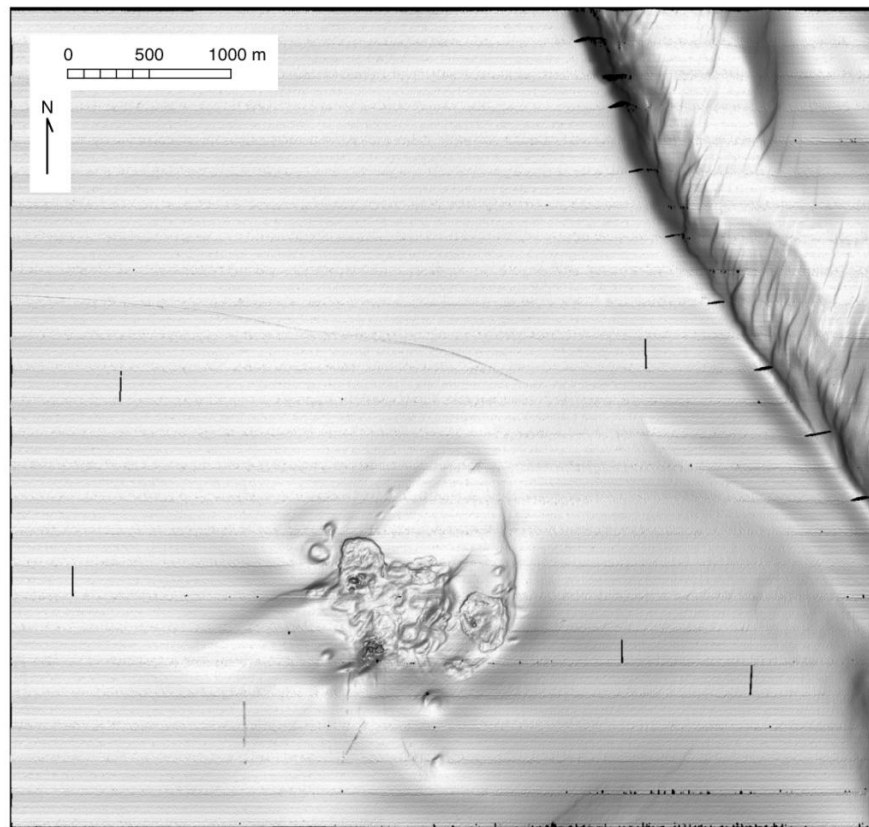


Figure 2. Multibeam image of Mississippi Canyon 118. Data acquired by C&C technologies and reprocessed by The University of Mississippi and University of Rome, La Sapienza.

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.

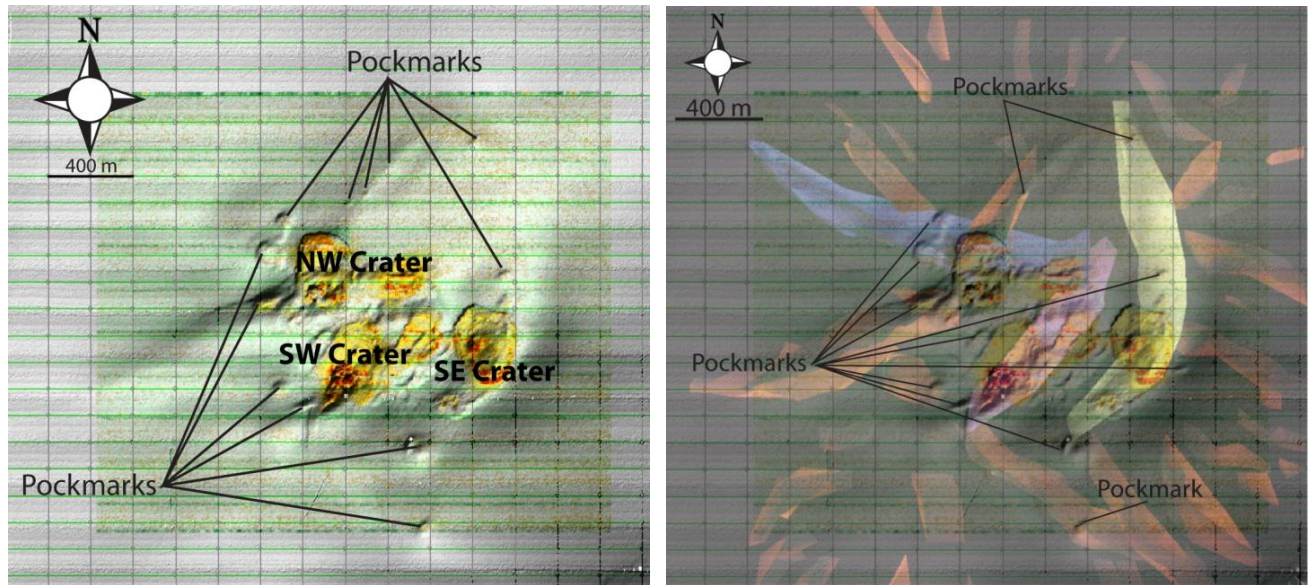


Figure 3. Woolsey Mound at MC118 has 3 distinct crater complexes. The image on the left shows bathymetry at the site. To the right, “master faults” – blue, violet, yellow – and shallower radiating faults – orange – are plotted with this same bathymetry to illustrate surface expression of the fault system.

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 (Figure 4). 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. The array deployments await appropriate sea/weather and equipment conditions.

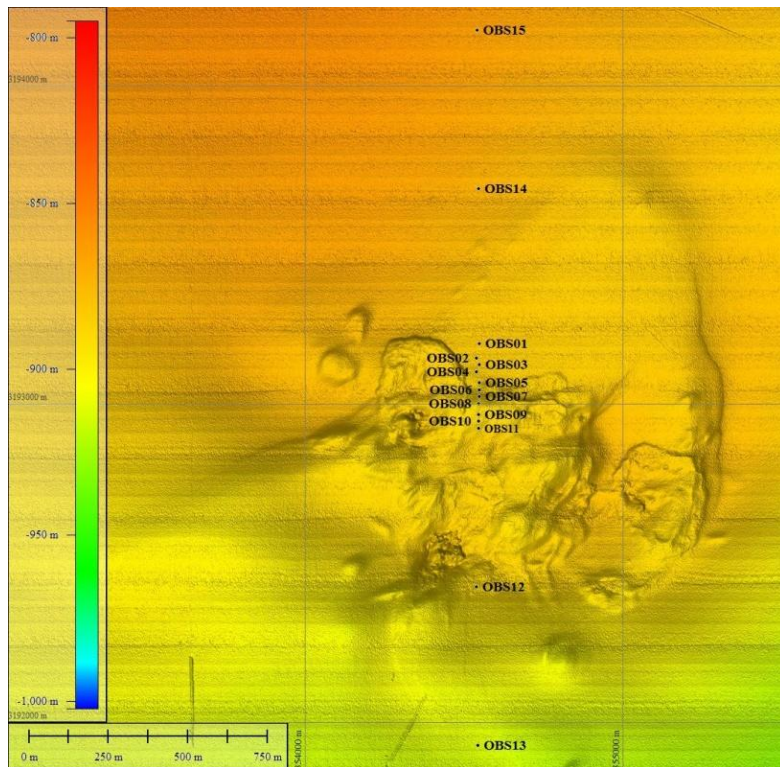
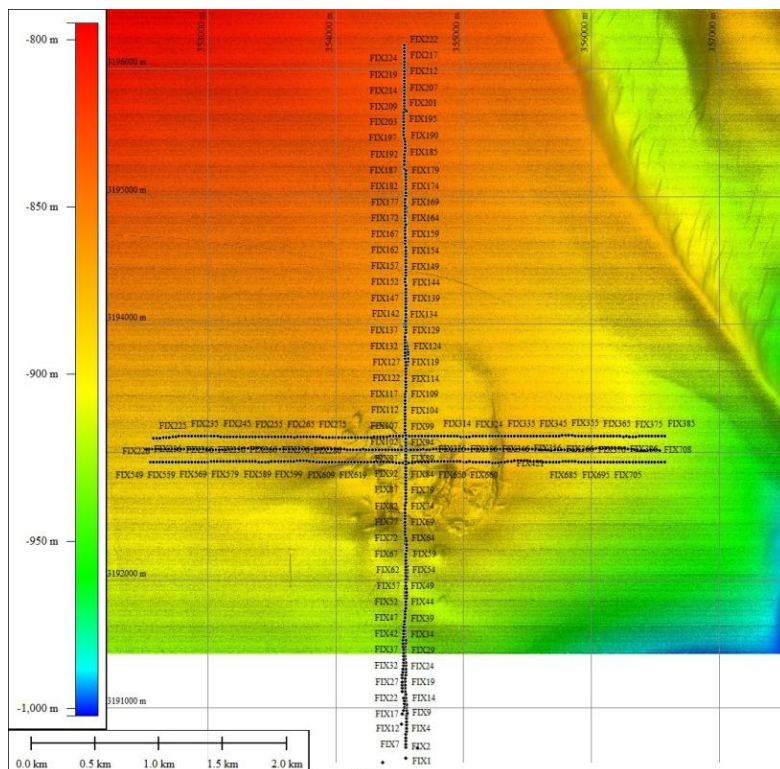


Figure 4. Ocean Bottom Seismometer (OBS) Survey. 15 OBSs were deployed in a North-South line across Woolsey Mound at MC118 (top). An active survey was conducted using a 105 cubic inch GI gun source and repeated using an 80 cubic inch water gun source, following the pattern portrayed in the lower image. In addition, the OBS instrument packages were deployed and were collecting ambient noise data during a severe storm event as well as during traverses of the ship over the Woolsey Mound.



Additional geophysical studies are either complete, underway or in the planning stages. With access to the NIUST AUV (Autonomous Underwater Vehicle), *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. Two hydrophone systems have been considered and the favored one, a fiber-optic array, is still in development but is due to be available to AUV engineers later in 2011. A Polarity Preserving/Discriminating Chirp sub-bottom profiler system is being developed 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. This system is expected to distinguish gas from hydrate. It has been purchased and was received (December, 2010), but many adjustments have had to be made in order for NIUST engineers to receive signal. It has been installed on the AUV and is scheduled for testing in 2011.

An additional industry data set acquired by Western Geophysical Company will provide deep subsurface information 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.

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 together with 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 (Figures 5 and 6). 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 7). 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.



Figure 5. A disk of solid hydrate was recovered in the core barrel ~1m from the bottom of the core, JPC-001.



Figure 6. 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.

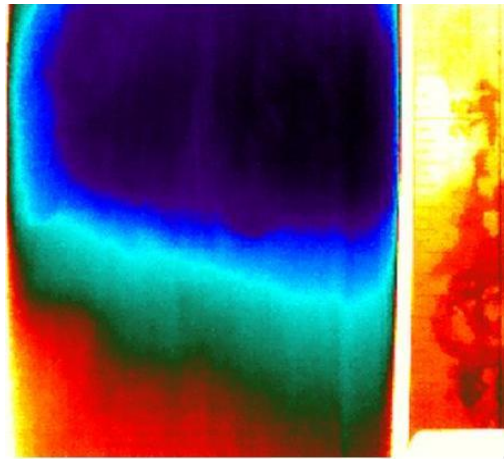
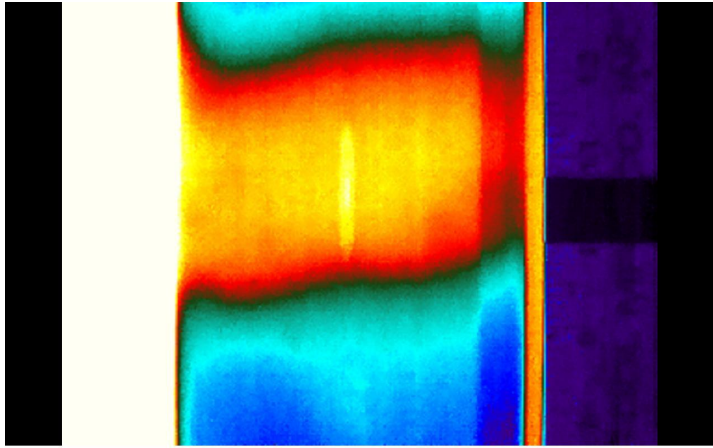


Figure 7. Images from the IR camera highlight areas of anomalous temperature. In the top example, a void space in the unopened core shows as warmer (warmer color). In the bottom example, a hydrated section shows as cooler (cooler color).

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.

Geochemical Sensor Systems

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. Most recently (see Phase 2, Task 6, below) experimental analyses of MC118 microbial consortia 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.

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 (ROV Assisted Recovery Device), at MC118 in September, 2010, and was recovered in June, 2011. Initial inspection of the data reveals good data truncated after 3 weeks due to battery failure. These data will be evaluated in detail on the near-future but seem to include very high resolution geochemical data. In addition, a similar, mobile system is being designed to run from an AUV, likely the NIUST *Eagle Ray*.

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 are underway with Contros concerning repair/replacement of the sensor as they would like to be able to market it to markets working at greater depths. The Woods Hole Oceanographic Institution's (WHOI) optic modem was used successfully to transfer data remotely from the BBLA to the ship.

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 (ROV Assisted Recovery Device, Figure 8) 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.

The high throughput filter water-column microbial filter – mass spectrometer water chemistry evaluation system have been successfully interfaced. On successful dives, water chemistry dictated the recovery of filtered sample (DOE). The potential for this system as a test-bed is being explored and tested. It has been used to recover samples from disturbed as well as undisturbed areas with positive results and is being adapted to collect additional chemistry as well as water samples, fitted with a camera and with water-sampling capability. It is due to be deployed in refitted mode in October, 2011.



Figure 8. 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 has long been discussed. In spring, 2005, the NIUST Director made competitive funding available for researchers

in microbiology to become involved in the mission of the MS/SFO. 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 9. 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 10 and 11). Additional cruises and projects, mostly carried out through affiliates of the CMRET, are scheduled in the remainder of 2011 and into 2012.



Figure 10. Bacterial mats and clams form part of a chemosynthetic community on the seafloor at MC118.

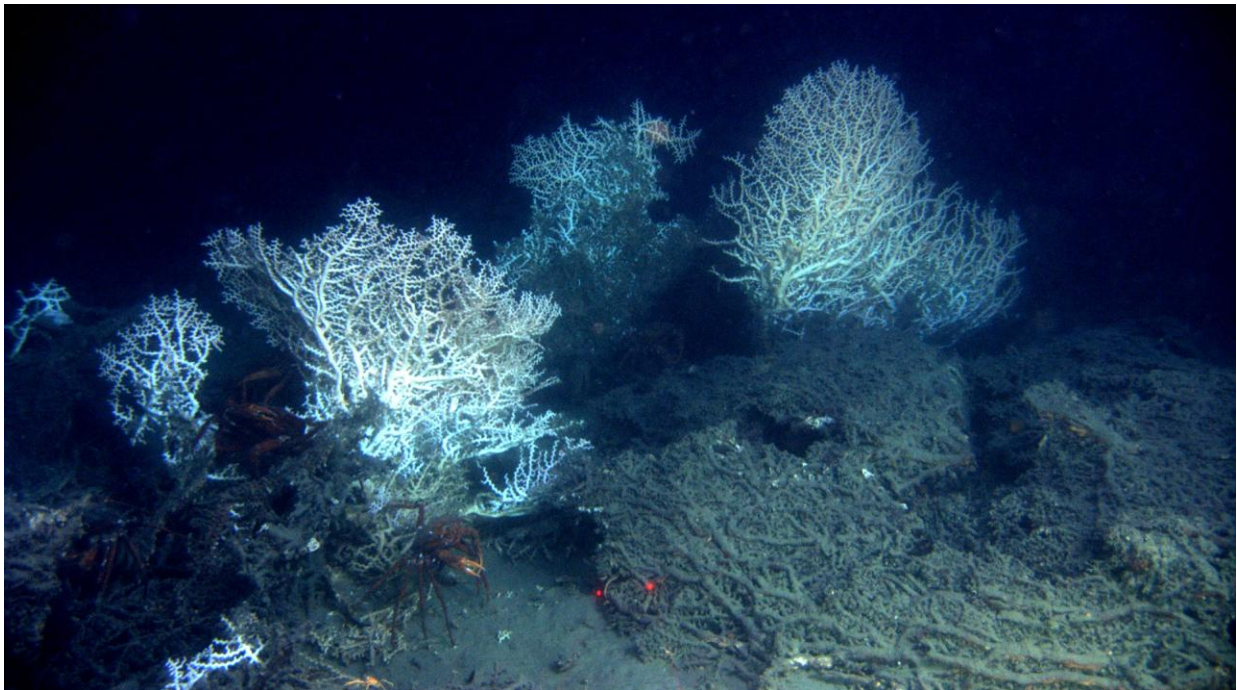


Figure 11. Deep Sea Corals at MC118. Reefs provide habitat, recruitment and nursery functions for a range of deep-water organisms including commercial fish species. Deep corals may provide windows into past environmental/ecological conditions (photo credit: Chuck Fisher, Chief Scientist Lophelia II cruise 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, 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; 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. Plans to collect test HLA data include “real” testing of this system in late 2011.

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, MMS; The SSD is a specially designed ROV-like system for use on level-two-equipped, dynamically positioned vessels (available at a much lower day rate than a level one) for the purpose of deploying station sensors and support equipment, i.e. hooking up wet-mateable connectors, etc. 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: a) multipurpose suspension cable acquired, terminated and tested, successfully, using a drift camera to survey the carbonate mound at 900m depth at MC118, within the MMS restricted zone (for hydrate research); b) deployment and recovery of microbial experiments and targeted – by virtue of its navigation capabilities and 3 cameras – push-cores (Figure 9). During the June, 2009 cruise, over 30 hours of resistivity data were acquired using the SSD as the transport for the 1100m towed cable. 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. The SSD will be the work horse in cable laying for the HLAs and their (and other instruments') subsequent underwater connection (to IDP).

F. Autonomous Underwater Vehicle (AUV), NOAA/NIUST: The AUV "*Eagle Ray*", acquired from ISE 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 payload 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 sea floor operation, data acquisition to sub bottom depths of 500 to 700m, navigation accuracy, noise reduction and reduction of survey time by a factor of four. A polarity-preserving chirp system,

designed to distinguish between gas and hydrate, has been designed, built and received. It is being installed on the *Eagle Ray* in anticipation of a test deployment in July, 2011.

G. Mola Mola AUV, NOAA/NIUST: This vehicle 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 2011 cruise season.

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 and an October, 2011 effort is scheduled.

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.

Abstract

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

Introduction

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

Summary of Activities

In April, 2011, the MMRI arranged and effected the collection of ambient noise data from the MC118 Observatory site, via the OBS instruments deployed and recovered from the *Bunny Bordelon* by the WHOI and MMRI teams. Dr. Gerstoft and prospective Post-Doctorial student Olivier Carriere participated in the cruise. The data will be evaluated for potential utility to the Consortium effort. A full-time post-doc, Olivier will pursue this effort and will begin work at UCSD in August, 2011.

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 and MMRI will send 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.

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 will be exhausted when the PI travels 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 SDR 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 desired 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 free 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 cruises 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 January through July 2011, we participated in the Jumbo Piston Core (JPC) cruise and after cruise activities, conducted a time-lapse analysis and comparison of two industry quality 3D seismic data volumes, and have calibrated our rock physics with the data from the Mallik wells in Northwest Territories, Canada. This report summarizes our technical contributions as follows:

- Jumbo Piston Core Cruise and After Cruise Analysis

- Time-Lapse Seismic Analysis
- Rock Physics Model Calibration

USC prepared three poster presentations for the 7th International Conference on Gas Hydrates, held in Edinburgh, Scotland, July 2011.

During the second half of 2010 we refined the rock physics models that were developed prior. Based on frictional interaction between sediment grains, the updates provide an additional degree of freedom to calibrate the model against measured field data. A presentation and poster of the rock physics model development were made, respectively to the Annual Meeting of the GoM-HRC in October 2010 and to the Annual Fall Meeting of the American Geophysical Union in December 2010.

Jumbo Piston Coring Cruise

In order to test the plausibility of our model based on gas hydrates accumulation in the vicinity of certain faults mapped on the TGS-Nopec and Western Geco seismic volumes, in January 2011, a dedicated cruise of Jumbo Piston Coring (JPC - maximum penetration 20m) was carried out. The JPC cruise was on board of the *R/V Brooks McCall* and Antonello Simonetti represented USC. This cruise had the following relevant objectives:

- sample upper 20 m of the stratigraphic section;
- calibrate seismic datasets for lithology;
- characterize sediments in the vicinity of faults that seismic interpretation suggests are active and compare those with sediments removed from fault;
- ground-truth high frequency seismic back-scatter on the SSSR data;
- provide age control for recent movement on deep-seated master faults (Blue, Pink, Yellow);
- calibrate the high resistivity anomaly "A" identified by Dunbar et al. 2010.

Post-Cruise Activities

- Assist with core description (J. Salazar)
- Integration with high-resolution seismic datasets (J. Salazar)
- Evaluate rock properties from acoustic logs (D. Terry)
- Integrate age constraints with 3-D seismic interpretation (A. Simonetti)

JPC targets selection

USC proposed 4 out of these 5 sites (Figure 12) based on analysis of the 3D seismic data. The JPC samples are still being analyzed. However, preliminary onboard studies have confirmed some of the suggested hypotheses. In particular, the attempt to ground truth the presence of solid gas hydrates in the vicinity of the active faults system, in the vicinity of the greatest resistivity anomaly previously found (Dunbar et al., 2010) and where the high frequency seismic back-scatter had been individuated on SSSR data, was successful. Figure 2 shows JPC1 and JPC3 cores locations on a SSSR profile, N-S oriented. JPC1 was intended to sample a portion of the subsurface where the SSSR data highlighted recent growth section along the blue fault (note the difference in thickness of the yellow section between JPC1 and JPC3) and the high

frequency scatter, while JPC3 was located over a "normal" spot where, based on our predictions, gas hydrates should not have been present. Also, JPC1 was taken above one of the previously discussed shallow seismic anomalies interpreted as free gas at the base of the GHSZ.

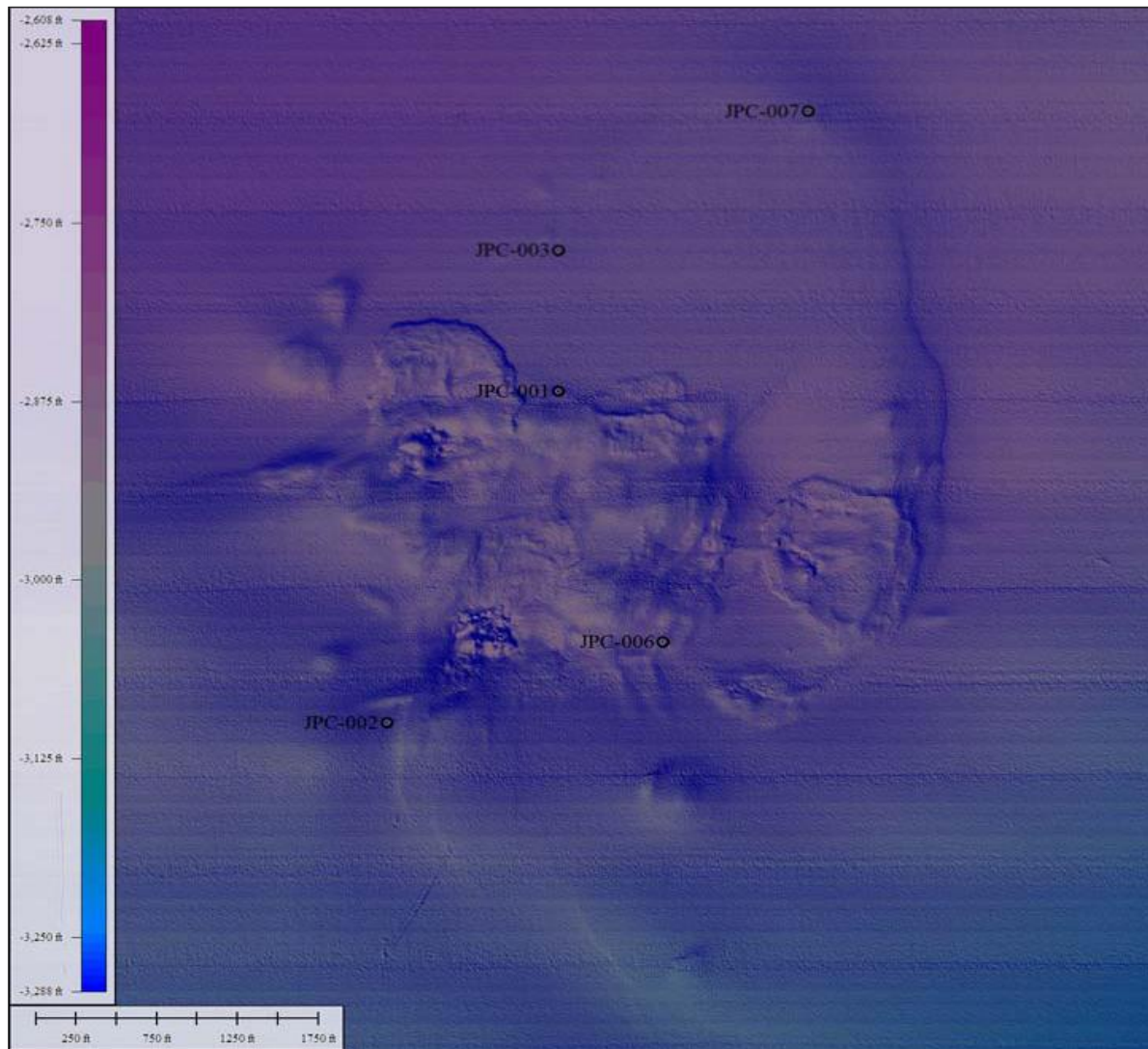


Figure 12. Site locations of the five Jumbo Piston Cores collected at *Woolsey Mound* in January 2011.

Cores were intended to calibrate a recent growth sequence (Figure 13, highlighted in yellow) along one of the main faults which was thought to be acting as a preferential pathway for thermogenic hydrocarbons. While JPC1 was collected in the very vicinity of the "blue" master fault, where also the "high frequency seismic back scatter" occurs, JPC3 was taken 200m away from the fault and where no seismic anomalies were seen. Thus, we were able to compare JPC3's composition with JPC1 and test our model based on faults/fractures and gas hydrates occurrence.

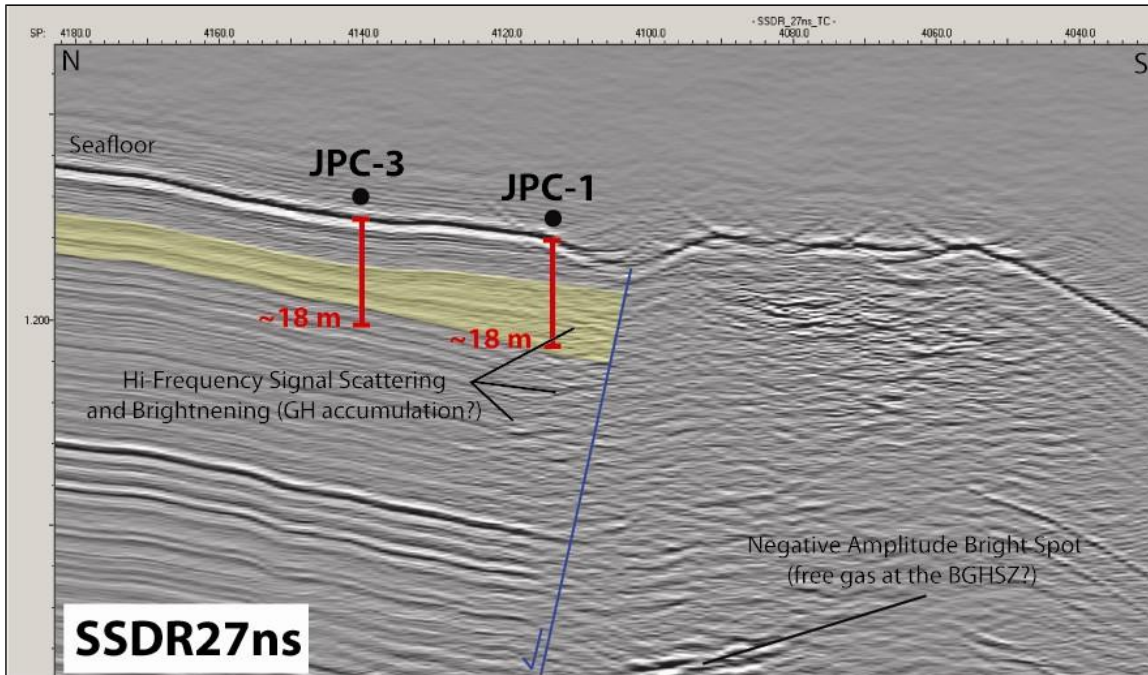


Figure 13. SSDR seismic profile showing the locations of JPC1 and JPC3 cores.

Figure 14 shows pictures of JPC1 being recovered aboard the research vessel. The core recovered hemipelagic mud with large hydrate inclusions (JPC1 was the only core which recovered gas hydrates), mostly occurring in fractures. Geochemical characterization, such as hydrocarbon composition determination and $\delta^{13}\text{C}$ isotope analysis, were carried out on hydrate samples and they revealed a thermogenic source for the hydrocarbons involved (R. Wilson, *Florida State University*, personal communication).

Oppositely, in JPC3 which was taken about 200m away from one of the Master Faults, gas hydrates were not found and only hemipelagic mud was recovered, as expected from our predictions.

The Jumbo Piston Coring Cruise can be considered a very successful achievement. We had the opportunity to test our theoretic model based on gas hydrate accumulation in the vicinity of certain faults, previously identified as migration pathways for thermogenic hydrocarbon gas.



GAS HYDRATE DISK (2cm thick and ~10 cm wide)



GAS HYDRATES (chunks, blades)

Figure 14 (left), JPC1 during on board core-sectioning operations; the picture shows a gas hydrate disk with diameter equal to the PVC liner; (bottom), JPC1 during on board core-opening activities; the picture shows JPC1, dark-grey hemipelagic mud with large hydrate inclusions (white), mostly occurring in fractures (chunks, blades and nodules). Photos courtesy of MMRI, University of Mississippi).

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Dunbar, J., A. Gunnell, P. Higley, M. Lagmanson, **2010**, *Seafloor resistivity investigation of methane hydrate distribution in Mississippi Canyon, Block 118, Gulf of Mexico*, (expanded abstract), Symposium on the Application of Geophysics to Engineering and Environmental Problems, v. 23, p. 835-844.

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 CO₂ sequestration monitoring activities (Chadwick et al., 2005). On the other hand, time-lapse seismic analyses in natural cold seep areas are poorly documented in literature (Riedel, 2007), due to the unpredictable behavior of such complex environments; therefore, a very careful experimental approach is required.

It mainly consists in 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, CO₂, and maybe gas hydrate).

After we had evaluated and proposed the time variant mechanism for the processes observed at Woolsey Mound's GHSZ (Figure15), we decided to move further and to perform 4D seismic analyses at the site by getting another set of multi-channel 3D standard data set from Western Geophysical Company (Western Geco), so that we could compare them with the already available TGS data.

The analysis is being carried out essentially using the 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 Western Geco data were acquired in 2002, namely ~2.5 years later than the TGS data. The reason why we could not perform a true time-lapse seismic monitoring by using TGS data (acquired in 1999-2000) and SDR data (acquired in 2006) stems from the fact that the latter have geometry and acquisition/processing parameters completely different compared to the TGS. Also, we wanted to verify if we could find significant changes in the sub-surface anomalies even in a shorter time frame than 6 years, for instance two-three years.

As mentioned previously, when it comes to perform 4D analyses and compare two seismic data sets, preferably the data sets 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 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 seismic parameters, some processing steps were needed in order to have the two data sets looking as similar as possible. The first step in doing 4D seismic consisted in setting a data set (usually it has to be the oldest) as reference, and the newer or the newest as monitor. In our case, TGS data were chosen as reference and the Western Geco data, as monitor.

The processing sequence applied consisted of:

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

Two processing steps, a *phase matching* and a *shaping filter*, still need to be addressed on Western Geco data in order to be fully compared to the TGS data. However, preliminary results from the time-lapse seismic monitoring are encouraging, showing that some sub-surface anomalies related to the Woolsey Mound's subsurface (i.e. hydrocarbon and gas hydrate anomalies) are different on the two data sets, thus confirming a dynamic GHSZ at Woolsey Mound even within a short time frame.

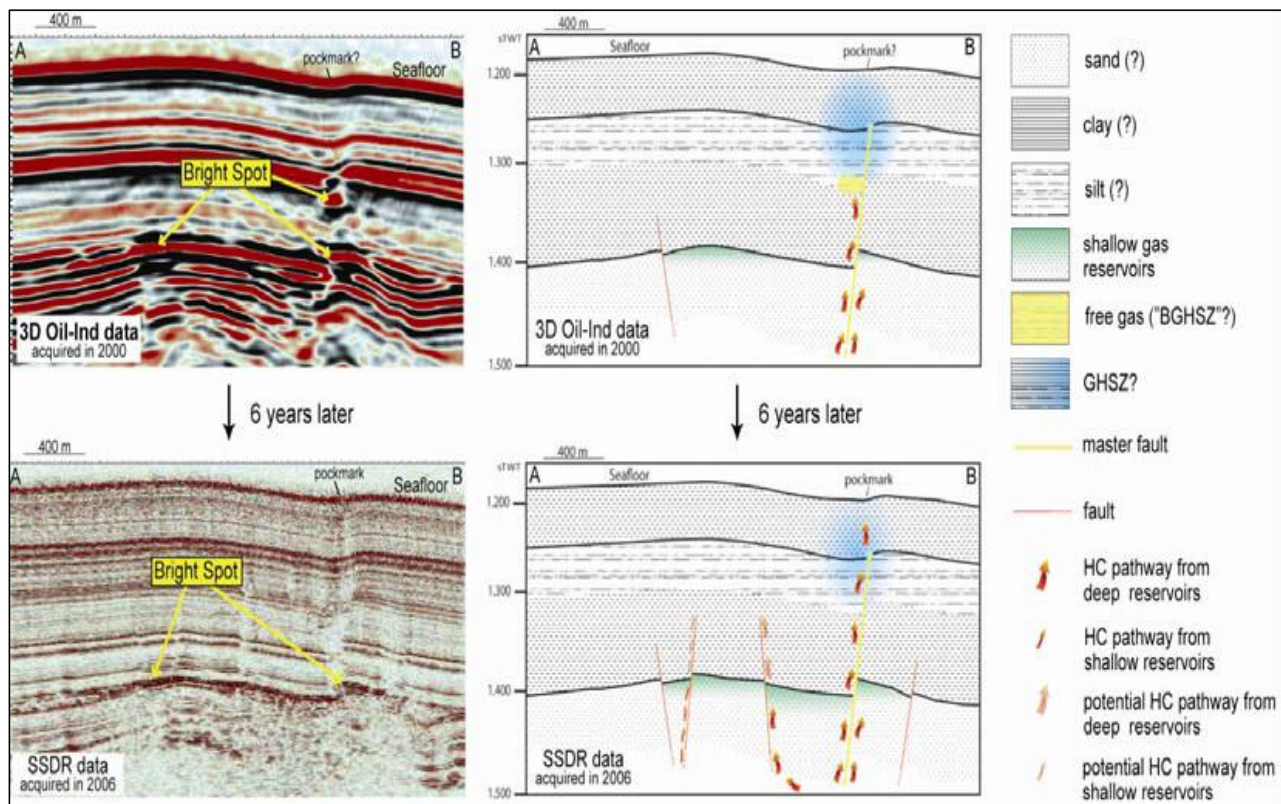


Figure 15. Time variant mechanism proposed for processes observed at the Woolsey Mound's GHSZ. During tectonic activity, upwardly transient hydrocarbon migrating from deep sources may perturb hydrate stability in terms of pressure and temperature, causing dissociation. Such processes provide a supply of hydrocarbons into the GHSZ. These partially escape through the seafloor and in part lead to a subsequent hydrates formation during tectonic quiescence. The new gas hydrate formation provides the sealing mechanism for free gas coming from below the GHSZ, until a new fault-related venting (hydrate dissociation) episode occurs. This hypothesis is corroborated by some of the pockmark-related gas anomalies, that are present on the 3D data (collected in 2000) but seem to be no longer present on the SDR data, collected in 2006.

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Rock Physics Model Calibration

During the current reporting period we continued with development of the effective-medium rock physics models for unconsolidated sediments. Concentration of effort was in three areas: 1) updating the Hertz-Mindlin effective-medium model to incorporate smooth sphere grains, and 2) calibrate our model for rough sphere grains against previously published models, and 3) calibrate our model against field data.

I. Extended Effective-Medium Model

Two versions of a Hertz-Mindlin effective-medium model have seen frequent use in modeling studies of unconsolidated sediments (Helgerud et al, 1999) and interpretation studies for the presence of gas hydrates (Sava and Hardage, 2006). The effective-medium model of Walton (1987) considers the surface characteristics of the spherical grains and therefore develops two separate models. One is for infinitely rough spheres in which slip between the grains is prevented; the other is for perfectly smooth grains with slip. A few years later, and independently with slightly different assumptions, Dvorkin and Nur (1996) developed a model for infinitely rough spheres that is equivalent to the rough sphere model of Walton (1987). In a so-called extended Walton model, Jenkins et al. (2005) introduced the friction parameter alpha, α , to incorporate the rough and smooth sphere models of Walton (1987) into a single model. In this extended model, $\alpha=0$ and $\alpha=1$, respectively, are the end states of perfectly smooth sphere grains (frictionless interaction) and infinitely rough sphere grains (fully frictional, or no-slip).

In the current work we adopt the extended Walton model to use as our effective-medium model, but use the nomenclature from Dvorkin and Nur (1996). Similar to Dvorkin and Nur (1996), we use an expression for bulk modulus in place of the Lamé coefficient. Therefore, our Hertz-Mindlin effective-medium model is written:

$$K_{HM} = \left[\frac{k^2(1 - \phi_c)^2 G^2}{18\pi^2(1 - \nu)^2} P \right]^{1/3}$$
$$G_{HM} = \frac{1}{5} \left[\frac{3k^2(1 - \phi_c)^2 G^2}{2\pi^2(1 - \nu)^2} P \right]^{1/3} \frac{[2 - \nu + 3\alpha(1 - \nu)]}{(2 - \nu)}$$

where K_{HM} and G_{HM} are the Hertz-Mindlin effective bulk and shear moduli, respectively; ϕ_c is the critical porosity; k is the consolidation number; P is the confining pressure; G is the grain material shear modulus, and ν is Poisson's ratio.

II. Calibration With Mallik Well Data

In Xu et al. (2004) and Dai et al. (2004) comparisons were made among several competing approaches to predict seismic velocities from gas hydrate saturation values with comparison against derivative well-log data. Results of the comparison clearly favor the Helgerud et al. (1999) model. Helgerud et al. (1999) is based on rough sphere grains, uses the framework of Dvorkin et al. (1999) for unconsolidated sediments, and assumes a rock-matrix grain-pore morphology. Though performing

better than the other models, this model over predicts the compressional velocity and significantly over predicts the shear velocity (Xu et al. 2004; Dai et al. 2004). Sava and Hardage (2006) suggest the smooth grain model as a solution to this over prediction.

To implement our extended effective-medium model we adopt the framework for unconsolidated sediments as in Dvorkin et al (1999) and Helgerud et al (1999). In generating our results below, we exercised our model to compare with previous results (Xu et al. 2004; Dai et al. 2004; Dai et al. 2008); compare against Mallik well data; and compare rough and smooth sphere grain models against each other.

The data sets for our comparisons and calibration are from the same wells used in Dai et al. (2004) and Dai et al. (2008). We apply the model to the data from the Mallik wells, 2L-38 and 5L-38. Following a similar approach, we plot theoretical curves of the model overlain on the data derived from the well-logs of the Mallik 2L-38 and 5L-38 wells.

| | Bulk Modulus (GPa) | Shear Modulus (GPa) | Density (g/cc) |
|-------------|--------------------|---------------------|----------------|
| Gas hydrate | 5.6 | 2.4 | 0.90 |
| Ice | 8.8 | 3.9 | 0.92 |
| Water | 2.3 | 0.0 | 1.04 |
| Quartz | 36.0 | 45.0 | 2.65 |
| Clay | 21.0 | 7.0 | 2.60 |
| Methane | 0.1 | 0.0 | 0.235 |
| Pore fluid | 2.60 | | |

The model parameter values used in our calculations include $\alpha = 0.6$, $k = 8.5$ for coordination number (average number of contacts per particle), and $\Phi_c = 0.40$ for critical porosity. Depth = 1000.0 m was used. We used a clay/quartz ratio = 40/60.

In the plots below, we have red curves for the rough sphere model; blue curves for the smooth sphere model; yellow curves for alpha = 0.6. Solid curves are for compressional waves with dashed curves for shear waves.

II.A. Mallik 2L-38 Well

The Mallik 2L-38 well-log data were available in analog form and had to be digitized. The well log data, reported in Collett et al. (1999, figure 1, oversized), is available for three resistivity measurements and for the sonic measurements which were used to derive gas hydrate saturation values, and are used to generate scatterplots of compressional and shear velocities against gas hydrate saturation. We generated theoretical curves at several porosities, 0.30, 0.35, 0.40, and 0.45. Physical properties the rock properties are detailed in the Table above. For each value of porosity three cases are calculated; i.e. rough sphere (red curves), smooth sphere (blue curves), and alpha = 0.6 (yellow curves).

Description. Runs of the theoretical model are made at four different values of porosity, and shown in the scatterplots of Figure 17. The scatterplots, velocity vs. gas hydrate saturation, allow comparison of the Mallik 2L-38 well log data with the theoretical model. We consider the best match to be obtained for the porosity value of 0.40. Based on looking at the rough sphere curves our results are comparable to the match shown in Dai et al. (2004). However, we note a few differences in preparation of our data. These include: 1) the log data were digitized 0.1 m interval from Dallimore et al. (1999) since we did not have access to the field data at the time; and 2) we used all the data within the interval from 850m to 1150m instead of just the intervals where gas hydrate was identified. Both may account for the greater density of data and the greater scatter.

Dai et al. (2004) used a load-bearing rock matrix model for his model 3 based on Helgerud et al. (1999) and Dvorkin et al. (2003); therefore their model 3 is essentially identical to our rough sphere model.

Xu et al. (2004) and Dai et al. (2004) note their model 3 closely matches their scatterplot data. Using the same elastic properties we are able to obtain a comparable result. Not particularly surprising given that we use an essentially identical model. Xu et al. (2004) and others have noted the tendency of the model to overestimate S-wave velocities at high gas hydrate saturations. Some (Savage and Hardage) have suggested the smooth sphere model of Walton (1987) as the solution to the overestimation. Results of this algorithm are plotted in Figure 17 as the black curves. Assuming a porosity of 0.40 is correct, the smooth sphere model underestimates to the same degree the rough sphere overestimates the velocities. Jenkins et al. (2005) proposed rewriting the rough sphere and smooth sphere models as a single model; following the approach of Jenkins et al. (2005) led to our model in which we set $\alpha = 0.60$ for the results in Figure 17.

For the porosity of 0.40, when considering the S-wave data, either using α as an extra degree of freedom to obtain a good match, or to use the rough sphere and smooth sphere to bracket the most of the data seem viable approaches. However, this does seem a little less viable for the P-wave data, but probably still acceptable. Two minor deficiencies are noted: 1) the separation between the rough and smooth curves is less for the P-wave model and the scatter in the plot of the P-wave data seems to be greater; 2) slight underestimation of P-wave velocities at very low porosities.

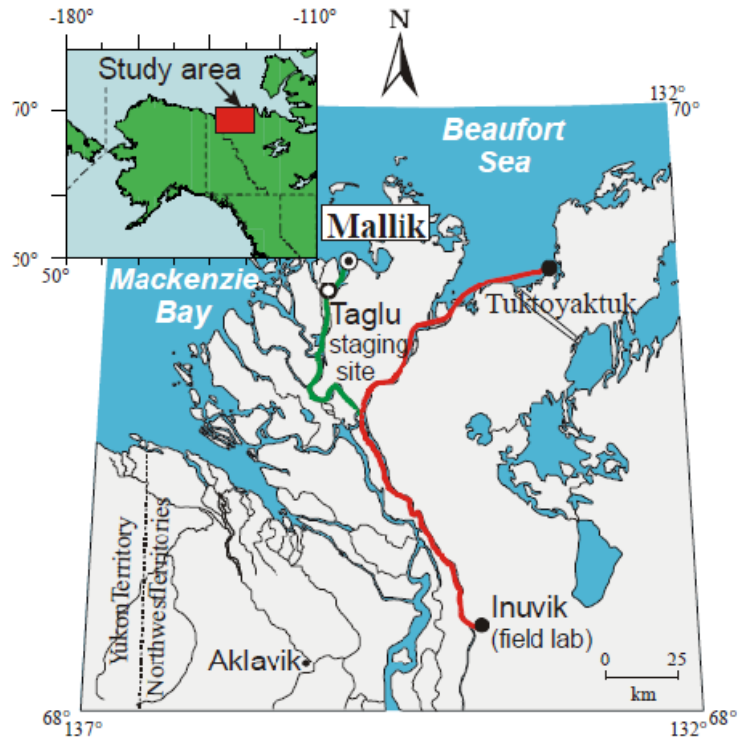


Figure 16. Location map of Mallik wells (ICDP Newsletter - English).

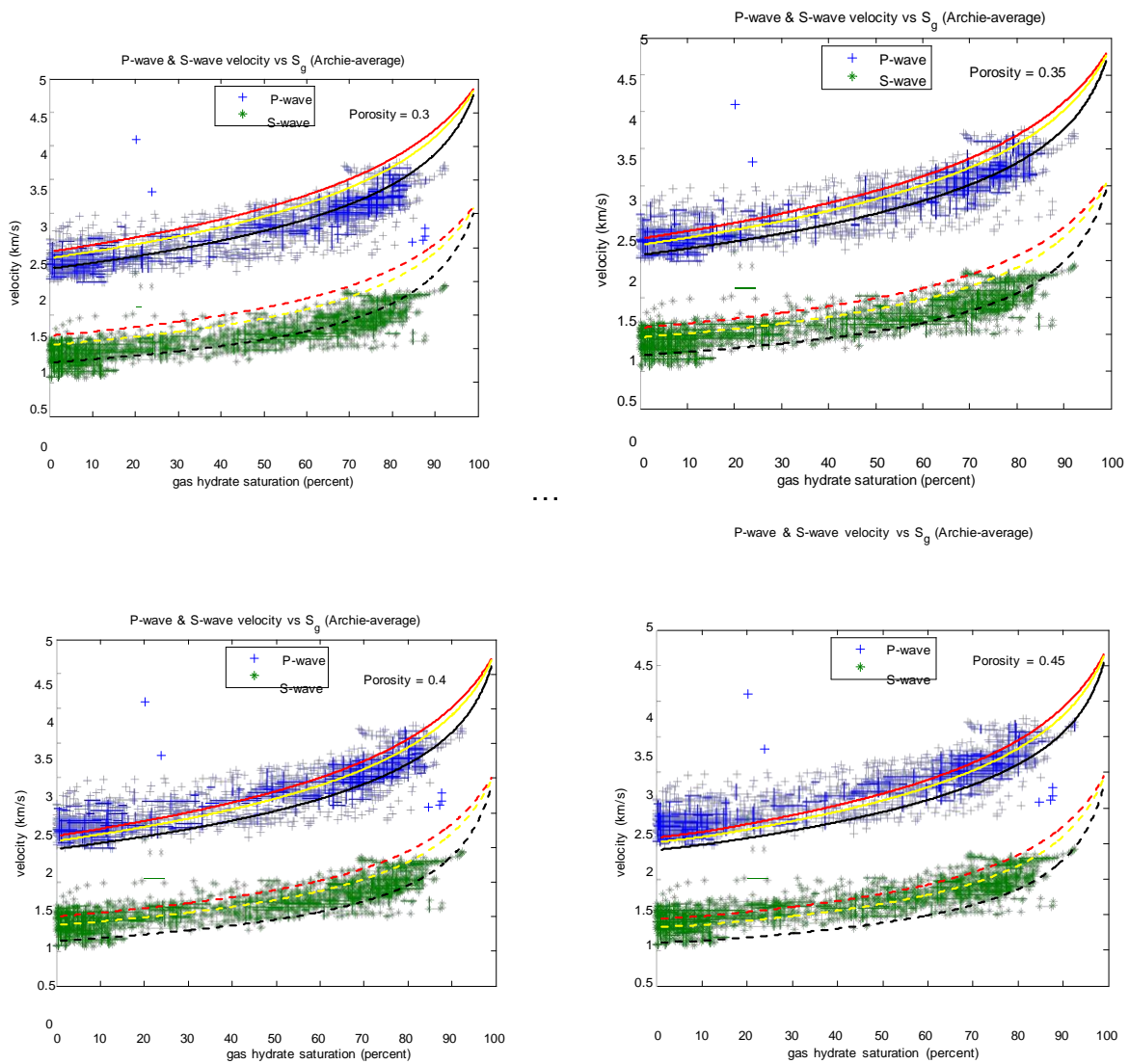


Figure 17. Scatterplots of compressional (V_p) and shear (V_s) velocities vs gas hydrate saturation (S_g) from the Mallik 2L-38 well, along with results from the theoretical model at porosities of 0.30 (top left), 0.35 (top right), 0.40 (bottom left), and 0.45 (bottom right). V_p , V_s , and S_g scatterplot values are digitized from Collett et al., 1999. 1) for Archie-average resistivity. Red curves for rough sphere model, black curves for smooth sphere model, yellow curves for $\alpha = 0.60$. Solid curves are for P-wave model and dashed curves for S-wave model.

II.B. Mallik 5L-38 Well

We located data from the Mallik 5L-38 in digital format on the website for Geological Survey of Canada, Bulletin 585 (See Collett et al, 2005). For Mallik well 5L-38 we downloaded the digital logs from a project website. Datasets were available for a single compressional sonic sensor and each of two shear sonic sensor configurations, referred to as Lower and Upper. As a scatterplot, the two shear sonic datasets are almost indistinguishable from each other, and therefore we only show results for the Upper sensor configuration here. Again, we calculated theoretical curves for several porosities, but only show the result for a porosity of 0.40. Again, we used rock property values from the Table above.

Curves are calculated at four different porosities, 0.30, 0.35, 0.40, and 0.45, for compressional and shear velocities vs gas hydrate saturation. In each case the theoretical curves are overlaid on the Mallik 2L-38 well data, where the gas hydrate saturation is computed using an Archie equation using the average resistivity.

The scatterplot data in Figure 19 encompass the entire interval from 891 to 1107m. We have not selected data just within the identified gas hydrate intervals, yet we note that the vast majority of the data fall within a region bounded by rough and smooth spheres for the grains when the models are run for a porosity of 0.40. The neutron porosity log of Figure 18 (c) shows that as a consistent value of 0.40.

The sections of Figure 18(b) colored in yellow mark the position of the major gas hydrate bearing sediments.

IV. Calibration With Gulf of Mexico Well Data

JIP Leg I. Future work will be to calibrate the models with well-log data from the Gulf of Mexico using data from the Joint Industry Project (JIP) wells. Logging while drilling (LWD) and conventional wireline (CWL) logs were planned for JIP Leg I; the LWD logs were available but did not contain sonic and resistivity data; attempts to obtain conventional wireline logs, which included resistivity and sonic, were aborted with collapse of the wells.

JIP Leg II. Conventional wireline logging was not part of the JIP Leg II logging program, but the LWD suite including advanced sensors for resistivity and sonic data. We anticipate access in the near future.

JIP Leg III. Conventional wireline logs and LWD logs are part of the JIP Leg III planning, along with plans to stabilize the wells for longer time periods; i.e. up to 170 hours.

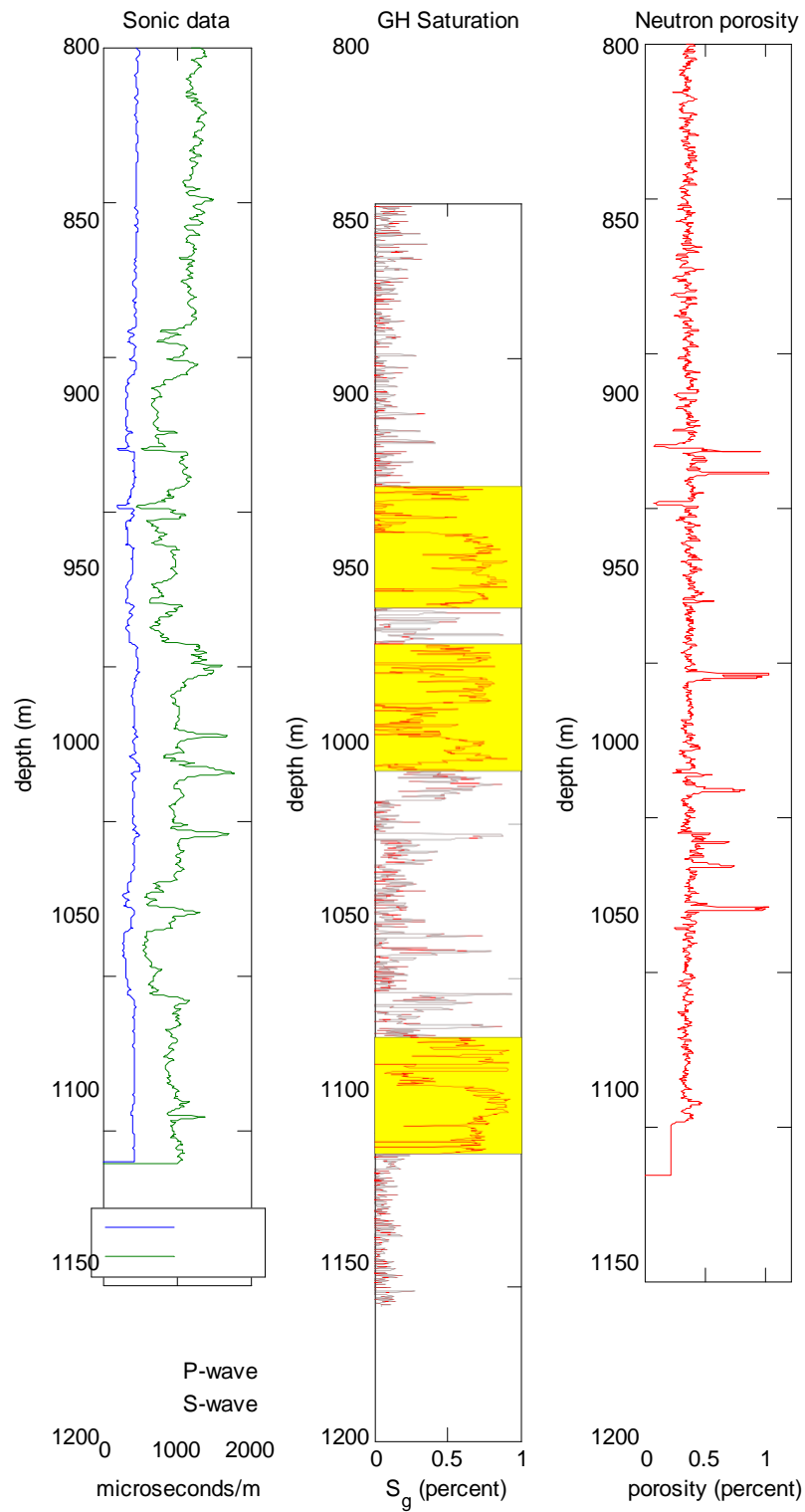


Figure 18. Mallik 5L-38 well logs from Dallimore and Collett (2005, website): a) sonic log, b) gas hydrate saturation, and c) thermal neutron porosity.

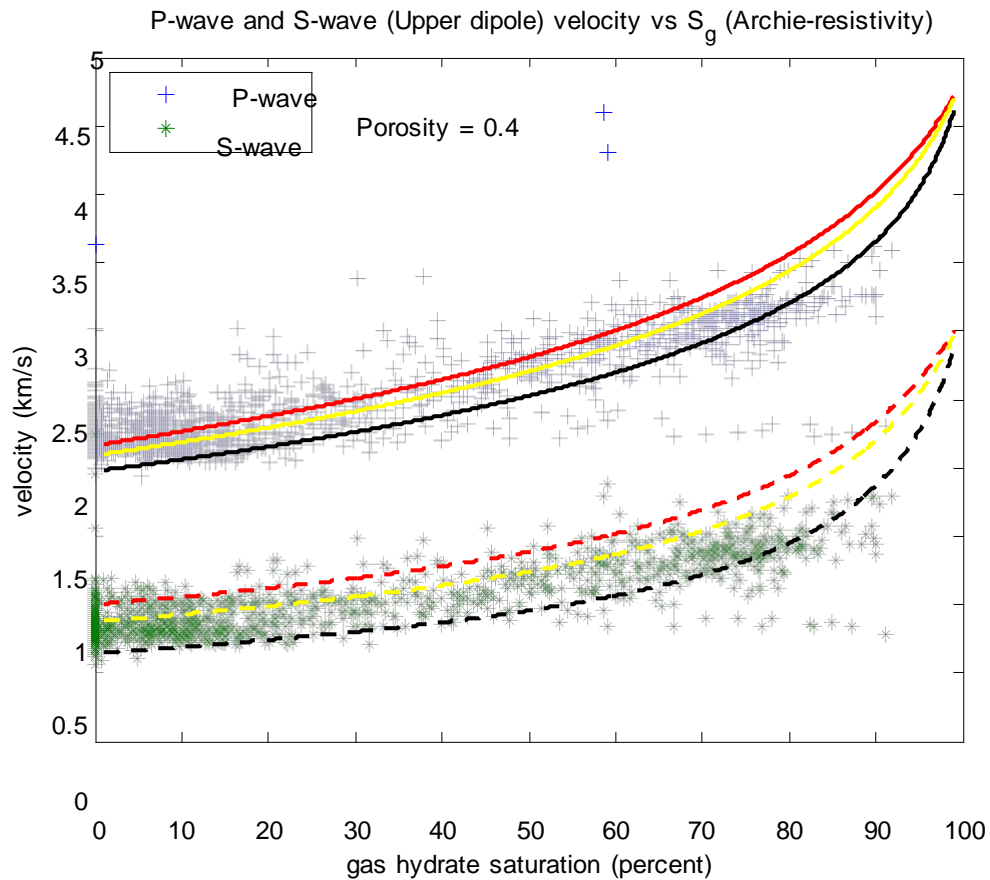


Figure 19. Scatterplot of compressional (V_p) and shear (V_s) velocities vs gas hydrate saturation (S_g) for the Mallik 5L-38 well, along with results of the theoretical model at a porosity of 0.40. V_p , V_s , and S_g scatterplot values are from Dallimore and Collett (2005, website) for Archie-resistivity. Red curves for rough sphere model, black curves for smooth sphere model, yellow curves for $\alpha = 0.60$. Solid curves for P-wave model and dashed curves for S-wave model.

Conclusions

We incorporate the effective-medium models from the work of Walton (1987), Dvorkin and Nur (1996), and Jenkins et al. (2005) into a single model that preserves the nomenclature of Dvorkin and Nur (1996). This “extended” model incorporates the smooth sphere component of Walton’s (1987) model and the capability of Jenkins et al. (2005) extended Walton model to partition between rough and smooth grains.

We incorporate the extended effective-medium model into the framework for unconsolidated sediments (Helgerud, 2001) using the rock matrix configuration for grain placement. Calculations from this theoretical model are overlain on scatterplots of seismic velocities vs gas hydrate saturations from the Mallik wells (Mckenzie River Delta, Northwest Territories, Canada) 2L-38 and 5L-38.

Results appear to be in agreement with previous theoretical results for rough sphere grains; Dai et al. (2004) and Xu et al. (2004) for Mallik 2L-38 and Dai et al. (2008) for Mallik 5L-38. We have rerun the cases with the partitioning parameter α set to 0.60; results in our opinion show an improved fit with the measured data. We note, at least for the shear model, the rough grain and smooth grain results nicely bracket the most of the data.

This is less so for the compressional model because the separation between the rough and smooth grain results is much less than the scatter in the data. Yet, except for very low values gas hydrate saturations, the fit of the compressional model is better for a partition parameter α of 0.60 than it is for the rough grain run.

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Papers, Posters, Presentations

Poster Presentations, 7th International Conference on Gas Hydrates 2011, Edinburgh International Conference Centre, Edinburgh, Scotland, United Kingdom 17-21 July 2011.

- Simonetti, A.; Macelloni, L.; Knapp, J.; Knapp, C.; Lutken, C.; 2011. Defining the hydrocarbon leakage zone and the possible accumulation model for marine gas hydrates in a salt tectonic driven cold seep: Examples from Woolsey Mound, MC118, Northern Gulf of Mexico. Paper P744, in preparation.
- Terry, D. A.; Knapp, C. C.; Knapp, J. H.; 2011. Effective-Medium Models and Rock Physics Analysis for Marine Gas Hydrates (in Northern Gulf of Mexico). Paper P170, in preparation.
- Wood, W. T.; Knapp, C.; Knapp, J.; 2011. Using Refractions Observed in Long-Offset, Multichannel Seismic Data to Achieve Diagnostic P-Wave Velocities in the Gas Hydrate Stability Zone. Paper P754, in preparation.

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. No progress has been made on this project as we

have not yet been notified that TDI Brooks can work us into their heat-flow schedule, work for which one of their vessels must be specifically equipped and mobilized.

Subtask 2.2. Recipient shall contract to have giant piston cores collected from areas of interest at the Observatory site. TDI Brooks, International contacted MMRI in early November regarding a spot in their Jumbo Piston Coring schedule near MC118. The proposed late November cruise was ultimately cancelled due to weather but a rescheduled effort put on the books for January. Five Consortium members – 2 geologists, 2 graduate students in geochemistry and a geophysics graduate student - participated in this cruise aboard the R/V *Brooks McCall*. Five Jumbo Piston Cores (JPCs) were collected from MC118. Sites cored were based on input from Consortium members. Suggestions and comments were solicited and many were received. The selected sites were designed to constrain lithologic, paleontologic and stratigraphic parameters at the observatory site, and to ground-truth shallow seismic data (chirp, SSSR, resistivity, multibeam, backscatter) already collected from MC118. Geochemists wanted core material from sites believed to be experiencing fault/fracture-related activity in the recent past. Further discussion of core-site selection is included in Phase 3, Task 2 and in Task 2.4, below.

In general, sites were targeted because they showed one or more of the following prospects:

1. tie-in to geophysical datasets,
2. revealing the geologic section to greater depths than previous coring efforts (10m maximum)
3. providing information regarding geophysical/seismic anomalies (high frequency scatter, blanking, hot spots, pockmarks),
4. providing information regarding faulting noted in seismic data,
5. confirming presence of resistivity anomalies found in a survey conducted in 2009.

Five cores were recovered from the area of the mound and its periphery. Cores were sectioned, tops photographed and sampled for geochemical parameters, closed, and scanned for temperature anomalies using infrared imagery. A subset of these sections was tested for shear strength using minivane techniques. Top sections were windowed and sampled for sulfate and methane. In one case, a core section was opened and examined for hydrate occurrence based on readings from the new infrared (IR) camera. This section was found to contain hydrate as massive chunks, blades, nodules and disseminated grains/granules. Some of the hydrate was collected for chemical analyses. The cores were transported to the Navy Research Laboratory at Stennis Research Facility where analyzed with a GeoTek logger for resistivity, compressional strength, density and magnetic susceptibility. They will be opened, examined visually, photographed, logged, subsampled for additional geochemical analyses and bio- and lithostratigraphy.

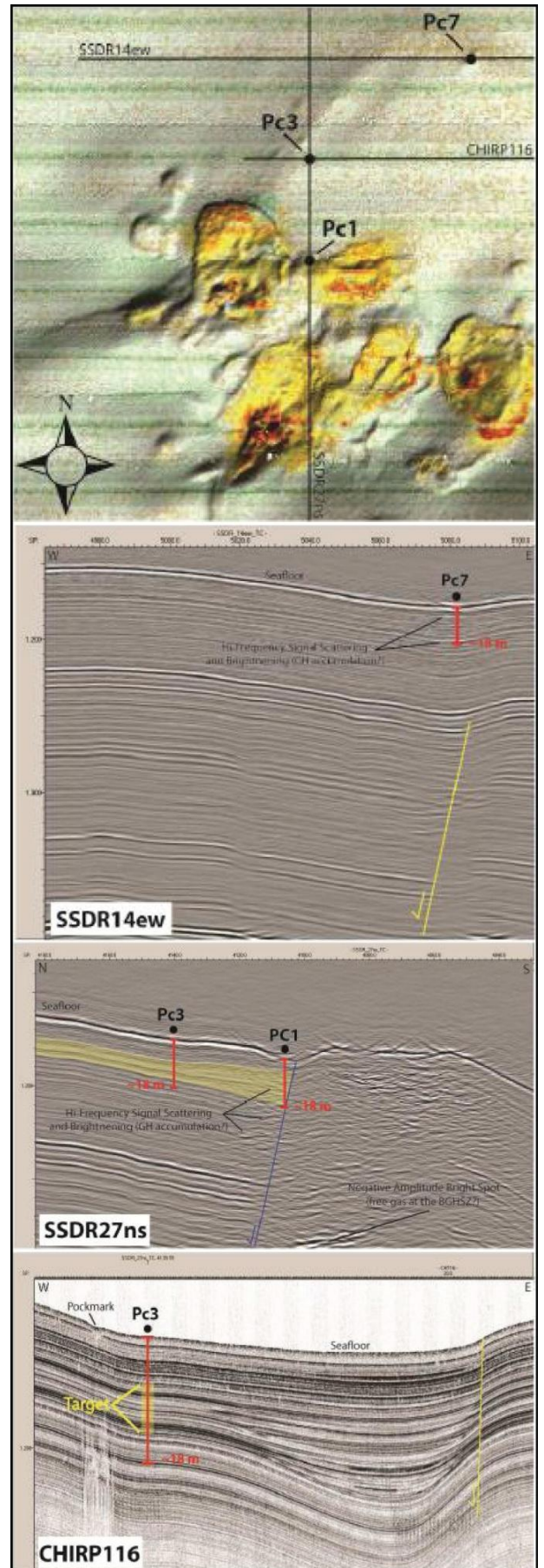
Geochemists are analyzing chemical samples collected onboard; results will be used to determine sites from which to collect heat-flow data as well as future coring efforts to extend the range of geologic and geophysical characterization of Woolsey Mound.

Figure 20, at the right illustrates the integrated approach used to select core sites. This series shows the identification of surface features on sonar backscatter and seismic data profiles. Figure 21, a multibeam seafloor bathymetry map shows the five locations that were cored, with the rationale behind each location choice.

Figures 22 and 23 illustrate the JPC apparatus. Figures 24 and 25 show the results of gas expansion following the recovery and sectioning of JPC-006. This late January cruise saw the successful recovery of hydrate in a core location with the greatest known resistivity anomaly as well as high frequency chatter in the SSSR data. Figures 26, 27, 28, 29, 30 and 31 are photographs of JPC-001 and show the recovered hydrates and the disturbed sediments hosting them.

An important set of developments on this cruise derive from the successful initial use of the IR camera (see Figures 32, 33, 34, and 35). Although far from refined, this system correctly identified hydrates (coldest sections on any core) and voids (high-temperature anomalies). The carriage system is being refined and the software adjusted accordingly. This tool holds great potential and will be incorporated into future coring efforts.

Figure 20. Criteria used to select core sites include identifying surface features on seismic data profiles: top to bottom; bathymetry and transect locations; SSSR west-east transect; SSSR north-south transect; close-up CHIRP west-east transect. Note that target Pc1 occurs atop a fault on a bathymetric low with signal scattering in the subsurface; that Pc3 exhibits none of these characteristics; that Pc7 is located in a pockmark, or gas expulsion feature. Also, notice the expanded section intercepted by proposed cores Pc1 and Pc3.



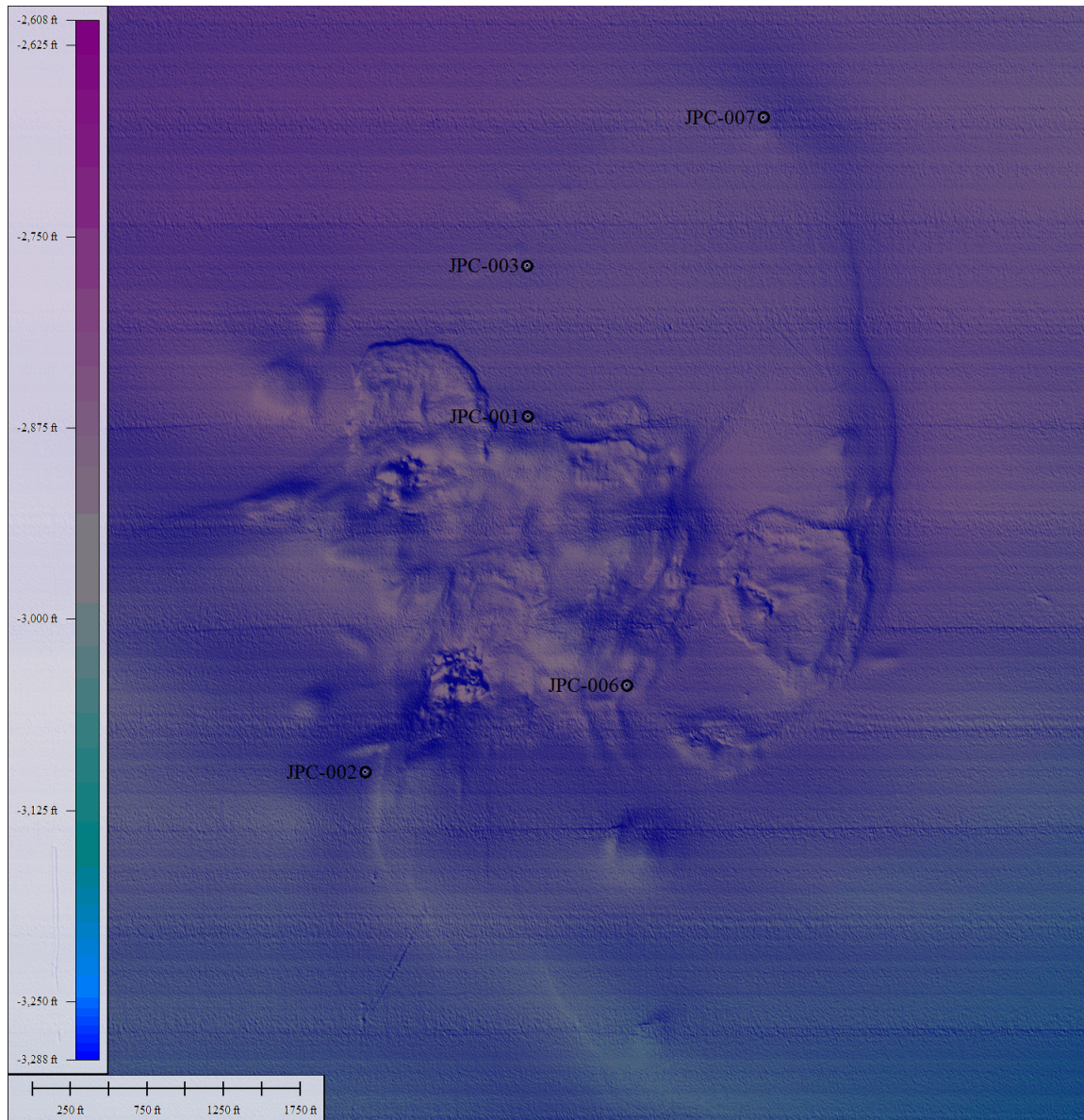


Figure 21. Locations of the 5 Jumbo Piston Cores recovered from Woolsey Mound, January, 2011.

JPC-001 Justification: growth section along the “Blue Fault”, ground-truth on SSSR data; about 100 m west from high resistivity anomaly A.

JPC-002 Justification: south-west of the SW Crater Complex, in a compressed stratigraphic section, close to the “Pink Fault”.

JPC-003 Justification: calibration JPC-001, penetrate complete marker unit (age constraint for blue fault movement).

JPC-006 Justification: between SW and SE Crater Complexes, close to the Pink Fault, acoustic blanking on CHIRP data.

JPC-007 Justification: in the northern portion of the parabola, NE of Woolsey Mound, exhibits high-frequency scatter in SSSR data, it is in a pock mark and the surface expression of the “Yellow Fault”.



Figure 22. Recovery of the Jumbo Piston Corer to the deck.

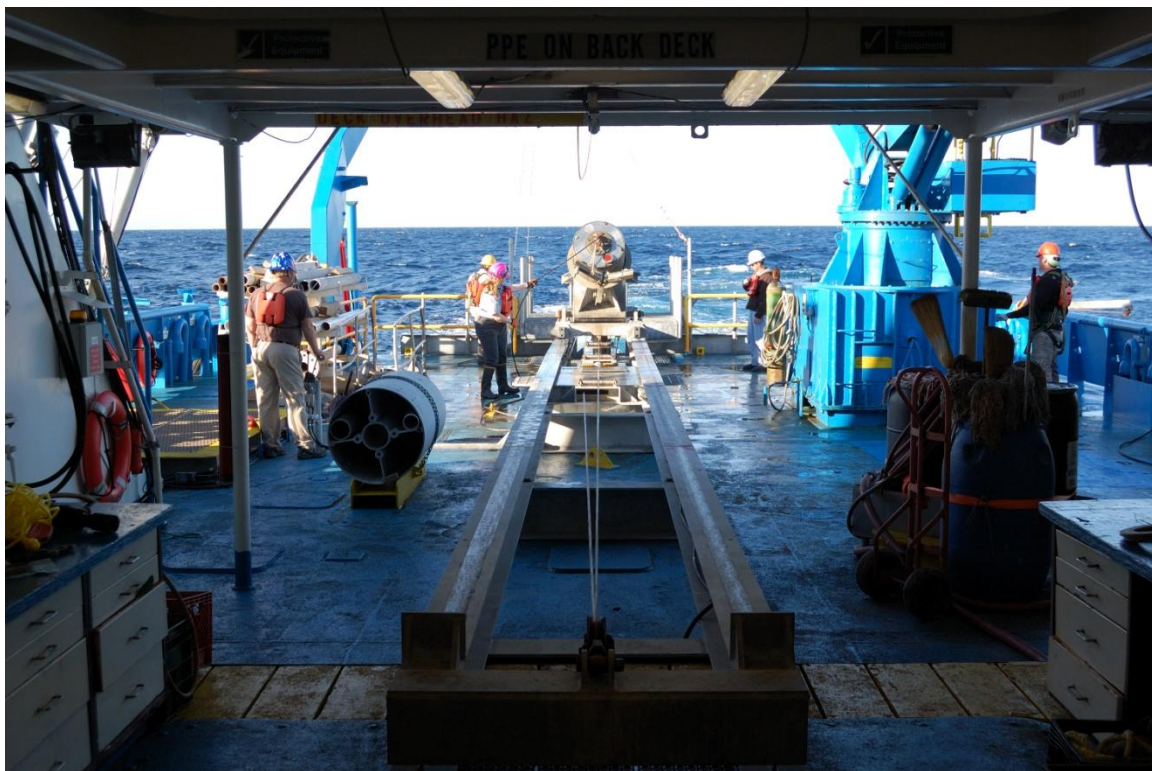


Figure 23. Launch and recovery tracks for JPC. Maximum possible recovery is 64 feet though normally about 50 ft recovery can be expected.



Figure 24. Sampled top of a section of JPC-006 shows high organic content and gas expansion.



Figure 25. Top pf JPC-006; Note gas expansion, typical of JPC-006.



Figure 26. Chunks of hydrate 6 feet from the base of JPC-001.



Figure 27. A disk of hydrates ~.8 in thick covered the entire cross-sectional area of JPC-001, 5.5 ft from the bottom of the core section.



Figure 28. Highly disturbed base of JPC-001.



Figure 29. Bottom 3 ft section of JPC-001 contained hydrate nodules, blades, grains and granules.

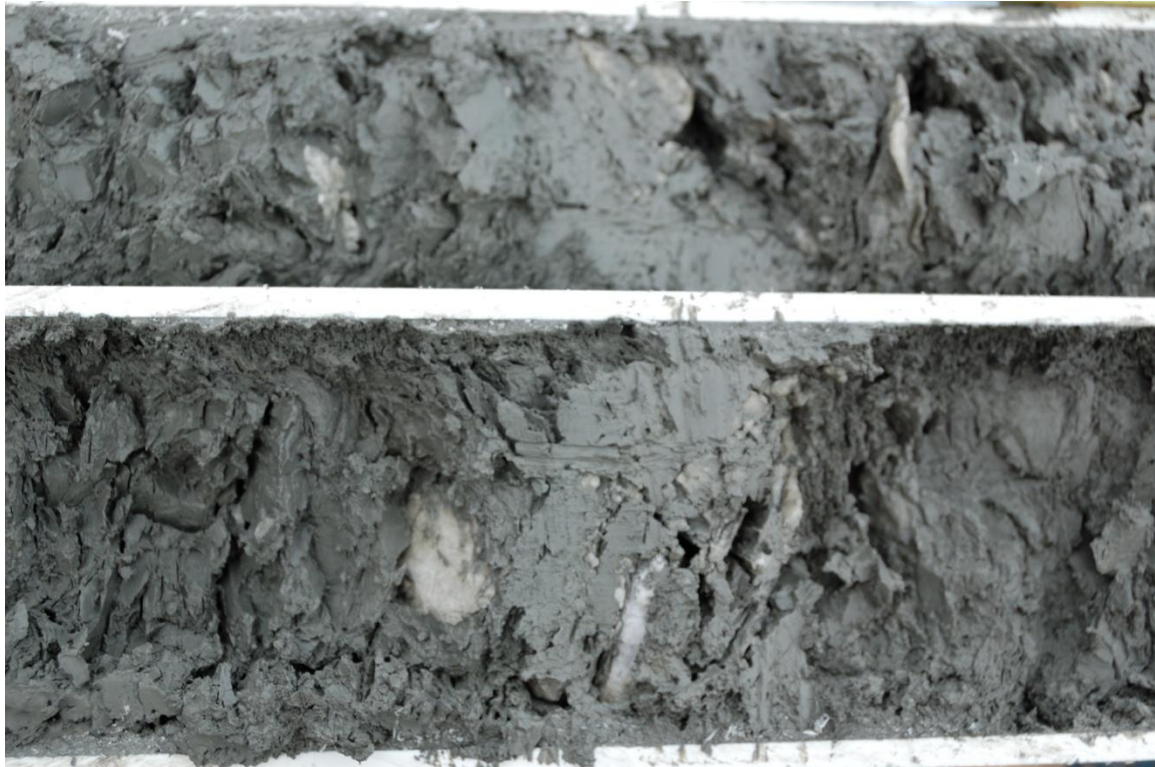


Figure 30. Extremely fine-grained material hosts hydrates at JPC-001 core-site.



Figure 31. After 2 hours on deck, hydrate can still be observed in the bottom sections of JPC-001.

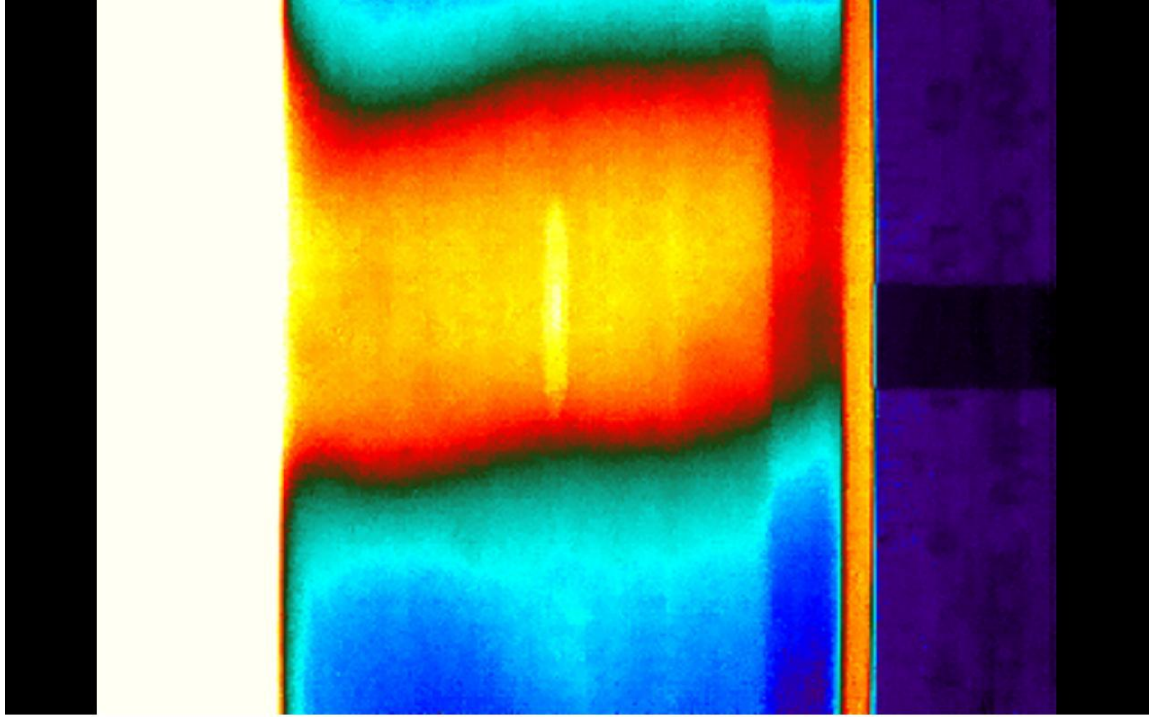


Figure 32. A void appears as a “warm spot” on the IR imagery.

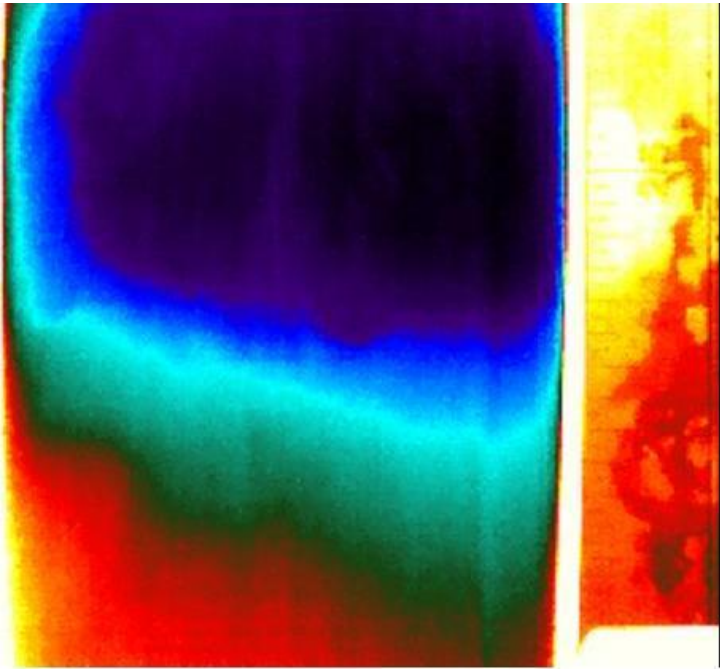


Figure 33. A “cold spot” appears as blue.

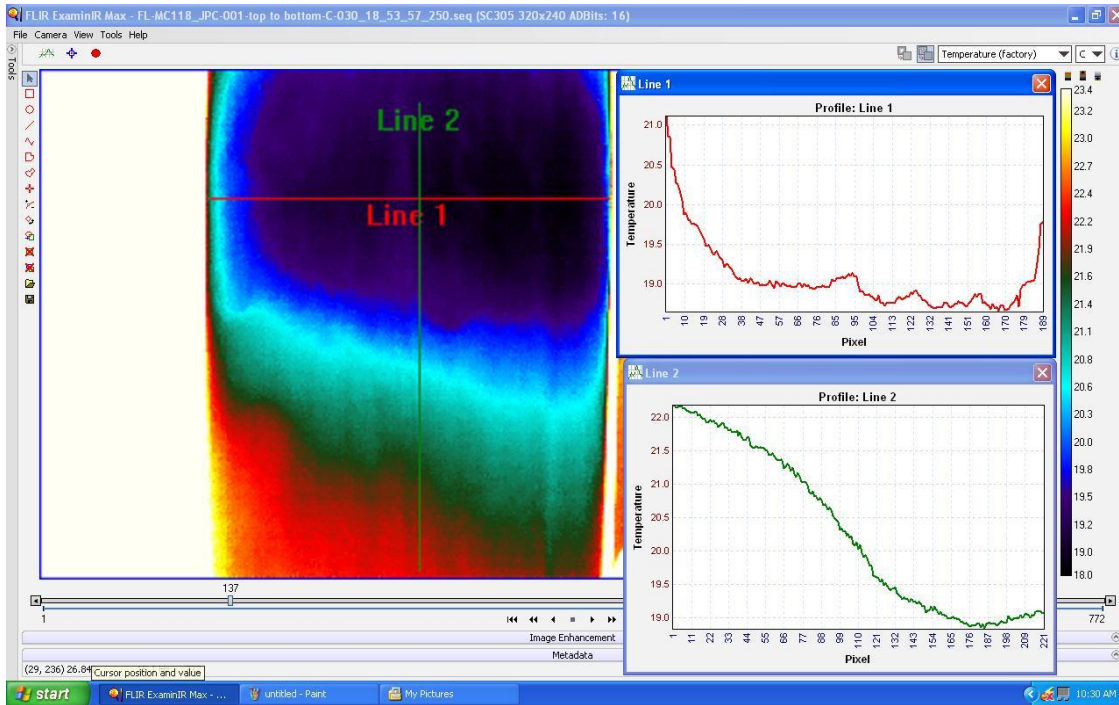


Figure 34. A screen-capture shows a 4"x6" section of core believed to contain hydrate (blue). The color-coded sections - green = longitudinal, red = transverse – show temperatures along/across the core.

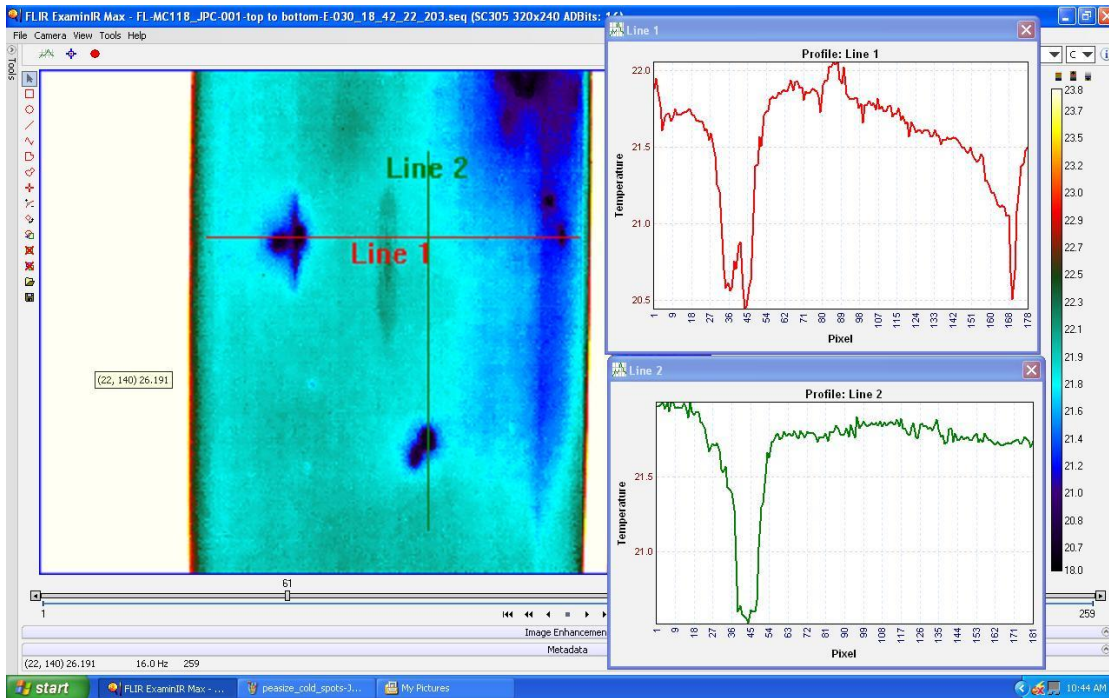


Figure 35. A screen-capture shows a 4"x6" section of core believed to contain grains of hydrate (blue). The color-coded sections - green = longitudinal, red = transverse – show temperatures along/across the core.

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 Geoacoustics custom-designed polarity-preserving chirp system was received in late December, 2010. Efforts to install the system on the NIUST *Eagle Ray* Autonomous Underwater Vehicle (AUV) could not begin until the vehicle was returned from its session at ISE where it was upgraded and new batteries were installed. Following some initial difficulties, centered about a faulty ribbon, MMRI set up a series of meetings with Geoacoustics (in the U.K.) and their shop, our STRC shop and the NIUST Underwater Vehicles Technology Center (UVTC) shop. These web meetings were designed to force the progress of this promising system. NIUST engineers have taken the lead in effecting changes in the systems software. Some minor problems have been corrected, the system installed on the *Eagle Ray* and a test (engineering) cruise is scheduled for mid-July, 2011.

It is hoped that this system will aid in the identification of a seismic signature for shallow, buried, hydrates by reflecting differences between sediments and fractures filled with gas hydrate and those filled with gas, to provide a better understanding of the upper part of the thermogenic fluids conduit system.

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 is due to open the JPCs in late July, thence to proceed with descriptions, photographing and beginning to perform laboratory analyses, including grain-size analyses, mineralogical analyses, microfossil analyses and lithologic analyses.

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 but they have not yet been fitted to the Station Service Device (SSD) Remotely Operated Vehicle (ROV). However, small samples of solid hydrate recovered in the JPCs in January were recovered from the cores, placed in small jars entirely full of sea water and sealed so that all contained gas must have evolved from the hydrate samples. These samples are being analyzed by the Florida State University geochemical team.

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. In the spring of 2007, the Gulf of Mexico Hydrates Research Consortium administration was advised by DOE management that, for the sake of expediency in deploying the horizontal line arrays (HLAs), a major component of the monitoring station/seafloor observatory, accelerometers should be removed from the FY06-funded HLAs, making them hydrophone-only arrays for the collection of passive

data. Geophysicists involved with the monitoring station/observatory project suggested an alternative way to recover the needed 4-C data that would have been provided by the accelerometers in the arrays from the seafloor. This alternative required the independent collection of 4-C data and processing it via new programming and software already developed by the University of Texas at Austin for the observatory project (Phase 1, Task 2). While installation of accelerometers as permanent components of the observatory – for the collection of shear data - is still a goal of the Consortium, the consensus is that a 4-C experiment would provide a vital component of the research at MC118 and serve to guide decisions regarding permanent installation of 4-C instruments.

The plan proposed (FY09) study included the lease or donation of 4-C nodes by CGGVeritas and the donation of the use of a source gun and shooting time all as a cost-share component. This was due to interest at CGGVeritas in using the shooting on the horizontal arrays as an experimental test of a technique they were considering incorporating into their reservoir monitoring program. However, personnel and priority changes at CGGVeritas occurred before the work could be scheduled; the donated nodes would have to be transported from Singapore; the Consortium would have to contract to be trained in the use of the nodes by a former CGGVeritas-employee as no one still with the company had any knowledge of how they should be used or maintained...Eventually (mid 2010) UT-Austin, seeing no way to make the data acquisition happen asked to be relieved of the contract. For several months, we searched for ways to satisfy both their request and the need for the shear information. At the fall, 2010 Consortium meeting in Oxford, it was suggested that Woods Hole Oceanographic Institution's Ocean Bottom Seismometer group might agree to contract to do the work if they were not completely booked with internal projects. When they were contacted, it turned out that they were already fully booked during traditional cruise season but that they could do the work during the spring of 2011 if their instruments could be returned to WHOI by mid-April in time to be refurbished for a May job on the west coast.

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, Ocean Bottom Seismometer (OBS) Group, Woods Hole Oceanographic Institution (WHOI)). Activities identified herein will be coordinated and carried out in conjunction with the CMRET and in support of those identified in Phase 2, Task 3. Activity by the Recipient under this task shall include, but not be limited to:

Subtask 3.1. The WHOI OBS Group will provide 15 short-period Ocean Bottom Seismographs, each containing a 3-component 4.5 Hz geophone and a hydrophone for a 4-C shear wave study at MC118, northern Gulf of Mexico. All four channels will be sampled at 200 Hz.

Subtask 3.2. WHOI will deliver the OBS units to the R/V *Pelican* (LUMCON) in a 20' ocean-going laboratory van and will ship them back to Woods Hole when the experiment is completed.

Subtask 3.3. WHOI will provide two technicians to participate in the experiment to

deploy and recover the OBS.

Subtask 3.4. Upon completion of the experiment, WHOI will provide to CMRET clock-corrected seismic data in two formats: (i) SEGY-formatted data cut according to a shot table that CMRET will provide, and (ii) the complete data in SEED format.

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. These will be used as an indication of progress towards achievement of results and shall be included in the required progress reports.

Woods Hole's responsibilities have been fully completed. An 8-day cruise, April 2-9, 2011, was devoted to acquiring the OBS data and included a CMRET as well as a WHOI team onboard the M/V *Bunny Bordelon*. 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 (Gerstoff) 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>

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. The venting activity has most likely changed over time. In addition to variable venting activity over time, the following observations are relevant to the modeling of hydrates at the 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) has 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. This work is more fully described in the following.

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. Because of late start and the complexity of the software under development, SAIC has requested a no-cost extension to the end of December 2011.

A paper based on the work performed under the contract (Garg and Pritchett, 2011) has been accepted for presentation at the 7th International Conference on Gas Hydrates (ICGH 2011), July 17-21, Edinburgh, Scotland, United Kingdom.

Technical Progress

During the current report period (January 1, 2011 to June 30, 2011), work was continued on the development of a multi-component equation-of-state.

We seek to describe a system consisting of up to three hydrocarbon gases (principally methane, with smaller amounts of ethane and propane) together with a saline brine in the pressure/temperature range at which hydrates may form (generally between 0°C and 35°C temperature and between 1 MPa and 100 MPa pressure). During Year 2 (2009-2010), we focused on the PVT properties for the hydrocarbon gases, and developed a module for computing the relevant properties for a gaseous mixture consisting of methane, ethane, and propane. In the following, we describe the development of a module for computing hydrate/liquid/gas equilibrium conditions.

Two methods for calculating hydrate/liquid/gas equilibrium conditions for aqueous/hydrocarbon systems are available in the literature. The first is a general-purpose first-principles statistical thermodynamic approach described by *Sloan* (1998); see in particular Chapter 5. This procedure has been embodied in a stand-alone computer program called CSMHYD, also available with *Sloan* (1998). The second approach is the much simpler and more heuristic “distribution coefficient” or “K-value” method, which permits equilibrium conditions to be estimated using algebraic formulae. This approach is described at considerable length by *Sloan* (1998).

It had been our original intent to employ the “K-value” approach in the development of the new STAR/THROBS compositional constitutive description for the three-component

hydrocarbon case. During the last reporting period (July-December 2010), we first undertook to use the formulation of *Mann et al.* (1989) (see *Sloan* (1998) for a discussion of various K-value formulations) to try to estimate equilibrium conditions as a function of temperature for a non-saline aqueous system (techniques for taking dissolved-salt effects into account are discussed below) in equilibrium with a gaseous phase consisting of 96% methane (CH₄), 3% ethane (C₂H₆) and 1% propane (C₃H₈) by volume. This composition is representative of the vent gases emanating from the Mississippi Canyon 118 hydrate site (*Sassen et al.*, 2006). Structure II hydrate was assumed. These “K-value” results were then compared to those from similar calculations using the more general-purpose CSMHYD program of *Sloan* (1998).

Unfortunately these comparisons suggested that the “K-value” approach, while useful for preliminary estimation purposes, is insufficiently robust for use in a general-purpose simulator. A comparison of the predictions for P_{eq} , the “equilibrium pressure” at which all three phases may coexist, showed that the two methods produce comparable results over a pressure range extending from approximately 2 MPa to 20 MPa, but outside that range the “K-value” method diverges markedly from the CSMHYD representation. For pressures less than about 1.7 MPa the “K-value” P/T relationship has a negative derivative, and the equilibrium temperature appears to diverge completely for pressures exceeding 50 MPa or so.

The clear superiority of the CSMHYD results mandated that this more general-purpose approach would be required for the development of our new constitutive model. But direct use of CSMHYD within the STAR or THROBS context would have been impractical, for several reasons. First is the fact that the CSMHYD source-code was not available to the present authors. Second, CSMHYD is a far more general-purpose description than is needed for the present purposes, and thus even if the source-code had been available, its direct use would have been much too computationally inefficient for practical calculations using the reservoir simulator.

In the progress report for the last period (July – December 2010), we described an intermediate approach. The CSMHYD program was exercised extensively to characterize three-phase equilibrium conditions for a three-component hydrocarbon gas (CH₄, C₂H₆ and C₃H₈) in equilibrium with H₂O as a function of temperature. The composition of the gaseous phase is specified by the values of two dimensionless parameters H and G :

$$H = (\langle \text{Ethane} \rangle + \langle \text{Propane} \rangle) / (\langle \text{Methane} \rangle + \langle \text{Ethane} \rangle + \langle \text{Propane} \rangle)$$

$$G = \langle \text{Propane} \rangle / (\langle \text{Ethane} \rangle + \langle \text{Propane} \rangle)$$

where:

$\langle \text{Methane} \rangle$ = number of moles of CH₄ in the gaseous phase,

$\langle \text{Ethane} \rangle$ = number of moles of C₂H₆ in the gaseous phase, and

$\langle \text{Propane} \rangle$ = number of moles of C₃H₈ in the gaseous phase.

CSMHYD calculations were carried out for temperature $T = 0^\circ\text{C}, 5^\circ\text{C}, 10^\circ\text{C}, \dots, 35^\circ\text{C}$,

for $H = 0.00, 0.02, 0.04, \dots, 0.10$ and for $G = 0, 0.125, 0.25, 0.375, 0.5$ and 1.0 . The calculated results for each of the 248 cases considered (equilibrium pressure P_{eq} and the equilibrium composition of the hydrocarbon mixture in the solid hydrate phase) were recorded.

The CSMHYD calculations described above were carried out for four-component systems (H_2O , CH_4 , C_2H_6 and C_3H_8) without dissolved salt ($NaCl$). Of course, in reality the “equilibrium pressure” (the pressure at which all three phases – hydrocarbon gas, solid hydrate, and aqueous brine with dissolved hydrocarbons – can coexist) may be regarded as depending upon temperature, brine-phase salinity, and the composition of the gaseous phase. Defining brine salinity as:

$S = \text{dissolved NaCl mass} / (\text{dissolved NaCl mass} + \text{liquid } H_2O \text{ mass})$

it is useful to define an “adjusted temperature” T_{adj} by:

$$T_{adj} = T + 60 \times S$$

where both T_{adj} and T (the actual measured temperature of the system) are expressed in degrees Celsius. The effect of non-zero salinity upon the equilibrium relations is to raise the equilibrium pressure (see e.g., Sloan, 1998; Garg *et al.*, 2008), so that the equilibrium pressure at (T, S) is essentially the same as that for pure water at $(T_{adj}, S = 0)$. So, the equilibrium conditions (equilibrium pressure, and the composition of the solid hydrate phase) may be regarded as a function of T_{adj} and the composition of the gaseous phase or “feedgas” (as specified by the H and G parameters – see above).

Using the above relation for T_{adj} , mathematical fits were formulated to the computed CSMHYD results listed in the Appendix which yield equilibrium pressure and the hydrate hydrocarbon composition (molar ratios of $CH_4:C_2H_6:C_3H_8$) as functions of T_{adj} ($= T + 60 S$) and the values of H and G describing the composition of the feedgas. These fits employ smooth interpolations (with continuous partial derivatives) among the values obtained from CSMHYD. Details of these fit were presented in the progress report for the July-December 2010 period.

During the current report period, we have coded the equation-of-state (HYDGAS) module. It is a relatively large code (over 15,000 lines; see appendix A). The code 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.).

Future Work

Because of the significant additional effort required to formulate the correlations for the hydrate-liquid-gas equilibrium conditions, the code development is somewhat behind schedule. During the next few months, we will continue to debug and test the HYDGAS equation-of-state package. On completion of the HYDGAS package, we plan to perform preliminary calculations to characterize the effect of a gaseous mixture on hydrate formation at the Hydrate Mound.

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Appendix A: HYDGAS package - status as of July 7, 2011

Total source code size: ~570 kilobytes.

Total lines of Fortran source code: 15,531.

List of source code elements:

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

ABSTRACT

Peeper instruments for collecting porewater samples in shallow subsurface sediment profiles were deployed on the ROVARD during the September 2010 cruise and recovered during the June 2011 cruise aboard the R/V *Pelican*. Pore Fluid Array samplers (PFA; Lapham et al. 2008) were constructed for deployment at MC-118 during 2011, one of these samplers was constructed to replace the PFA previously deployed at the northwest crater once the original has been recovered, scheduled for the 2011 cruise season. A second PFA was constructed to be attached to the ROVARD for its deployment in August 2011. Jumbo piston cores were collected during the RV *Brooks McCall* cruise in January 2011, and were analyzed for a suite of geochemical parameters. Results of these analyses indicate spatial variability in the methane source and microbial activity across the mound complex. Preliminary data suggest the presence of a transient lateral brine transecting at least one of the sites perhaps advecting via conduit channels resulting from fault features. Hydrate was obtained from one of the cores and isotopic as well as hydrocarbon composition indicate that the hydrate is of thermogenic origin. Evidence of microbially-produced methane was found at other coring locations. Geochemical evidence from the jumbo piston cores supports previous indications that spatial as well as temporal variability is high across the mound complex, highlighting the need for continued temporal sampling efforts as can be accomplished via the PFA instruments as well as increased coverage across the mound to better constrain spatial variability with relation to the mapped faults.

INTRODUCTION

Hydrates have been implicated as both a mechanism to “store” methane preventing its 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 its stability are perturbed. Unfortunately those factors governing hydrate stability are still poorly understood, especially the geochemical parameters necessary to maintain hydrate stability. Characterizing the chemical environment at hydrate-bearing sites in conjunction with estimates of hydrate dissolution rates will help us to further understand the parameters controlling hydrate stability and assess the potential for dynamic methane release. We are particularly interested in the feedbacks between the chemical environment and microbial activity at the site and how they affect hydrate stability. Because microbially-mediated anaerobic oxidation of organic matter (AOM) has been proposed as an important mechanism for removing methane from enriched porewaters and storing the carbon as authigenic carbonate before it can be released to the atmosphere (Joye et al. 2004; Orcutt et al. 2004) the mechanisms that may influence

oxidation rates, including substrate availability, are important to our understanding of the global carbon budget. While AOM is almost exclusively accomplished via sulfate reduction (SR), SR rates are only loosely coupled to AOM (Joye et al. 2004) perhaps due to the presence of other available substrates (Bowles et al. 2011). In addition to methane, upward-advecting porefluids in the southwest seep at MC-118 also contain additional hydrocarbons (ethane, propane, butanes) as well as oils, consistent with a deep thermogenic reservoir, which may also be oxidized via SR (Bowles et al., 2011).

MC-118 is located in the Gulf of Mexico along the Louisiana continental shelf. Large outcropping methane hydrates have been observed at this site over a period of at least 7 years. The presence of methane hydrates buried within the sediment is inferred from seismic data and the serendipitous coring of hydrate during geological coring surveys. The bathymetry at this site is dominated by a 1km diameter hydrate-carbonate mound-complex (McGee et al. 2009). Seismic profiling of the site has revealed an extensive fault system radiating from a salt diapir located hundreds of meters below the surface (McGee et al. 2009). It was hypothesized that SSSR anomalies were related to the deep seismic faults that transect the site. Our aim was to monitor the surface expression of these faults via geochemical profiles to better understand the role of these faults as conduits for fluid flow. It has been hypothesized that the faults act as channels for deep thermogenic source reservoirs to connect with the surface (McGee et al. 2009). The presence of higher molecular weight hydrocarbons ($C_1 - C_4$) and the enriched isotopic values ($\delta^{13}C = -47\text{‰}$) of the methane from hydrates sampled at this site support a deep thermogenic hydrocarbon source (Sassen et al. 2006). Oxidation rates are controlled by the availability of substrates provided by upward flux from below (methanotrophy) and downward advection from above supplying sulfate necessary for anaerobic oxidation of organic matter within the sediments (Joye et al. 2004). Our objectives were to understand the chemical environment that results from the feedbacks between physical supply of substrates and biological consumption/production that play a key role in the chemical environment of the hydrates. This chemical environment is hypothesized to influence the stability of hydrates *in situ* (Lapham et al. 2008; 2010).

MATERIALS AND METHODS

Five coring locations were chosen based on the presence of acoustic anomalies in the seismic data and surface expressions of faults (Figure 36). Piston-assisted gravity cores (TDI Brooks International) were conducted at each of the five sites to collect sediment samples. These cores are capable of collecting up to 20m of sediment under ideal conditions; however, actual recovery is limited by substrate hardness. Once on deck, the core was capped, and the crew cut the core into 3-foot sections capping at each cut, the core lengths were then brought into the lab for sampling. Cores were sampled at the top of each 3-foot interval. Additional samples were taken at closer intervals within the first 1m of two cores.

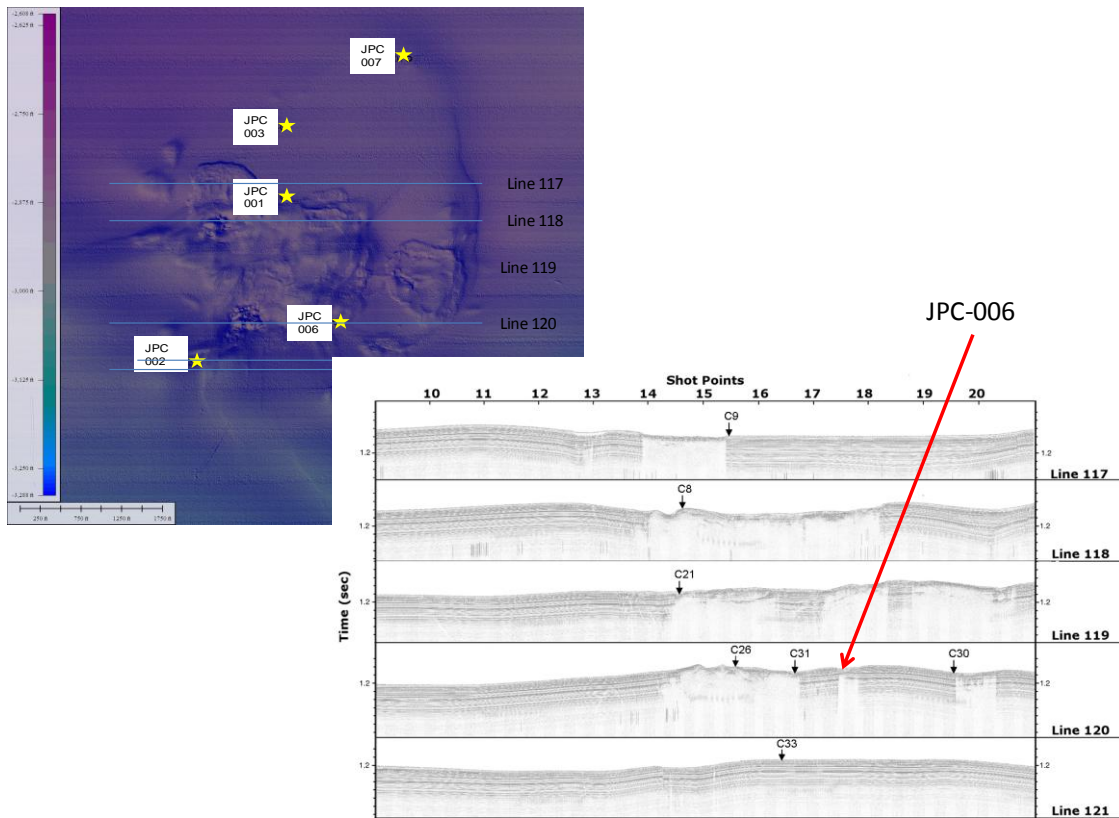


Figure 36: Bathymetry map of MC-118 mound complex and SSSR data showing acoustic anomalies targeted in the coring survey. (Bathymetry and chirp data courtesy of Antonello Simonetti).

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)/ $\delta^{13}\text{C}_{\text{DIC}}$ 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 at Florida State University, following completion of the coring cruise.

Dissolved methane concentrations were measured on a Gas Chromatograph following headspace equilibration (Lapham et al. 2008). Sulfate and chloride concentrations were obtained on a Dionex Ion Chromatography (Sunnyvale, California) following the methods of Martens et al. (1999) and Lapham et al. (2008). Carbon isotope ratios 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: $\delta^{13}\text{C} = (R_{\text{sample}}/R_{\text{standard}} - 1) * 1000$, where $R = {}^{13}\text{C}/{}^{12}\text{C}$. $\delta^{13}\text{C}_{\text{DIC}}$ were obtained following acidification of the samples with 43% nitric acid.

RESULTS

One core (JPC-002) was collected in sediments where seismic data suggests compressed stratigraphy. JPC-003 was collected north of a high resistivity anomaly in the SDR data that is thought to correspond with a fault. The objective in collecting this core was to constrain the spatial extent of the fault in the northward direction. Three of the cores (JPC-001, JPC-006, and JPC-007) were collected in areas where SDR or chirp-line profiles indicated acoustic anomalies. Upon bringing JPC-001 onto deck, it was noted that the core was extremely “gassy”. 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 mud-line and the 3-foot 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. Various means were attempted to collect this hydrate. Pieces of hydrate were placed in canning jars, water was added. The jars were sealed with Teflon tape and brass rings before being frozen upside-down to trap the evolving gas. A subsample of the hydrate “disk” was subdivided into 4 pieces and each piece 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 and stoppered serum vials for hydrocarbon and stable isotope analysis. All hydrate gas samples were analyzed for methane concentrations and $\delta^{13}\text{C}$ using the same procedure as sediment samples.

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 37). 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 600 μM at 1113cmbsf. Methane in cores JPC-003 and JPC-007 reached maximum concentrations of 720 μM and 1.3mM respectively at the bottom of the sampled core. JPC-001 (where the hydrate was found) had higher methane concentrations over shallower ranges than the other cores. Methane concentrations were approximately 10mM by approximately 400cmbsf and then decreased to a constant 1.3mM over the range of 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 $\delta^{13}\text{C} = -40.4\text{‰} \pm 0.7\text{‰}$ ($n = 10$), the ethane/methane ratio was 0.15.

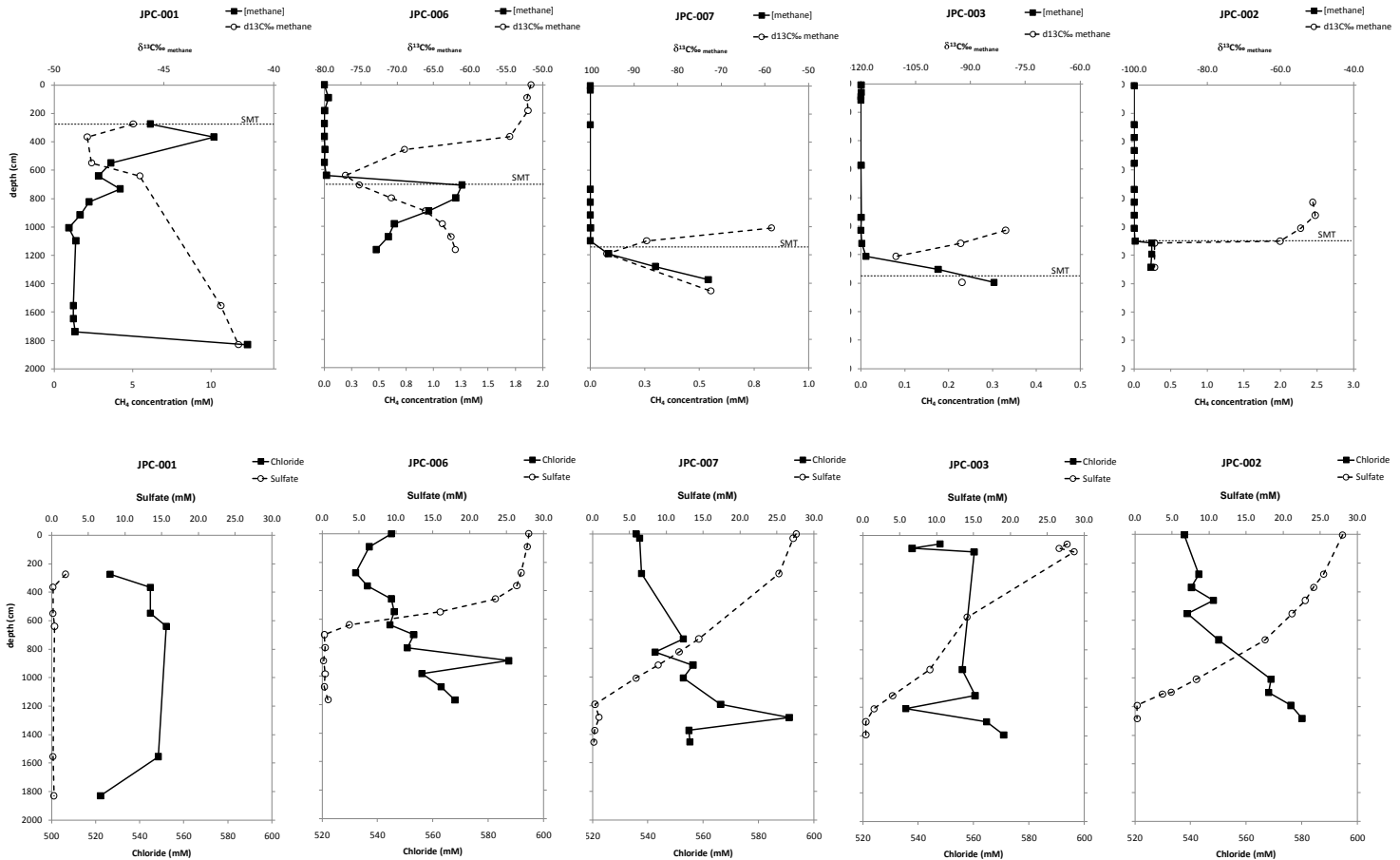


Figure 37: Methane concentrations, methane stable isotopes, sulfate and chloride concentrations from Jumbo Piston Cores.

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 38). With the exception of JPC-001, $\delta^{13}\text{C}_{\text{DIC}}$ 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, $\delta^{13}\text{C}_{\text{DIC}}$ began to be progressively enriched with depth. In JPC-001, the shallowest portion of the core was lost; the general trend is an increase in both DIC concentration and $\delta^{13}\text{C}_{\text{DIC}}$ enrichment. The $\delta^{13}\text{C}_{\text{DIC}}$ approaches 40‰ in positive δ -value!

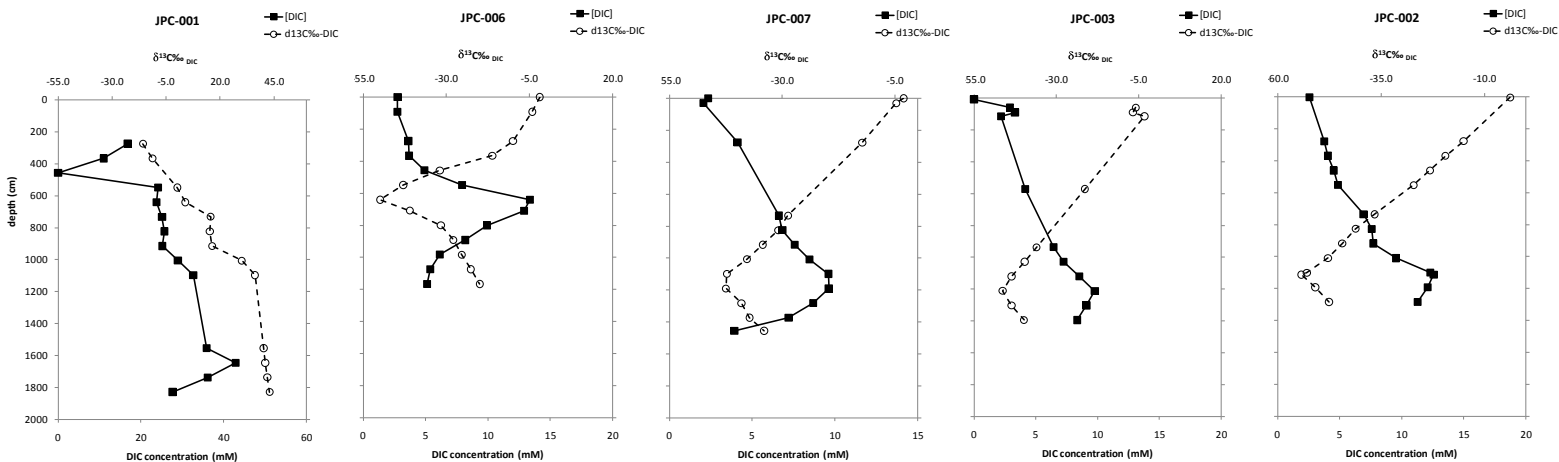


Figure 38: Dissolved inorganic carbon (DIC) concentrations and stable isotope ratios ($\delta^{13}\text{C}$) measured in the Jumbo Piston Cores.

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 $\sim 13\text{m}$ (Figure 37). Sulfate was found to about 11m in JPC-002. Sulfate depletion depth in JPC-006 was around 8m. Nearly all of the sulfate was depleted in JPC-001 by $\sim 3\text{m}$. These depths correspond well with the increase in methane concentrations as well as the inflection in $\delta^{13}\text{C}_{\text{DIC}}$ values in the cores and thus define 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. 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 JOC-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} .

DISCUSSION

In cores JPC-002, JPC-003, and JPC-007 sulfate, methane (Figure 37), and $\delta^{13}\text{C}_{\text{DIC}}$ profiles (Figures 38) are consistent with microbial anaerobic oxidation of methane coupled to sulfate reduction. 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; however they have not been visually examined as we were trying to preserve the integrity of the cores as much as possible during geochemical sampling for further anticipated analyses. Blanking in the acoustic data suggests the possibility that authigenic carbonates could be present in the vicinity of some cores (JPC-006 and JPC-001), although the seismic data are also consistent with the presence of hydrates or gas bubbles. Indeed, we actually sampled gas hydrates in JPC-001 (discussed below).

The average sulfur depletion rate in cores JPC-002, JPC-003, and JPC-007 of 0.023 mM cm^{-1} is similar to what Lapham et al. (2008) found in their “moderate” microbial

activity cores at the same site suggesting that methane advecting towards the surface is similarly fueling microbial processes at these sites. Although we do not have the uppermost sediment from JPC-001 to compare sulfate depletion rates, qualitatively we show that all of the available sulfur in this core has been reduced by 3m depth. In JPC-006, on the other hand, the sulfate concentration is still ~28mM at 3m and is not exhausted until more than 7m (Figure 37). This suggests that methane flux rates are much higher at JPC-001 compared to JPC-006. However, sulfate depletion rates in core JPC-006 are much higher than in any of the other three cores examined (Figure 37) over the 4-7m depth range.

Depth of the SMT was inversely correlated with the stable carbon isotope composition of the methane gas in the sediment porewater (Figure 38). The correlation between $\delta^{13}\text{C}_{\text{methane}}$ and depth of the SMT implies that microbial oxidation rates are higher in zones with increased fluid flux rates (i.e. higher methane supply). If this trend was simply the result of high rates of methanogenesis at depth in cores JPC-001 and JPC-006 that were being oxidized as the fluid advected towards the surface, 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 $\delta^{13}\text{C}_{\text{methane}}$ values to become increasingly enriched with depth. This could suggest a deep thermogenic source of methane mixing with MOG products at shallower depths (e.g. Lapham et al. 2008). Although the $\delta^{13}\text{C}_{\text{methane}}$ in core JPC-006 is not definitively thermogenic (-66.8‰), the ratios of methane to ethane (C_1/C_2) in the samples are about two orders of magnitude lower than biogenic ratios observed at other sites (e.g. Martens et al. 1991) lending further credence to the suggestion that thermogenic methane is contributing to the total methane pool sampled. Sulfate concentrations in JPC-006 are essentially the same value as seawater (28mM) up to a depth of >3m (Figure 37), below which the sulfate is rapidly consumed.

Chloride concentrations in JPC-006 generally increase with depth and reach a subsurface maximum between 8-10m. The overall trend taken in conjunction with the rapidly depleted sulfate at depth suggests a high-salinity brine advecting towards the surface. JPC-006 was chosen as a coring site due to its proximity to one of the faults that radiates from the salt dome to the surface, thus the spike in salinities ~900m (Figure 37) suggests a region of brine fluid transport. We suggest that the average direction of transport of this higher salinity, sulfate-depleted brine horizontally transects the region we cored. Chanton et al. (1993) have observed similar “horizontal creep” of brine fluids at the Florida escarpment, such high salinity, sulfate-depleted brines are confined to horizontal layers because of their increased density relative to seawater. Although Chanton et al. (1993) observed linear trends between sulfate and chloride profiles leading them to suspect diffusional mixing between the brine seep fluid and overlying seawater. We do not see a similar significant linear trend in our data; although, in general, there is a negative correlation between chloride and sulfate concentrations in the porewater. We propose that, in contrast to the Florida escarpment, our system is not at steady-state. Rather, it appears that an increased-salinity (~37.1‰) sulfate-depleted brine has recently (transiently?) intruded the 8-10m depth profile at this site. If this is the case, and if the intrusion continues, we would expect the sulfate profile to eventually assume a linear (rather than curvi-linear) decrease with depth. Further monitoring, including time-series data as per Lapham et

al. (2010), is essential to further our understanding of the physically-controlled geochemistry at this site.

DIC concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ are inversely correlated in all cores except JPC-001. In JPC-006, the DIC concentration and isotope profiles with depth further suggest non-steady-state conditions. We used the method of Hu et al. (2010) to determine the $\delta^{13}\text{C}$ of the DIC added ($\delta^{13}\text{C}_{\text{added}}$) over the depth range from the regression of $\delta^{13}\text{C}_{\text{DIC}} \cdot [\text{DIC}]$ vs $[\text{DIC}]$. The slope of this regression resulted in a $\delta^{13}\text{C}_{\text{added}} = -54.8\text{‰}$ ($R^2 = 0.95$). This is approximately 10‰ enriched relative to the average $\delta^{13}\text{C}_{\text{methane}}$ over the entire depth range and relative to the $\delta^{13}\text{C}_{\text{methane}}$ in the deepest section of the core (Figure 37) suggesting an additional source to the DIC pool. The $\alpha_{\text{DIC-methane}}$ value, 1.043, is slightly less than expected for AOM (1.06, Alperin et al. (1988) as cited by Joye et al. (2004)) suggesting additional sources to the DIC pool, perhaps the lateral pulse is bringing MOG methane and MOG-altered DIC into the core where it encounters this upward flux of thermogenic (enriched) methane.

Publications

- Luzinova, Y., G.T. Dobbs, L. Lapham, J.P. Chanton, and B. Mizaikoff (2011) Detection of cold seep derived authigenic carbonates with infrared spectroscopy. *Marine Chemistry* **125**: 8-18
- Joye, S.B., I. Leifer, I.R. MacDonald, J.P. Chanton, C.D. Meile, A.P. Teske, J.E. Kostka, L. Chistoserdova, R. Coffin, D. Hollander, M. Kastner, J.P. Montoya, G. Rehder, E. Solomon, T. Treude, and T.A. Villareal (2011) Comment on “A persistent oxygen anomaly reveals the fate of spilled methane in the deep Gulf of Mexico” *Science* **27**(332):1033

Cruise Participation

- Wilson participated in the January 2011 cruise aboard the RV Brooks McCall to collect Jumbo Piston Cores at MC-118.
- Wilson participated in the June 2011 cruise aboard the RV Pelican to retrieve the ROVARD instrument lander and attached instruments and to collect pushcores.

Meetings

- Chanton and Wilson attended the BOEMRE Information Transfer Meeting in New Orleans, LA March 22-24th 2011 and reported on the results from the Brooks-McCall Jumbo Piston Coring Cruise as well as the deployment of UNC-CH’s chimney sampler array deployment via ROVARD.

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

The University of Georgia has assigned the University of Mississippi/DOE grant number 037757-02. In addition, 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 requested to extend the working time to August 2012. General schematics have been drawn for the Lander components which include the underwater mass spectrometer and multi filtration system. The Lander and surface vessel will be linked by the same fiber optic cable as used for 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 39) and will 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 pre-filled with distilled water to prevent contamination from surrounding water during deployment. Once deployed and upon pump activation, the distilled water will be displaced with seawater at the desired depth and location. The pump will continue to move seawater through the filter until the desired volume has been reached or the filter has been clogged. After collecting a sample, the pump injector can move from one filter pack to another so that multiple filters can be collected with varying pore sizes per sampling location. Upon recovery, the filter packs have pressure relief valves that will aid in equalizing the internal pressure that could potentially build as a result of deep water sampling.



Figure 39. Filter assembly mounted on distilled water pumping station.

The Lander frame has been 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 40). 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*.

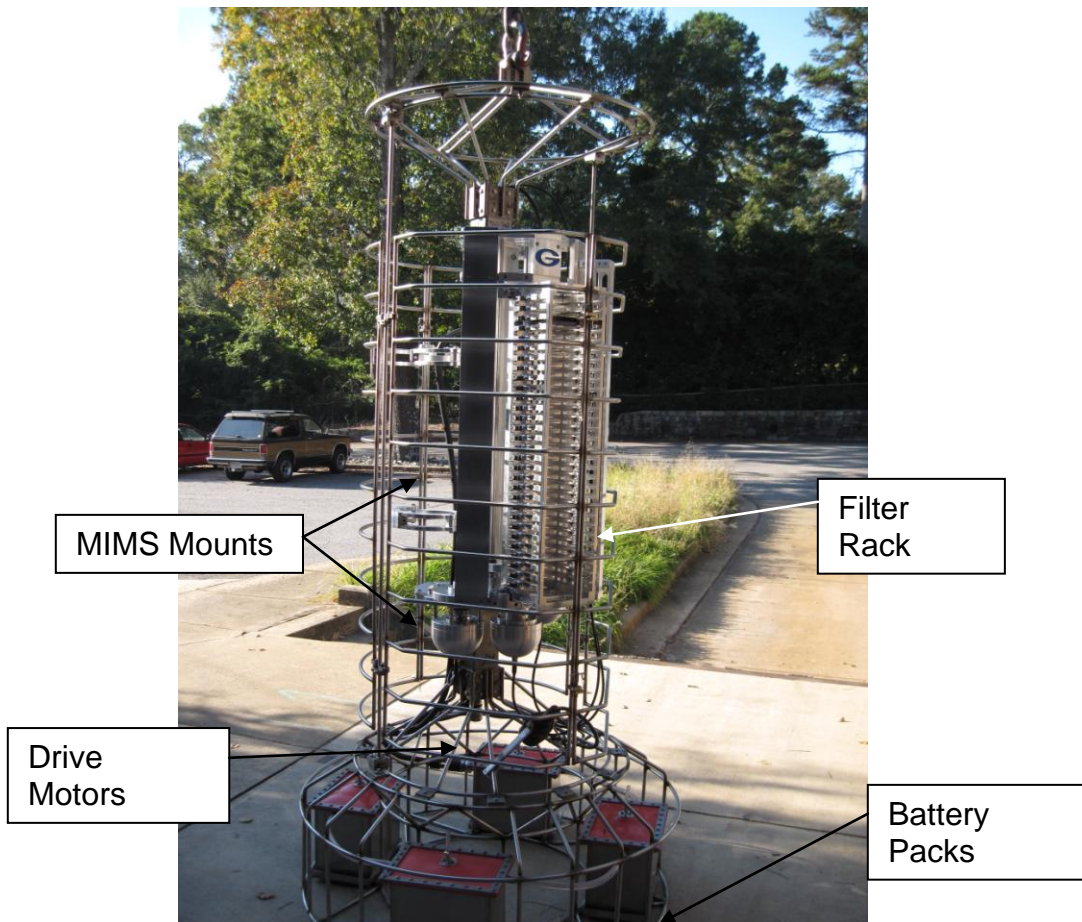


Figure 40. Lander Assembly

In January 2011, the Lander was transported to the Southwest Research Institute (SWRI) in San Antonio, Texas for a simulated deployment. The Lander was equipped with the filter rack, video, MIMS, conductivity/temperature/depth sensor (CTD), and altimeter (Figure 41). Prior to placing the Lander into the pressure chamber, communications were established between the Lander communication package and the MIMS. The Lander was placed into the 48" pressure chamber, chamber lid installed and filled with water (Figure 42). Once sealed in the chamber, the simulated deployment was initiated by slowly raising the pressure in the chamber. The chamber was pressurized to simulate a deployment to 1000m. Communication with the Lander was maintained throughout the simulated deployment. The MIMS, CTD and altimeter successfully sent a data stream through the Lander pressure housing to the bench top computer. Commands to the MIMS were successfully received with corresponding responses returned to the bench top computer. The video camera and lights continued to work successfully and could be turned on and off during the test deployment.

During the simulated deployment, one set back was experienced. At approximately 300m (simulated) depth, a bulkhead connection on one of the Lander drive motor housings controlling part of the filtration system leaked causing the motor to burn out. It was later determined that the connector was defective and it was replaced. The housing and new connector was later tested in Athens at the UGA shop to a simulated 1000m depth without failure.

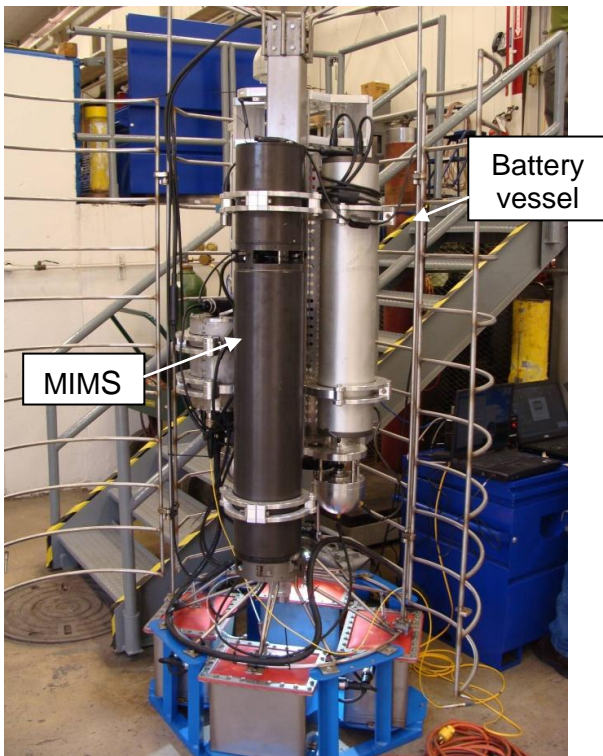


Figure 41. MIMS and battery pack loaded into the Lander.

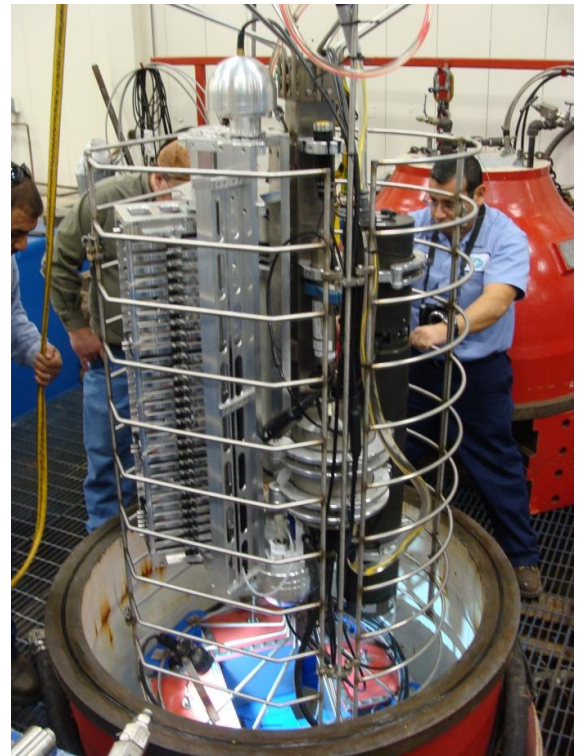


Figure 42. Loading the Lander into the SWRI pressure chamber.

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 will be a Model K508 Stirling cooler assembly from RICOR Cryogenic & Vacuum Systems. The cooler and two types of cold fingers were ordered through RMA Global, LLC and were received in late 2010. In order to minimize or eliminate condensation of water vapor on the cooler cold finger, the operational environment for the cooler must be evacuated or back-filled with a dry inert gas, such as argon. Consequently, a separate pressure housing was retro-fitted with a custom end cap for mounting the cooler and providing electrical connectors to power the chiller, and vacuum connections between the membrane inlet probe and the vacuum housing of the mass spectrometer (Figure 43).

The vacuum line between the membrane inlet probe and the MIMS vacuum housing will be routed through the cooler pressure housing through a custom cold-finger block to trap water vapor coming through the membrane inlet interface. Previous work by scientists at the Alfred Wegener Institute in Germany has shown that a temperature of -90 degrees C is sufficient to trap water vapor and improve their methane detection limit by over an order of magnitude (private communication). SRI plans to test the cooler system within the next two months to evaluate the improvement in methane detection limits for the MIMS systems. The system could then be implemented for in situ dissolved gas measurements at depth in the Gulf of Mexico.

The conceptual design for a new smaller and lower power MIMS instrument was established in late 2010 and all of the major internal components (e.g., mass analyzer, high vacuum pump, roughing pump, and water sampling pump) were ordered and have been received. An InficonE3000 200 atomic mass unit (amu) sensor will serve as the mass analyzer. This analyzer has a more rugged construction than the CPM200 sensor used in previous SRI underwater MIMS systems. It also has two filaments in the ion source that are designed for high water vapor environments. The two filaments provide redundancy in case one filament fails during deployment. The high vacuum pump for the new system is a Pfeiffer HiPace10 turbo pump, which is smaller and lower power than the Varian pumps used in prior instruments, and also allows use of a smaller lower power KNF diaphragm pump as the backing pump. Figure 44 is an engineering model of the new MIMS underwater system components and pressure housing (without electrical wiring). Figure 45 is a photograph of the major components of the new MIMS system (without the membrane inlet probe, power distribution board and microcontroller board) and Figure 46 is a photograph of the new pressure housing (rated and tested to 2000 m depth). The new system will not have an embedded computer. Instead all data will be stored on a removable storage device and all operations will be controlled by the microcontroller. The power distribution board has been designed and all components have been ordered. The microcontroller board is in the final stage of design review. Final assembly and testing is expected to be completed in the next two months.

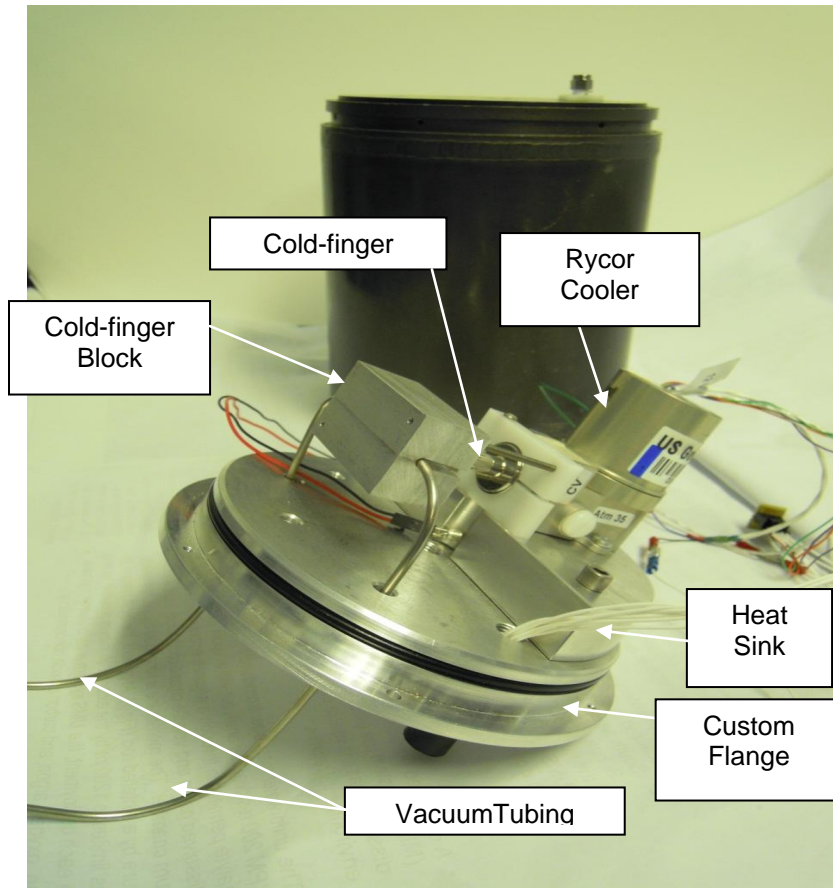


Figure 43. SRI cold-trap system for improving methane detection limits. Water vapor in the vacuum tubing will be trapped in the cold-finger block section at approximately -90 deg. C. Major components are labeled.

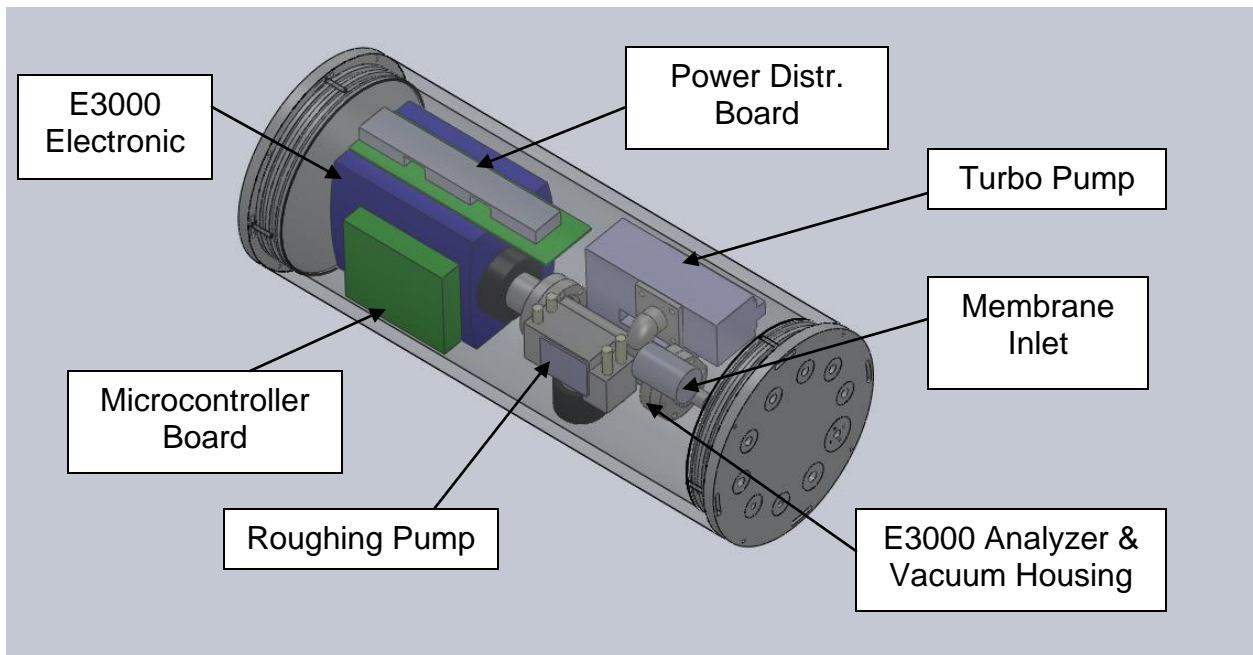


Figure 44. 3-D solid model of the new MIMS system. Major components are labeled.

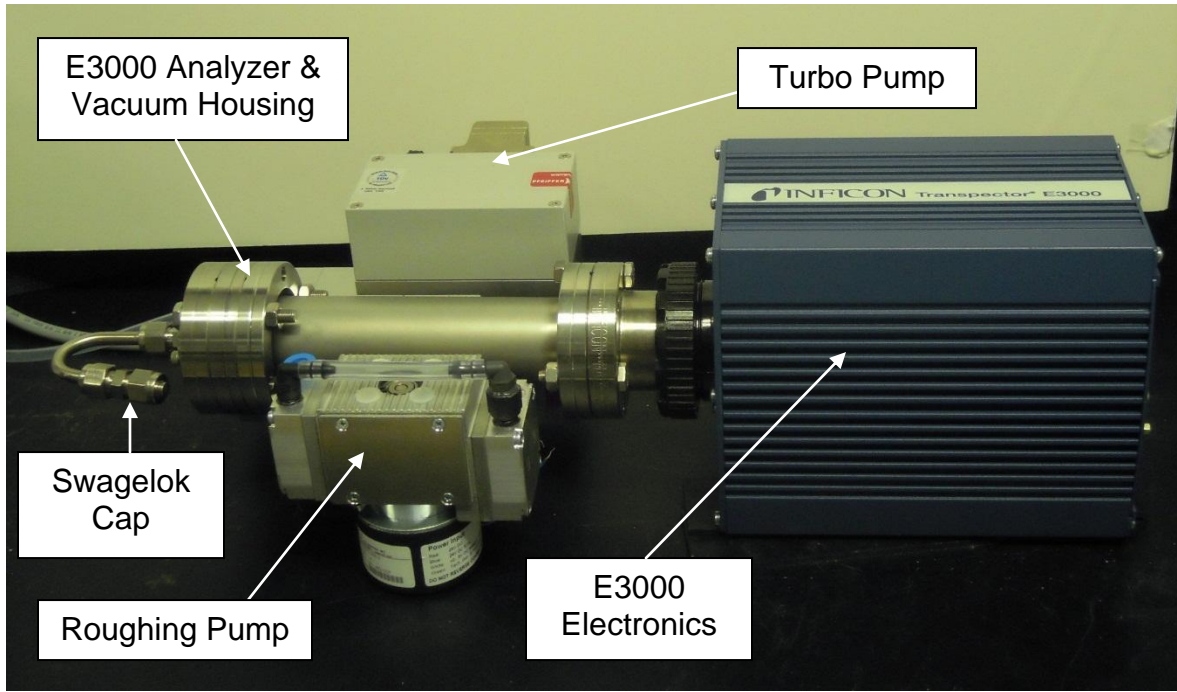


Figure 45. Major components of new SRI MIMS system. The membrane inlet module will replace the Swagelok cap noted in the figure. The roughing pump is not connected to the turbo pump at this time. The power distribution and microcontroller boards are currently under development and are not shown (as well as the internal wiring). All components will be mechanically supported on the feedthrough end cap.

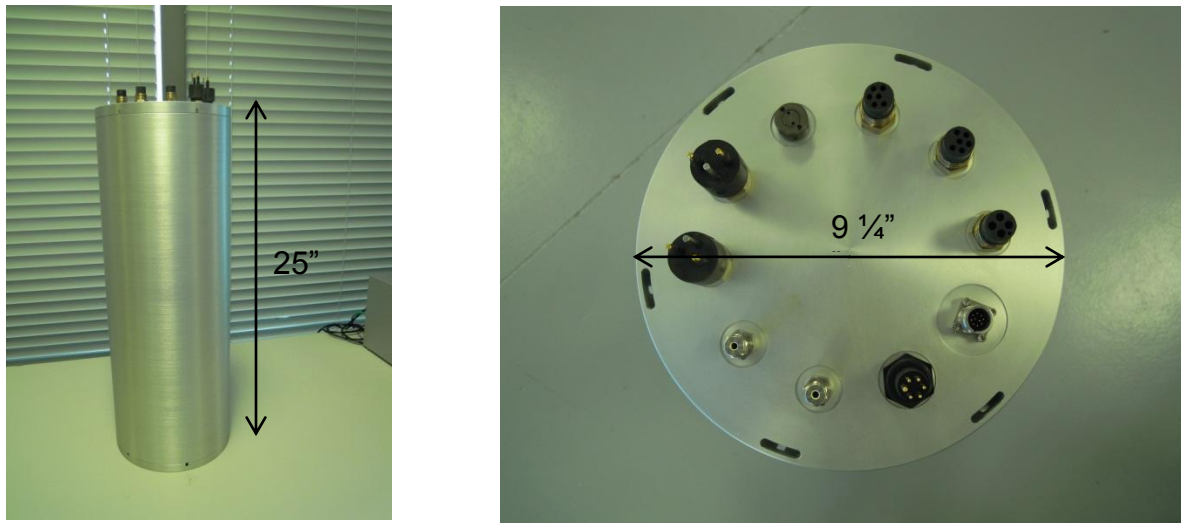


Figure 46. New SRI MIMS pressure housing. a) Side view; b) Top view showing all electrical and fluidic connections are on one end cap. The overall length of the housing is 25 in. and the outer diameter is 9 ¼ in.

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

EFFORT SUMMARY:

During a RV *Pelican* cruise in fall 2010, an attempt was made to measure methane and hydrocarbons in the air above MC118, following on results from the Hyflux experiment (2009) that showed seep methane reached the atmosphere. Unfortunately, electrical power instabilities prevented collection of useful data. On the return drive back to California, a unique methane data set was collected using generator power, demonstrating the system's functionality. Also deployed was a sonic anemometer system, which suffered from excessive noise. This was determined to arise from vibrations. Later it was found that this could be eliminated by guy-wires and a stiffer mounting-pole.

Also brought to the cruise was a multibeam sonar rotator / compass / benthic lander system. Unfortunately weather and rough seas prevented its deployment.

Over the last year, significant capability improvements have occurred. These include acquisition of a Picarro methane and carbon dioxide analyzer, which can measure methane at 10Hz to 0.1 ppb, allowing direct measurements of methane air-sea fluxes using the eddy flux covariance method.

Significant improvements also have been done on gas chromatography measurements. Current capabilities allow measurement of ethane to decane at levels of 50 ppt in the atmosphere on ten-minute timescales (C1-C5), as well as the ability to measure alkenes and BTEX. Significantly greater sensitivity has been achieved using trap and purge at

slower repeat times. In part these successes relate to improved power noise filtering.

In addition, a 1000-m mini-rosette water sampler has been acquired which can be used to collect gas samples and/or water samples (up to 12) from a ROV or tow sled.

In addition, a new electronics bottle has been developed which provides communication between elements of the benthic lander, sonar, embedded computer, and other sensors. The bottle incorporates a circuit board that eliminates troublesome molex connectors, as well as circuitry to protect against short circuits and overvoltage, and diagnostics. Furthermore, we have developed significant capability in making underwater cables for the deepsea.

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 42877R18 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. An extensive January report covered accomplishments of the JPC cruise.
- The Gulf of Mexico Hydrates Research Consortium held several web-conferences regarding the direction of the Consortium, the possibility of cabling the observatory to land via a platform in the Gulf, and future funding directions and procedures.
- We have continued evaluations of the effects of the DeepWater Horizon disaster. Recovery of chemical sensors and arrays reveals greatly diminished impact of oil breakdown products though effects are still being investigated. Consortium members have participated in NRDA cruises designed to investigate and document effects of the spill on deep-sea habitats, including deep-sea corals, environmental health indicators.
- 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-1 and GRI-3 (unsuccessful) have been pursued.
- Consortium scientists participated in and directed the efforts of a Jumbo Piston coring cruise aboard the *M/V Brooks McCall*, January 25-31. Five JPCs each ~12-15m in length, were recovered from a variety of environments at MC118. Core targets were selected using an integrated approach that included three

seismic datasets as well as multibeam and core data from gravity coring efforts. Hydrates were documented in the subsurface, ~ 10-12m subseafloor, verifying both resistivity and shallow-source-deep-receiver findings that indicated the possibility of hydrate in the shallow subsurface.

- A duplicate dataset has been acquired by CMRET from Western Geco to enable CMRET to assist in data analyses of this resource.
- USC has begun to integrate the multiple seismic datasets, including the 12sec Western Geco set, to provide a time dimension to the subsurface analyses of the block. Integration of these industry data sets with the high resolution SDR and chirp is providing amazing insights into the shallow subsurface geology and structure as well as the seafloor at MC118. This information proved to be critically important to the site-selection process for the Jumbo Piston coring effort and will be used in selection of heat-flow targets as well.
- An April 2-9 cruise was executed onboard the *M/V Bunny Bordelon* to recover 4-C data from MC118. A contract was negotiated with WHOI to do the 4C data collection using their OBS nodes and personnel aboard a CMRET chartered vessel. CMRET provided the source guns – 105 cubic inch GI gun and 80 cubic inch water gun - and the compressor to effect the survey. CMRET also served as deck crew and navigators for the surveys. A dataset was collected using each of the source guns. A noise “survey” was also collected via 20-foot seas.
- 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. UT will apply converted shear wave analysis to the dataset in hopes of identifying gas hydrates in the subsurface (standard P-wave analysis is not sufficient for identifying gas hydrates).
- Noise data have been delivered to UCSD for evaluation for their appropriateness to seafloor studies and in reference to the horizontal array emplacements.
- The Benthic Boundary Layer Array (BBLA) was collected on the *Bunny Bordelon* cruise following a seven-month deployment at MC118 with continuous measurements of salinity, oxygen, temperature, pressure, chlorophyll-a, dissolved organic matter and light hydrocarbons. Newly discovered diurnal and longer-term trends in benthic conditions are documented over an extended time period.
- 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. The data, being analyzed and processed in MMRI’s seismic data processing lab, will help to characterize small scale mound morphology better than ever before.
- CMRET organized and executed a research cruise to MC118 June 24 – July 1. Objectives of this cruise included deploying one or more horizontal line arrays

with data-logger(s) at the Observatory site and connecting to the integrated data power unit; Deploying the refitted BBLA with new modem and testing the modem (recovering data) on the SSD or a lander; Recovering PFA-2 box; Collecting push-cores from key sites (instrument locations, hydrate sites); Recovering the Rovard and the instruments deployed on it; conducting a resistivity survey using the SDI/Baylor developed towed cable on the SSD (CMRET, Baylor). A major electrical failure of the SSD caused us to abandon SSD-dependent efforts but all others were achieved.

- The ROVARD (remotely operated vehicle assisted recovery device) deployment/recovery lander was recovered successfully. Deployed at MC118 and equipped with instruments to characterize the benthic zone at MC118, the ROVARD improves the installation and recovery capabilities at the Observatory.
- The Chimney Sampler Array, deployed for ten months at MC118 to characterize the benthic zone, was recovered via the ROVARD. Initial results indicate high levels of turbidity at the seafloor associated with increased concentrations of dissolved methane. The results will be correlated with data from the Benthic Boundary Layer Array to identify oceanographic forcing factors associated with methane releases from the seafloor approximately 900m below sea level.
- The BBLA was redeployed in June 2011 with a new, high speed, wire-less data system using a new optic modem. The bandwidth is approximately 100 times that of standard acoustic modems and the new system makes it possible for large data sets to be transferred quickly. The array no longer needs to be recovered to download data.
- New instruments have been acquired or developed that will enable researchers to better quantify the volume of fluids venting from the seafloor at MC118 (i.e. 1000m water depth). The fate of these fluids is the heart of this effort.
- An increasingly versatile lander, developed by UGa and SRI is ready for testing with camera and increased sampling (simultaneous) and geochemical surveying (via mass spectrometer) capabilities.
- 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.).

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 olde reports, logs and other data posted this winter. 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.

CONCLUSIONS

This report covers the accomplishments of the six-month period from January 1 through June 30, 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: cruises to test, deploy and recover instruments have been made. OBS data, AUV acquired side-scan sonar, multibeam and photo data as well as ROV photodata have been acquired. Jumbo Piston cores have been recovered 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. Reports have been completed and web and paper updates to various components of the project completed. 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 is ready for installation and testing on the NIUST AUV. Additional devices and sensors have been acquired and others fabricated. A busy cruise schedule has characterized 2011 and has included AUV and ROV surveys, major deployments, additional test deployments and retrieval of instrumentation that remains on the sea-floor. Every effort has been – and will continue to be – made to maximize Consortium members’ access to and benefit from the cruises scheduled for 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.

ACRONYMS AND ABBREVIATIONS

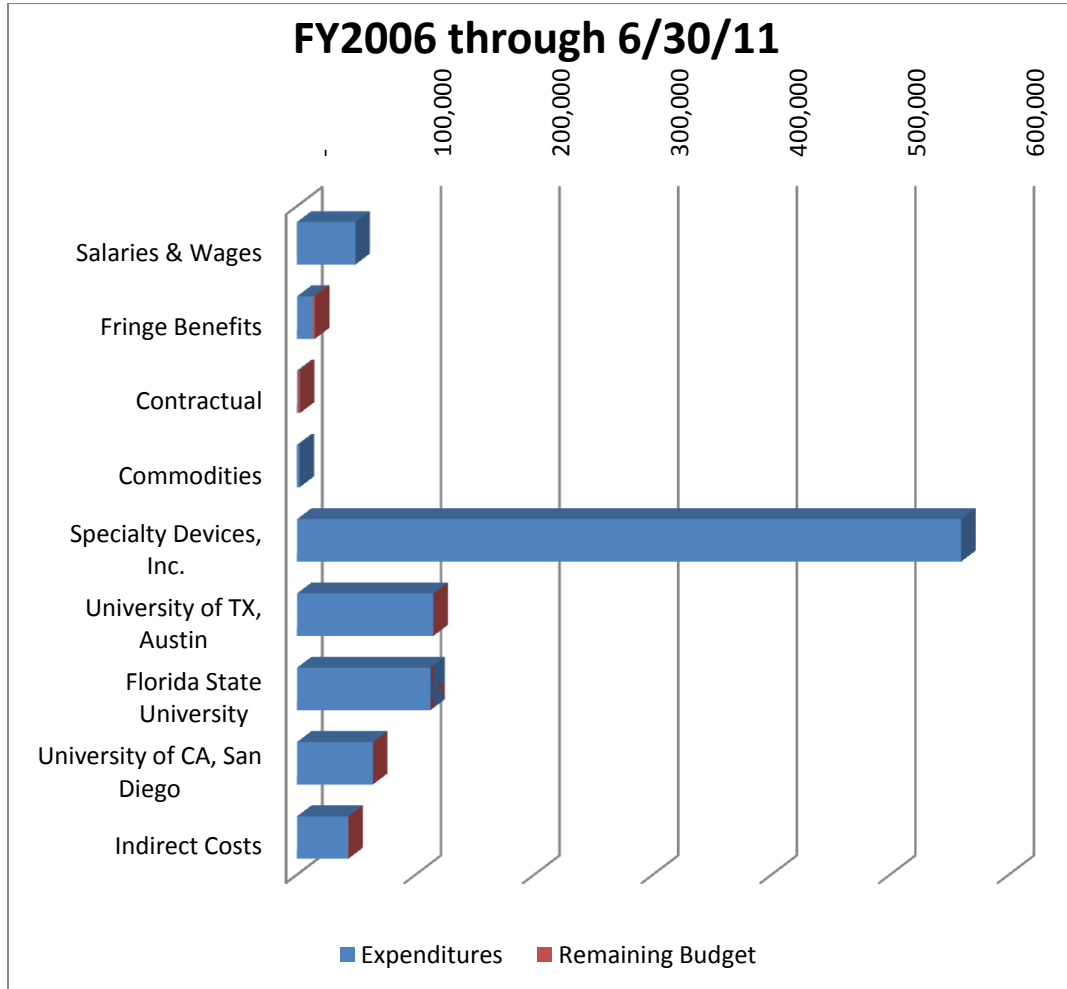
| | |
|-------|---|
| 3-D | 3-dimensional |
| 4-D | 4-dimensional |
| 4-C | four component |
| ABCMS | Automated Biological Chemical Monitoring System |
| AGM | Absorption Glass Mat (battery) |
| AOM | anaerobic oxidation of organic matter |
| AUV | autonomous underwater vehicle |

| | |
|------------|--|
| AVO | amplitude vs. offset |
| BBLA | Benthic Boundary Layer Array |
| BEG | Bureau of Economic Geology (University of Texas) |
| BOEMRE | Bureau of Ocean Energy Management, Regulation, and Enforcement |
| BSR | bottom-simulating reflector |
| C&C | Chance and Chance |
| 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 |
| CWL | Conventional wireline log |
| 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 |
| GRI | Gulf of Mexico Research Initiative |
| 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 |
| JIP | Joint Industry Project |
| 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 |
| MPa | Mega-pascal |

| | |
|---------------|--|
| MS/SFO | monitoring station/sea-floor observatory |
| M/V | Merchant Vessel |
| NETL | National Energy Technology Laboratory |
| NIUST | National Institute for Undersea Science and Technology |
| NOAA | National Oceanographic and Atmospheric Administration |
| 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 |
| <i>P-wave</i> | 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 |
| 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 |

COST STATUS

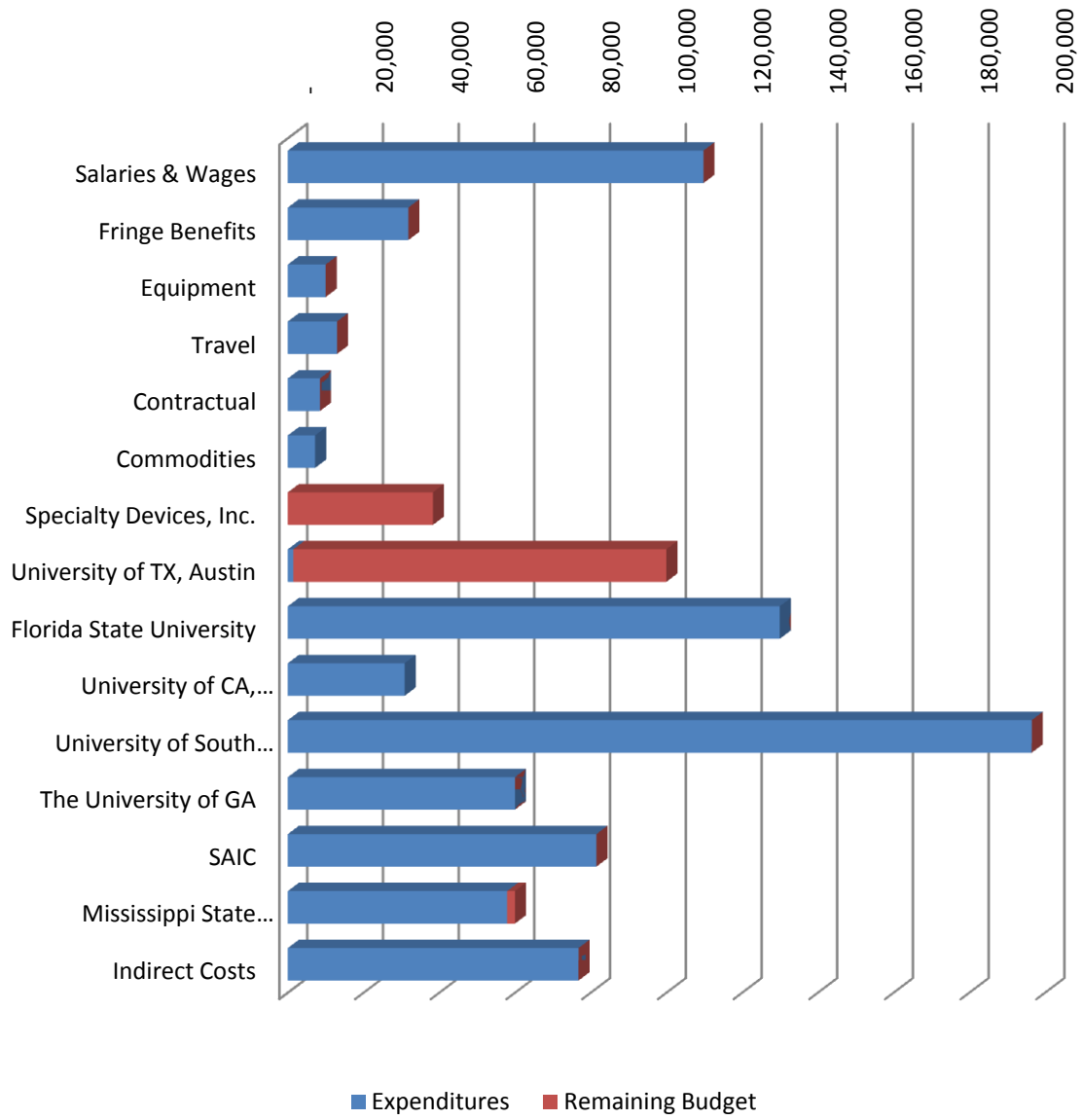
As can be seen in the figures and tables that follow, Phase 1 (FY06) funds are essentially spent. Funds remaining in Phases 2 and 3 (FY08 and FY09) are primarily the 4C experiment and the speed of sound probe. The 4C experiment should move quickly now that the data have been acquired. The probe is a priority for the off-season this year. We hope to conduct the coring work that will test this system in 2012. Subcontracts for Phase 4 (FY10) are well underway though spending is proceeding at a more cautious rate due to the lack of continued support for FY11.



Mississippi Mineral Resources Institute
DOE DE-FC26-
06NT42877
Funding Status as of
6/30/11

| 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 |

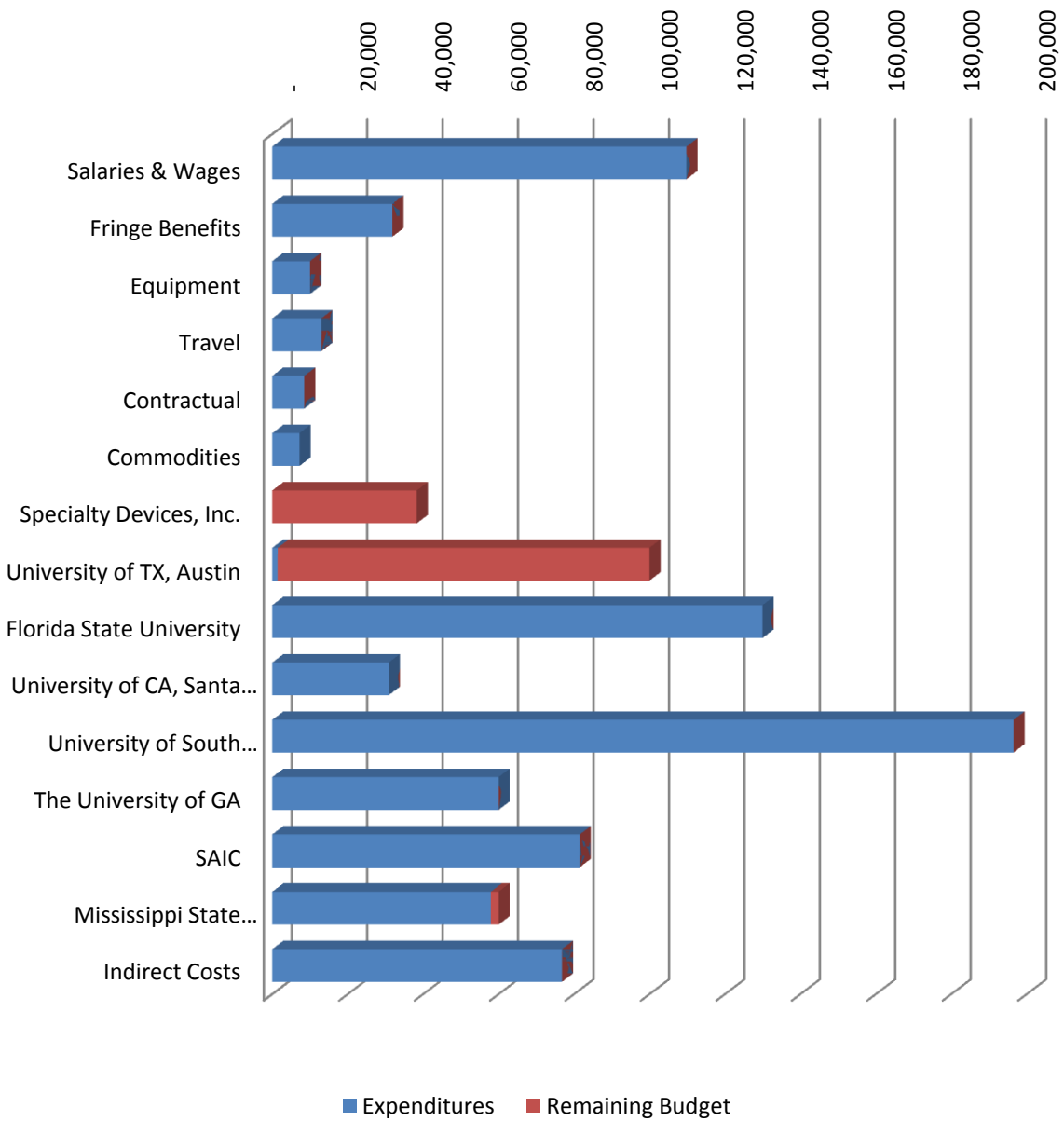
FY2008 through 6/30/11



Mississippi Mineral Resources Institute
DOE DE-FC26-06NT42877
Funding Status as of
6/30/11

| 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 | 57,934 | 2,068 |
| Indirect Costs | 76,796 | - |
| Total | 815,441 | 138,959 |

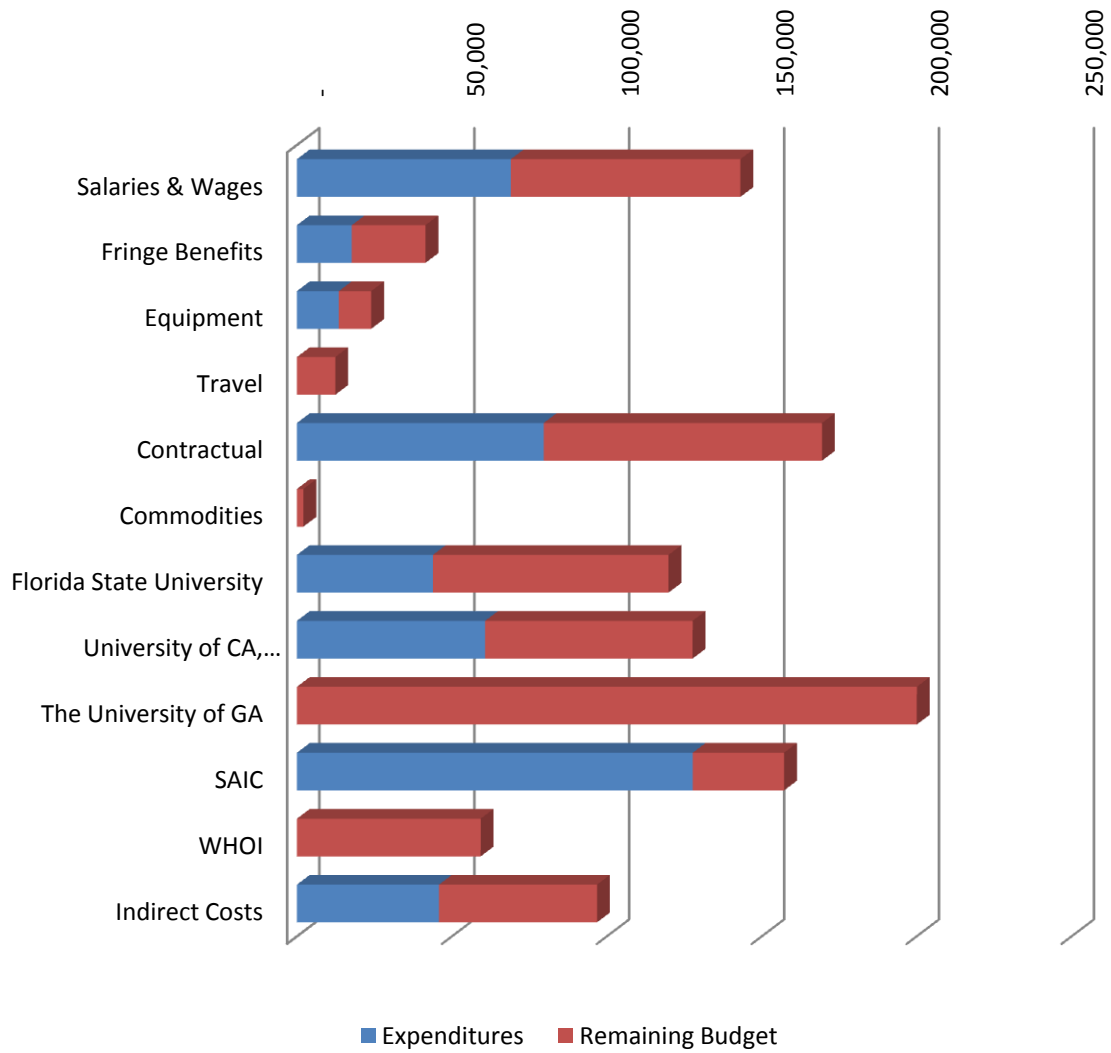
FY2008 through 6/30/11



Mississippi Mineral Resources Institute
DOE DE-FC26-06NT42877
Funding Status as of
6/30/11

| FY2009 | Expenditures | Remaining Budget |
|--|---------------------|-------------------------|
| Salaries & Wages | 87,602 | - |
| Fringe Benefits | 25,405 | - |
| Equipment | 13,544 | (3,544) |
| Travel | 7,400 | - |
| Contractual | 8,717 | - |
| Commodities | 2,664 | 4,104 |
| Florida State University | 88,508 | - |
| University of CA, Santa Barbara | 78,118 | - |
| University of South Carolina | 177,254 | 107,646 |
| The University of GA | 134,385 | 60,644 |
| SAIC | 158,252 | - |
| WHOI | 79,834 | 35,716 |
| Indirect Costs | 41,775 | - |
| Total | 903,458 | 204,566 |

FY2010 through 6/30/11



Mississippi Mineral Resources Institute
DOE DE-FC26-06NT42877
Funding Status as of
6/30/11

| FY2010 | Expenditures | Remaining Budget |
|--|---------------------|-------------------------|
| Salaries & Wages | 69,052 | 74,099 |
| Fringe Benefits | 17,734 | 23,780 |
| Equipment | 13,544 | 10,456 |
| Travel | 5 | 12,395 |
| Contractual | 79,657 | 89,843 |
| Commodities | - | 2,108 |
| Florida State University | 43,922 | 76,059 |
| University of CA, Santa Barbara | 60,755 | 66,988 |
| The University of GA | - | 200,121 |
| SAIC | 127,771 | 29,488 |
| WHOI | - | 59,328 |
| Indirect Costs | 45,873 | 51,022 |
| Total | 458,313 | 695,687 |

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 with the analysis of additional industry standard data from WesternGeco. An additional multibeam survey and a side-scan survey of extremely high resolution have been obtained (May) 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 will aid in constraining the shallow data. Chemical surveying has added valuable information to the site baseline characterization. The polarity-preserving chirp system has been received and is being installed on the NIUST AUV for survey work at MC118, simultaneously with the debugging and adjustments to the accompanying software. The photo-AUV, Mola Mola is scheduled to survey MC118 in July, 2011.

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

Major recoveries were achieved during this period: the BBLA and the ROVARD, both with multiple instruments and datasets. Additional attempts to recover instruments – primarily the PFA-2 - are scheduled for 2011 and 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. All four arrays are ready for deployment but will likely be deployed in installments as deck-space and maneuvering have turned out to be even more challenging than anticipated.

Milestone 4: Complete installation of all Observatory components and collect geophysical data for input into model (Task 9). Due to deployment logistics, this milestone will necessarily follow the deployment of the horizontal arrays and collection of geochemical sensors. However, time-series pore-fluid and JPC data will be soon be available to modeling efforts.

Milestone 5: Complete additional surveys – SSSR, 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. will use our 2005 survey to calibrate a new AUV they are testing for the Navy. The hydrophone array – necessary for the SSSR 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.

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.

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 are still being 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 August, 2011. This task depends on TDI's schedule. We hope to collect these data in the fall of 2011..

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 June, 2011. This task has slid as the April cruise had to be cancelled in light of certification issues with the vessel. We will reschedule 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 estimated to be complete by October, 2011. 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 is the goal of an October, 2011 AAPG meeting.

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 are very promising and work is ongoing to improve the carriage and scale display. The goal is to use it on our 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.

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 are incomplete. Additional devices are designed to be deployed on

the next ROVARD deployment.

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. An October cruise is scheduled but will likely not include the lander. If delayed until 2012, the new MIMS should be ready to include and this would be a great advance.

ACCOMPLISHMENTS

Major accomplishments of this reporting period include:

Advances in mapping capabilities

First seafloor habitat maps from MC118 have been drafted (paper in prep)

Recovery of jumbo piston cores from targeted positions on Woolsey Mound

Proven ability to maximize chances of recovering hydrate via use of integrated systems approach (primarily seismic)

Collection of 4-C data via OBS instruments; both active and passive source data acquired

Successful proof of concepts and recovery of data in support of CH₄ plumes in the water-column near MC118

Successful tests and repeat performances of additional functions of the SSD (push-cores, video-surveying)

Deployments: ADCP mooring, BBLA

Recovery of data remotely via optic modem

Innovative deployment method – ROVARD – proven instrument recovery capability

Recovery of geochemical data and sediment samples from the near-seabed and shallow seabed – BBLA and CSA and ROVARD

Coordination of multiple methods of water-column chemical evaluation

High-Definition side-scan sonar data from MC118

New Multibeam survey from MC118

PROBLEMS/DELAYS

The majority of delays in the program derive from one of two sources, or a combination of the two: weather and electronics at 900m water depth. Deep Water Horizon spill continues to complicate our work schedule as many Consortium members are obligated to the recovery effort. This is a major factor in the cancellation of our August cruise – the mass spectrometer will be in use 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 tow of our four shop guys gone (1 retired; 1 at another job) We have hired one replacement but are still feeling very shorthanded, having lost 40 years of experience at sea between these two employees. Having cancelled two cruises has 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 deployment of the HLAs has been rescheduled but the projects that are depending upon this critical achievement remain in “stand-by” mode. The ROVARD was designed, built and employed in an effort to alleviate some of the

back-log. It is currently being evaluated for corrosion and will be rebuilt/refitted with new/refurbished instruments for a fall or spring deployment.

Weather dictates cruise scheduling and successes. Although extra cruises have been scheduled for 2011, 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. Additional Western Geco dataset for coordinated (with USC) use at CMRET
2. 4C data
3. JPCs and associated data
4. New multibeam survey
5. Very high resolution side-scan sonar survey
6. Additional modeling
7. Cruise accomplishments and deployments: proof of ROVARD, optic modem, CSA, peepers
8. Progress Report from July– December, 2010
9. Publications and presentations at national meetings – many in press

REFERENCES

References for individual reports follow the appropriate section directly.

RECENT PUBLICATIONS BY CONSORTIUM MEMBERS:

2011

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