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Covering research during the period
1 June, 2002 through 30 September, 2008

Support of Gulf of Mexico Hydrate Research Consortium: Activities to Support Establishment of a Sea Floor Monitoring Station Project

Submitted by:
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SUPPORT OF GULF OF MEXICO HYDRATE RESEARCH CONSORTIUM: ACTIVITIES TO SUPPORT ESTABLISHMENT OF A SEA FLOOR MONITORING STATION PROJECT

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FINAL TECHNICAL REPORT
1 APRIL, 2008 THROUGH 30 SEPTEMBER, 2008

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PREPARED BY THE MANAGEMENT TEAM,
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FY03 Subcontractors:

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Task 2: Construction of the Prototype Sea Floor Probe

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Task 3: Acoustic System for Monitoring Gas Hydrates

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Task 4: Construction and Testing of an Electromagnetic Bubble Detector and Counter

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Task 5: Mid-Infrared Sensor Systems for Continuous Methane Monitoring in Seawater

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FY04 Subcontractors:

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Task 2: Applications of VSP Technology for Evaluation of Deep-Water Gas Hydrate Systems*

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

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Task 4: Microbial Activity Related to Gas Hydrate Formation and Sea-floor Instabilities

FY05 Subcontractors:

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Task 1: Data Management and Archiving System and Matched Field Inversion Software Development for the Sea-floor Monitoring Station

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Task 2: Experiment to generate Shear Waves in the Sea-floor and Record them with a Horizontal Line Array

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

* includes seismo-acoustic characterization of sea-floor properties and processes at the hydrate monitoring station until vertical seismic profile (VSP) data can be collected

DISCLAIMER

ABSTRACT

The Gulf of Mexico Hydrates Research Consortium (GOM-HRC) was established in 1999 to assemble leaders in gas hydrates research that shared the need for a way to conduct investigations of gas hydrates and their stability zone in the Gulf of Mexico *in situ* on a more-or-less continuous basis. The primary objective of the group is to design and emplace a remote monitoring station or sea floor observatory (SFO) on the sea floor in the northern Gulf of Mexico, in an area where gas hydrates are known to be present at, or just below, the sea floor and to discover the configuration and composition of the subsurface pathways or "plumbing" through which fluids migrate into and out of the hydrate stability zone (HSZ) to the sediment-water interface. Monitoring changes in this zone and linking them to coincident and perhaps consequent events at the seafloor and within the water column is the eventual goal of the Consortium. This mission includes investigations of the physical, chemical and biological components of the gas hydrate stability zone – the sea-floor/sediment-water interface, the near-sea-floor water column, and the shallow subsurface sediments. The eventual goal is to monitor changes in the hydrate stability zone over time.

Establishment of the Consortium succeeded in fulfilling the critical need to coordinate activities, avoid redundancies and communicate effectively among those involved in gas hydrates research. Complementary expertise, both scientific and technical, has been assembled to promote innovative methods and construct necessary instrumentation.

Following extensive investigation into candidate sites, Mississippi Canyon 118 (MC118) was chosen by consensus of the Consortium at their fall, 2004, meeting as the site most likely to satisfy all criteria established by the group. Much of the preliminary work preceding the establishment of the site - sensor development and testing, geophysical surveys, and laboratory studies - has been reported in agency documents including the Final Technical Report to DOE covering Cooperative Agreement DE-FC26-00NT40920 and Semiannual Progress Reports for this award, DE-FC26-02NT41628.

Initial components of the observatory, a probe that collects pore-fluid samples and another that records sea floor temperatures, were deployed in MC118 in May of 2005. Follow-up deployments, planned for fall 2005, had to be postponed due to the catastrophic effects of Hurricane Katrina (and later, Rita) on the Gulf Coast. SFO completion, now anticipated for 2009-10, has, therefore, been delayed.

Although delays caused scheduling and deployment difficulties, many sensors and instruments were completed during this period. Software has been written that will accommodate the data that the station retrieves, when it begins to be delivered. In addition, new seismic data processing software has been written to treat the peculiar data to be received by the vertical line array (VLA) and additional software has been developed that will address the horizontal line array (HLA) data. These packages have been tested on data from the test deployments of the VLA and on data from other, similar, areas of the Gulf (in the case of the HLA software).

During the life of this Cooperative Agreement (CA), the CMRET conducted many cruises. Early in the program these were executed primarily to survey potential sites and test sensors and equipment being developed for the SFO. When MC118 was established as the observatory site, subsequent cruises focused on this location. Beginning in 2005 and continuing to the present, 13 research cruises to MC118 have been conducted by the Consortium. During September, 2006, the Consortium was able to secure 8 days aboard the R/V *Seward Johnson* with submersible Johnson SeaLink, a critical chapter in the life of the Observatory project as important documentation, tests, recoveries and deployments were accomplished during this trip (log appended). Consortium members have participated materially in a number of additional cruises including several of the NIUST autonomous underwater vehicle (AUV), *Eagle Ray*. Activities reports summarize cruise activities, including objectives, how they were met or not met, and challenges. Deployment cruises are scheduled for 2009 that are designed to complete installation of the major observatory components.

Semiannual and Annual Meetings of the Gulf of Mexico Gas Hydrates Research Consortium were held in Oxford, Mississippi, each fall and spring during the life of this CA, with the exception of fall, 2006.

The seafloor monitoring station/observatory is funded approximately equally by three federal Agencies: Minerals Management Services (MMS) of the Department of the Interior (DOI), National Energy Technology Laboratory (NETL) of the Department of Energy (DOE), and the National Institute for Undersea Science and Technology (NIUST), an agency of the National Oceanographic and Atmospheric Administration (NOAA). The project is administered by the Center for Marine Resources and Environmental Technology (CMRET) at the University of Mississippi. The CMRET arranges and hosts Consortium meetings, cruises and cooperations and provides a single point of contact between funding agencies and Consortium participants. The CMRET is responsible for all reporting related to this CA including technical reporting, informal monthly reports and reports of meetings and cruises.

Subcontractors have fulfilled their technical reporting requirements in previously submitted reports; with the exception of Barrodale Computing Company, all are appended here. For Barrodale, brief summaries are here provided. Their entire programming report is available in the CMRET's reports to DOE, 41628R12 (June 1, 2005 – September 30, 2005) and 41628R14 (October 1, 2005 – March 31, 2006).

Briefly, the following projects, funded by DOE have been completed:

FY03: Task 1: Continuation of Work on the Vertical Line Array (VLA): The VLA, built and tested as a stand-alone acoustic array under CA 40920, led to the production of an improved VLA integrated into the observatory and linked, fiber-optically to a data recovery system.

Task 2: Construction of the Prototype Sea Floor Probe (SFP): The SFP has been completed, used to recover 10m cores and to deploy probes (to date, thermister and pore-fluid probes). It is available for additional deployment

and recovery operations.

Task 3: Acoustic System for Monitoring Gas Hydrates: This system was designed but not built.

Task 4: Construction and Testing of an Electromagnetic Bubble Detector and Counter: The bubble-counter was successfully tested under laboratory conditions, in shallow water at a known vent, and at MC118.

Task 5: Mid-Infrared Sensor Systems for Continuous Methane Monitoring in Seawater (MIR): The MIR was designed, built and laboratory-tested but the cost of construction of a suitable pressure chamber to enable its use at 1000m depth was never met.

Task 6: Seismo-Acoustic Characterization of Sea Floor Properties and Processes at the Hydrate Monitoring Station: The shear sled was built and tested and the technology incorporated into other systems for shear-wave generation and data recovery.

FY04: Task 1: Data Management and Processing Software for the Sea-floor Monitoring Station: The software has been written and tested and now awaits data input from the observatory. Barrodale has agreed to debug the product when data arrive.

Task 2: Applications of vertical seismic profiling (VSP) Technology for Evaluation of Deep-Water Gas Hydrate Systems: A data-processing code has been developed to analyze 4C OBS P-wave and S-wave data acquired with receivers positioned on the seafloor and with seismic sources positioned at the sea surface and has been used successfully on data from other sites.

Task 3: Coupling of Continuous Geochemical and Sea-floor Acoustic Measurements: A variety of pore-fluid sampling devices have been deployed at the observatory site. Samples retrieved have defined areas of brine and methane rich fluids with distinct isotopic signatures.

Task 4: Microbial Activity Related to Gas Hydrate Formation and Sea-floor Instabilities: Hydrate formation rates and crystal initiation times in a series of core samples from MC798 and MC118 were measured in the laboratory as a function of depth below seafloor and as a function of lateral displacement at the seafloor surface. Results suggest sulfate zone depth, bioactivity, pore-water salinity, mineral content, bioproducts coating sediment particles, and sediment particle sizes impact hydrate nucleation and formation in near-surface sediments.

FY05: Task 1: Data Management and Archiving System and Matched Field Inversion Software Development for the Sea-floor Monitoring Station: The software has been written and tested and now awaits data from the observatory. Barrodale has agreed to debug the product when data arrive.

Task 2: Experiment to generate Shear Waves in the Sea-floor and Record them with a Horizontal Line Array: The in-water test was performed with successful recovery of accelerometer shear data generated from the MMRI-developed seismic gun shear-sled. The shear data exhibited

excellent signal to noise ratios.

Task 3: Coupling of Continuous Geochemical and Sea-floor Acoustic Measurements: A variety of pore-fluid sampling devices have been deployed at the observatory site. Samples retrieved have defined areas of brine and methane rich fluids with distinct isotopic signatures.

Final Reports, prepared by the subcontractors, are appended to this report.

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INTRODUCTION/BACKGROUND

The Gulf of Mexico Gas Hydrates Research Consortium (GOM-HRC) was organized in 1999, with the goal of establishing a sea-floor observatory (SFO) to monitor and 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 SFO with a variety of sensors that would enable the determination of a steady-state description of physical, chemical and thermal conditions in its local environment as well as to detect temporal changes of those conditions: hydrate formation and dissociation, fluid venting to the water column, associated microbial and/or chemosynthetic communities' dynamics. Models developed from these studies should provide a better 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.

Many portions of the SFO have changed or evolved since the original design was conceived; however, the purpose – to monitor the sea-floor and near sea-floor for changes deriving from hydrate formation and/or dissociation – remains unchanged. The project is cosponsored by Minerals Management Services (MMS - Department of the Interior, DOI), The Seabed Technology Research Center (STRC) branch of the National Institute for Undersea Science and Technology (NIUST), a part of the National Undersea Research Program (NURP) of the National Oceanic and Atmospheric Administration (NOAA), Department of Commerce (DOC), and the National Energy Technology Laboratory (NETL), Department of Energy (DOE). While each of the sponsoring agencies has its own area of particular interest (MMS: the impact of formation or dissolution of hydrates on sea-floor stability/instability; DOE: hydrates as a significant potential energy resource; NOAA: hydrate dissolution products – hydrocarbon fluids, water, and greenhouse gases – venting to the water column and, eventually the atmosphere), they acknowledge the advantage to all in the cooperative effort to establish a functioning observatory in the hydrate stability zone. 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

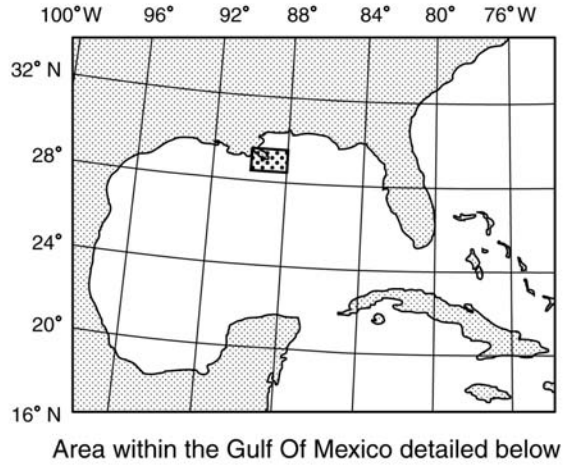
A consortium has been assembled for the purpose of consolidating both the laboratory and field efforts of leaders in gas hydrates research. Established at and administered by the University of Mississippi's Center for Marine Resources and Environmental Technology (CMRET), the Consortium, has, as its primary objective, the design and emplacement of a remote monitoring station or sea-floor observatory (SFO) on the sea floor in the northern Gulf of Mexico by the year 2009. 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 begun assembling 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. Central to the establishment of the Consortium is the need to coordinate activities, avoid redundancies and promote effective and efficient communication among researchers in this growing area of research. Complementary expertise, both scientific and technical, has been assembled; collaborative research and

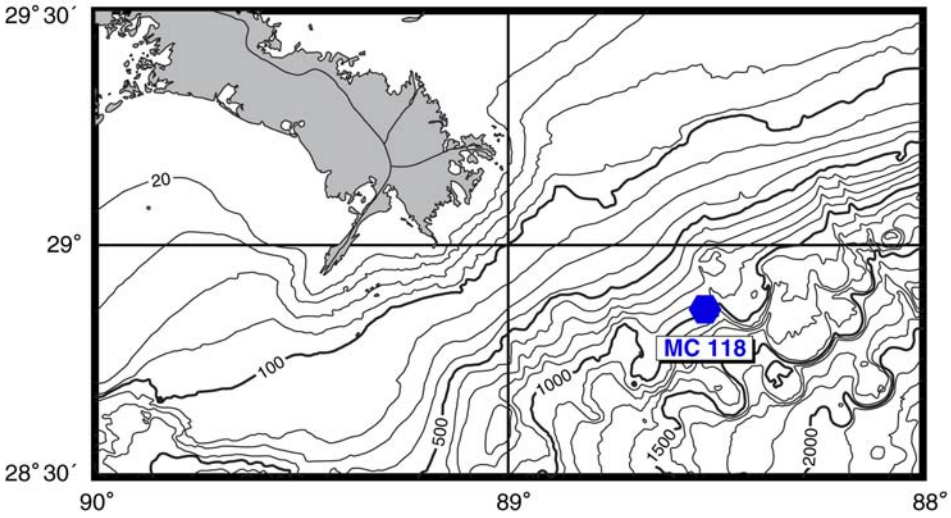
coordinated research methods have grown out of the Consortium and design and most construction of instrumentation for the sea-floor station are essentially complete.

Following several years of careful investigation and sensor research, development, and testing, Mississippi Canyon 118 (MC118) was selected by unanimous consensus of the Consortium members attending their fall meeting, 2004, as the site most desirable for the location of the SFO. In spring, 2005, the First Phase Sea-floor Probe (SFP) installation was completed successfully. Two sub-sea-floor arrays were emplaced in the sea-floor at MC118, the site of the SFO; a thermistor array (TA), and a geochemical, pore-fluid chemistry, and pressure sensor array (PFA) were deployed using the MMS gravity-driven SFP. The Second Phase SFO installation, scheduled for September, 2005, was disrupted by the severe hurricane season in the Northern Gulf of Mexico. However, cruise time was eventually secured and test deployments of nearly all station systems took place from 2006 through spring 2008.

The SFO was designed to accommodate the possibility of expanding its capabilities to include biological monitoring. A portion of FY04 funding from the MMS was directed toward this effort to support the study of chemosynthetic communities and their interactions with geologic processes. In addition, results will provide an assessment of environmental health in the area of the station. NOAA -NURP has, as a focal point, investigations of the effects of deep sea activities on world atmosphere and therefore, weather. In July of 2005, the Director of the National Institute for Undersea Science and Technology (NIUST) of NOAA-NURP made a portion of that agency's budget available *via* competitive grants to researchers with proven expertise in microbial research. A sea-floor microbial observatory is an objective of that agency and these sponsored projects sited at the SFO are designed to fulfill that directive.

The centerpiece of the monitoring station, as originally conceived, is a series of vertical line arrays of sensors (VLAs), to be moored to the sea floor. Each VLA was to have extended approximately 200 meters from the sea-floor. Sensors in the VLAs include hydrophones to record water-borne acoustic energy (and measure sound speed in the lower water column), thermistors to measure water temperature, tilt meters to sense deviations from the vertical induced by water currents, and compasses to indicate the directions in which the deviations occur. During discussions among the members of the geophysical subgroup of the Consortium, it was discovered that the project may be better served if some vertical arrays are converted to horizontal line arrays (HLAs). The horizontal water-bottom arrays were to have consisted of hydrophones and 3-component accelerometers laid upon, and pressed into, the soft sediment of the sea-floor, arranged in a cross so that they simulate two perpendicular arrays. The contract for the construction of the HLAs has been rewritten to reflect some of the findings of the June, 2007, cruise as well as the input of the geophysicists working with noise data and shear data. The new configuration of the arrays is designed to maximize the likelihood that they may later be useful for monitoring seismic events and hurricanes. Four hydrophone arrays, each 500m in length, will be deployed on the surficial deposits of the sea-floor at the SFO at MC118. They will be capable of collecting compression-wave data, via hydrophones, and sending them to the integrated Data Power Unit (IDP). Accelerometers will be added to the MS/SFO at a future date.



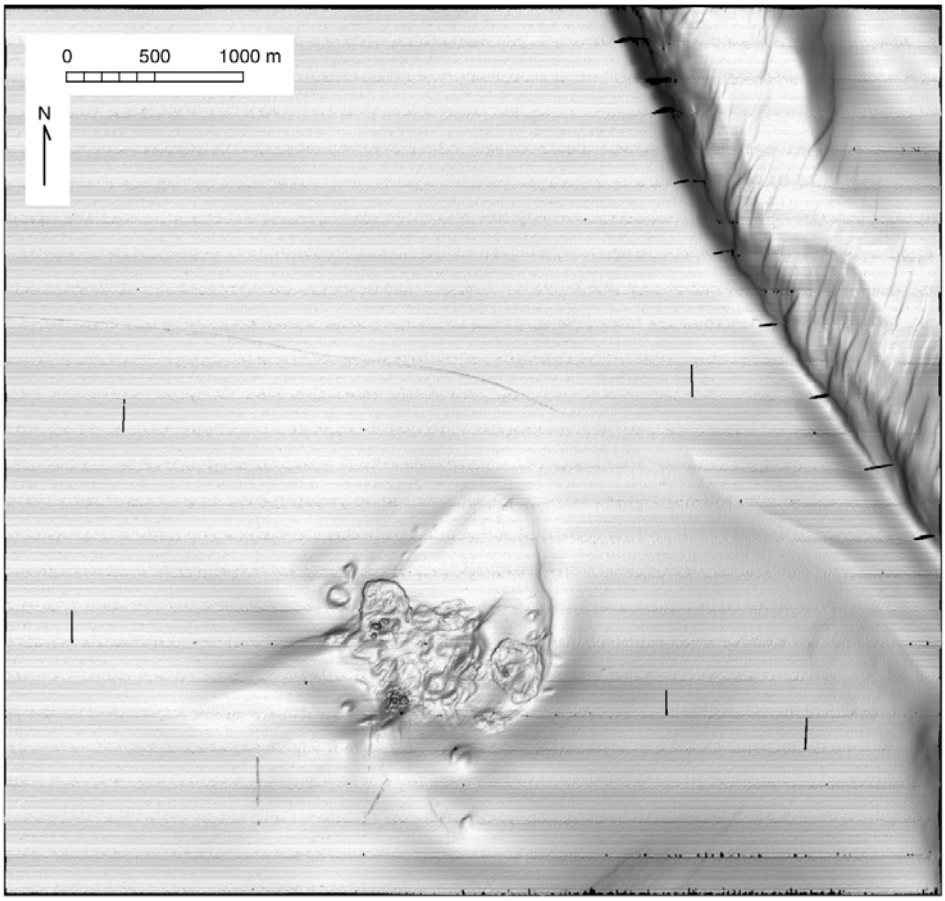


Site of the GOM-HRC's Monitoring Station/Sea-Floor Observatory, MC118

The prototype DOE-funded VLA has been completed and tested together with the associated data-logging and processing systems. Processing techniques have been developed for vertical array data by Consortium participants funded by the MMS.

In May, 2005, the Sea-Floor Probe (SFP) was used to retrieve core samples from MC118 as part of the effort to select sites appropriate for deployment of the geophysical and geochemical probes. The northwestern portion of the mound area defined on images recovered during a C&C (Chance and Chance) autonomous underwater vehicle (AUV) survey April 30-May 2, 2005, was selected for probe deployments based on information from these cores. Both the pore-fluid array and the geophysical line array were deployed *via* SFP at MC118 in May, 2005.

Additional SFO deployments, scheduled for September and October, 2005, were delayed due to the devastation of the Mississippi Gulf Coast and environs by Hurricane



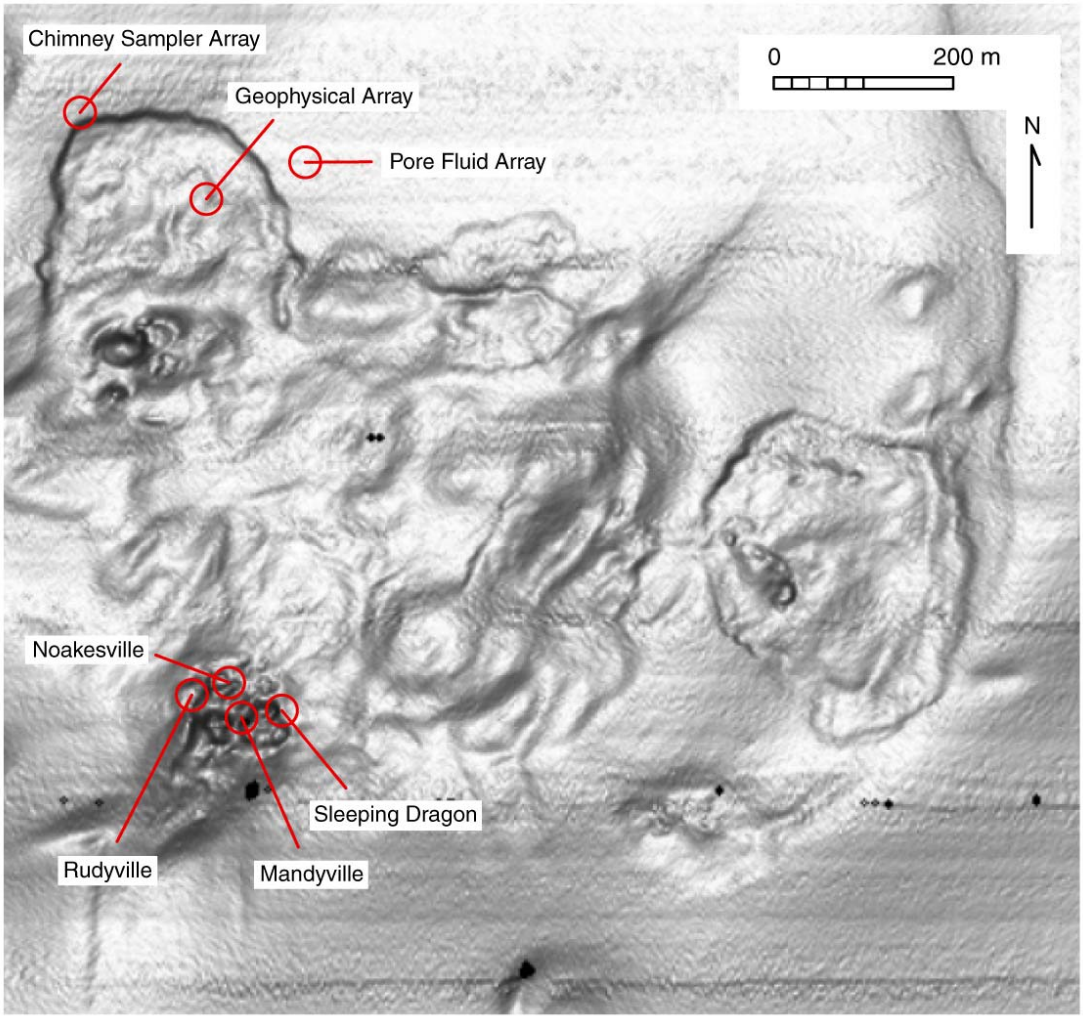
Backscatter image of the sea-floor at MC118

Katrina and, to a lesser extent, the Louisiana Gulf Coast by Hurricane Rita. The immediate cause for delay was the removal of the *M/V Ocean Quest*, the vessel that, with its two submersibles, was to have provided the platform from which many of the bottom-founded sensors would have been deployed and cable connections made. It would also have provided the visual survey needed to make optimal choices of deployment sites for station components

In October, 2005, March, April and June, 2006, the CMRET conducted a series of cruises to MC118 aboard the *R/V Pelican*. These cruises accomplished many of the tasks that had been planned for the *Ocean Quest*, including the recovery of more samples from MC118 and the deployment of a microbial filter device. A complete SSDR (surface-source/deep-receiver) high resolution seismic survey was made and a drift camera designed, deployed and used successfully to survey the sea-floor, visually. An ultra-short base-line system (USBL) was added to the SFP, providing pin-point accuracy for core sites and for deployments made using this system. However, a submersible or ROV was still required to accomplish many of the missions for which precise placement of instruments on the sea-floor was required.

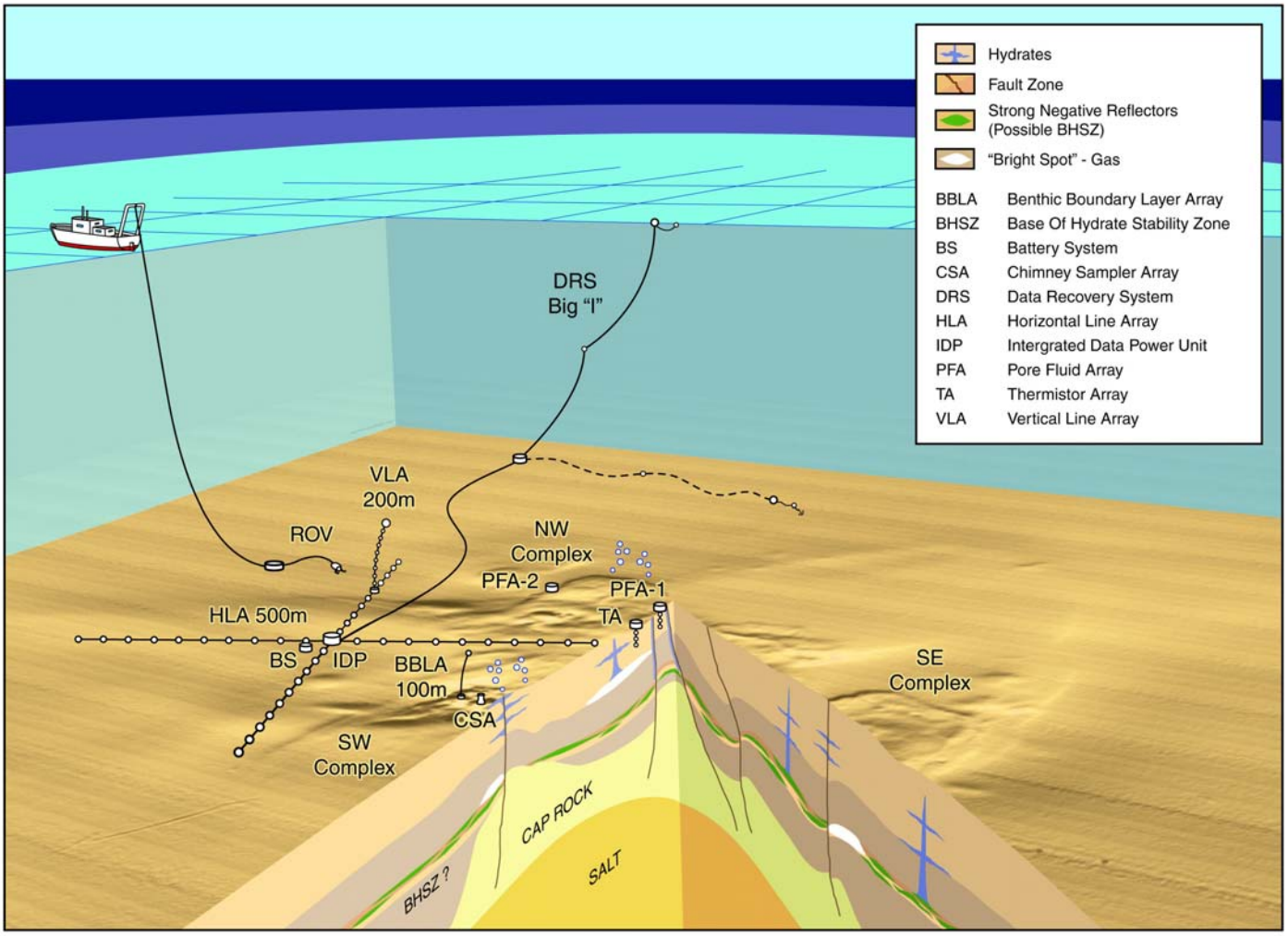
Following several “false starts”, anticipating the use of other vessels which never did become available, the CMRET eventually secured seven days of ship time aboard the R/V

Seward Johnson with use of its manned-submersible, the Johnson SeaLink. This vessel combination was used to retrieve the osmopump packages from the PFA and data-loggers deployed in 2005, to conduct visual surveys of the observatory site at MC118 and to deploy, and in some cases recover, sensors and experiments. Experiments designed to assess microbial communities and activities, hydrate host materials, and composition of pore-fluids were left on the sea-floor for several months' data collection. Cruises to recover these instruments and data-loggers were scheduled for 2007. Delays attributable to hurricane activity in the Gulf of Mexico caused scheduling and deployment difficulties but many sensors and instruments were completed during this period. A second PFA osmosampler was placed on the sea-floor near the southwestern crater at the site designated "Rudyville". Pore water equilibrators or "peepers" were installed at three sites at MC118. In addition to samples and data collected from these instruments, methane concentration and isotope samples were collected from 8 cores that were collected using the SeaLink at a variety of sites along transects across microbial mats.



Locations of Monitoring Station/Sea-floor Observatory instruments, on the hydrate/carbonate mound at MC118 (image acquired by C&C Technologies and reprocessed by Leonardo Macelloni and Alessandro Bosman).

After 1.5 years, the Pore-Fluid Array's (PFA's) instrument package was recovered and replaced successfully during the September Johnson SeaLink dives. The four ports collecting pore-fluids *via* OsmoSamplers were located in the overlying water and 1.2 m, 3.2 m, and 8.5 meters below the seafloor (mbsf). During the months following the retrieval of the sample box, pore-fluids were extracted from the sampler coils and measured for chloride, sulfate, and methane concentrations and methane isotope ratios. Normal seawater conditions were found in the overlying waters, while at 8.5 mbsf, chloride concentrations provide compelling evidence for the intrusion of brine fluids. Brine was further indicated by the absence of sulfate. As expected with brine fluids, they were characterized by high methane concentrations.



Gas Hydrate Sea-Floor Observatory - Mississippi Canyon Block 118

Defining mechanisms of sea-floor hydrate formation to aid in locating hydrates on the sea-floor is a long-term component of Consortium efforts. Laboratory findings relating to hydrate induction time and formation rates have shown that hydrate formation is catalyzed by biosurfactants, products of microbial activity. The microbes' bioproducts' hydrophobic moieties collect methane while the hydrophilic moieties collect and structure

water, thus emplacing the components necessary for hydrate formation. This in turn, explains the close affiliation of particular bacteria with hydrate outcrops on the sea-floor and leads to further questions regarding their interactions. Some generalizations can be made regarding hydrate formation: formation rates increase with depth until a maximum is reached and induction time decreases with depth until a minimum is reached. These generalizations are influenced, and in some cases overcome, by other factors influencing hydrate formation such as salinity, the depth of the sulfate zone, availability of gases, bioactivity, clay mineral composition, bioproducts coating sediment grains, and sediment size.

Software has been written that will accommodate the data that the station retrieves, when it begins to be delivered. In addition, new seismic data processing software has been written to treat the peculiar data to be received by the vertical line array (VLA) and additional software has been developed that will address the horizontal line array (HLA) data. These packages have been tested on data from the test deployments of the VLA and on data from other, similar, areas of the Gulf (in the case of the HLA software).

Researchers at the Exploration Geophysics Laboratory (EGL) have developed a new approach to processing 4-component (4C) seismic data acquired with multicomponent sensors deployed on the seafloor. Utilizing the large elevation difference between source and receiver allows deep-water 4C data to be processed with algorithms similar to those used to make images from vertical seismic profile (VSP) data (also acquired with a large elevation difference between source and receiver). This processing approach produces images that have much higher resolution of geology located near the receiver station than do standard 4C data-processing techniques.

New 4C ocean bottom cable (OBC) seismic data-processing software structured to optimize image resolution in the immediate vicinity of seafloor seismic sensors has been written by EGL researchers. While this novel data-processing strategy offers no advantage for imaging deep geology, it produces optimal images of geology immediately below seafloor sensor stations where hydrate systems are embedded. Preliminary tests of this software have produced impressive high-resolution images of near-seafloor strata. 4C data are scheduled to be acquired across MC118 in late 2009. Both active (airgun) and passive (ship and wave noise) sources will be used to record responses on both industry nodes and Consortium HLAs. Comparison of results of the two data-collection techniques will provide researchers from both academia and industry with a novel data comparison of the two techniques.

Several series of cores have been collected from MC118. These cores have been logged and are in the process of being transformed into digital files for posting on the world wide web for greater accessibility to all Consortium researchers. Many noteworthy studies have resulted. Of particular interest, however, are the cores that were recovered in April, 2008, with hydrate intact. This information from an area of proven hydrate activity on the shallow subsurface was used to locate Florida State University's second pore-fluid probe on the western flank of the northwestern crater complex. With the use of USBL transducers on the SFP for both core collection and PFA deployment, the PFA was reliably located within 3m of the hydrate site.

The University of Georgia's microbial filter and the University of South Florida's mass spectrometer have been deployed and operated separately and in concert with excellent results.

Dives of the Station Service Device (SSD) have verified locations of sea-floor markers and instruments left on the sea-floor on previous site-visits. Pin-point accurate locations have been acquired for them as the SSD frame now carries its own USBL. In November, 2007, remarkable changes on the sea-floor were noted despite the extremely murky water at depth due to the amazing amount of particulate matter in the water column. The source of this suspended material and debris covering the instruments is possibly related to the changes observed in the hydrate outcrops – diminished and exhibiting slump features.

At the Annual meeting of the Consortium in Oxford, February 26-27, 2008. The keynote presentation was made by students who have synthesized their work at MC118 into a cohesive picture of the chemistry and structure of the mound at MC118, thus laying the foundations for future federally funded work at the SFO.

Partly in response to DOE's comments resulting from the peer review process, the CMRET arranged a meeting of Consortium members making key contributions to the subsurface investigations at MC118. This meeting took place the week of February 3, 2008, at the University of South Carolina (USC), Columbia, South Carolina, under the supervision of Camelia Knapp. The goals for this meeting were to synthesize subsurface data collected from MC118 and to prepare both oral and written presentations of the data and findings to date. Three students who have completed their doctorates doing hydrates research at MC118 via Consortium funding, Laura Lapham, Brad Battista, and Leonardo Macelloni, assimilated their data and presented it to three Consortium professionals – experts in marine geophysics and chemistry - for review and comment. The group established a list of priorities with which to go forward in order to establish, fully, the history and character of the hydrate-carbonate mound at MC118.

TASK SUMMARIES

Brief summaries of the tasks funded directly by DOE are presented. Some of these continue into the current cooperative agreement (DE-FC26-06NT42877) while others have been completed, changed, incorporated into new devices or technologies or, in some cases, discontinued.

FY03: Task 1: Continuation of Work on the Vertical Line Array (VLA): The VLA, built and tested as a stand-alone acoustic array under CA 40920, led to the production of an improved VLA integrated into the observatory and linked, fiber-optically, to a data recovery system. Together with the cross of four 500m HLAs, and possibly a Borehole Line Array (BHA), the VLA comprises the heart of both active and passive monitoring at the observatory. The VLA has been tested successfully under a variety of environments and has performed well except in one deployment during which its pressure (depth) restrictions were violated. The VLA is ready to be deployed at MC118.

Task 2: Construction of the Prototype Sea Floor Probe (SFP): The SFP has been completed, used to recover 10m cores and to deploy probes (to date, thermister and pore-fluid probes). The SFP has become one of the workhorses of the Consortium toolbox, reliably recovering cores under

appropriate circumstances and failing only when attempts have been made to collect gravity cores on the hardground of the mound. The incorporation of the ultra-short base-line transponder into the frame of the SFP has enabled Consortium coring project researchers to locate samples with accuracy not anticipated at the onset of this project as locations are determined at the sea-floor rather than the sea's surface. This capability has resulted in the greatly improved geological and sedimentological definition of the shallow subsea-floor at MC118.

Task 3: Acoustic System for Monitoring Gas Hydrates: The report addresses the theory of using such a system and lays out its design. Unfortunately, this system was never built and subsequent funding was not provided.

Task 4: Construction and Testing of an Electromagnetic Bubble Detector and Counter: The bubble-counter was successfully tested under laboratory conditions, in shallow water at a known vent, and at MC118. The bubble counter was deployed and recovered using the SeaLink in September, 2006. Although it functioned well, parameters of its deployment make it not very useful to a project of this scope. The Consortium needs to develop a process whereby to calculate bubble volumes over a broader area/volume than was possible using this device.

Task 5: Mid-Infrared Sensor Systems for Continuous Methane Monitoring in Seawater (MIR): The MIR was designed, built and laboratory-tested but the cost of construction of a suitable pressure chamber to enable its use at 1000m depth was never met. This system proved to be of appropriate sensitivity and may, at some future date, be incorporated into the SFO. However, at this time, the cost projected to preserve its integrity at 900m water depth is prohibitive for the Consortium

Task 6: Seismo-Acoustic Characterization of Sea Floor Properties and Processes at the Hydrate Monitoring Station: The shear sled was built and tested and the technology incorporated into other systems for shear-wave generation and data recovery. This system can still be used as an active source of shear-wave energy but it is likely not appropriate to the vicinity of the HLAs, designed primarily for the capture of passive energy.

FY04: Task 1: Data Management and Processing Software for the Sea-floor Monitoring Station: The software has been written and tested and now awaits data from the observatory. Barrodale has agreed to debug the product when data arrive. For a detailed report, see the Consortium's report to DOE, 41628R12 (June 1, 2005 – September 30, 2005).

Task 2: Applications of VSP Technology for Evaluation of Deep-Water Gas Hydrate Systems: A data-processing code has been developed to analyze 4C OBS P-wave and S-wave data acquired with receivers positioned on the seafloor and with seismic sources positioned at the sea surface and has been used successfully on data from other sites. An appropriate test at MC118, performed in cooperation with CGG Veritas, is planned for 2009.

Task 3: Coupling of Continuous Geochemical and Sea-floor Acoustic Measurements: A variety of pore-fluid sampling devices have been deployed at the observatory site. Samples retrieved have defined areas of brine and methane rich fluids with distinct isotopic signatures. Chemical signatures indicative of atypical activity have been plotted against geophysical data from

MC118 and areas of suspected venting identified for further study.

Task 4: Microbial Activity Related to Gas Hydrate Formation and Sea-floor Instabilities: Hydrate formation rates and crystal initiation times in a series of core samples from MC798 and MC118 were measured in the laboratory as a function of depth below seafloor and as a function of lateral displacement at the seafloor surface. Results suggest sulfate zone depth, bioactivity, pore-water salinity, mineral content, bioproducts coating sediment particles, and sediment particle sizes impact hydrate nucleation and formation in near-surface sediments. These studies are being continued with particular attention to deeper sample recovery and peculiarities of sample mineralogy.

FY05: Task 1: Data Management and Archiving System and Matched Field Inversion Software Development for the Sea-floor Monitoring Station: The software has been written and tested and now awaits data from the observatory. Barrodale has agreed to debug the product when data arrive. For a detailed report, see the Consortium's report to DOE, 41628R14 (October 1, 2005 – March 31, 2006).

Task 2: Experiment to generate Shear Waves in the Sea-floor and Record them with a Horizontal Line Array: The in-water test was performed with successful recovery of accelerometer shear data generated from the MMRI-developed seismic gun shear-sled. The shear data exhibited excellent signal to noise ratios. This experiment will be repeated with alternative configurations and signal timings.

Task 3: Coupling of Continuous Geochemical and Sea-floor Acoustic Measurements: A variety of pore-fluid sampling devices have been deployed at the observatory site. Samples retrieved have defined areas of brine and methane rich fluids with distinct isotopic signatures. Chemical signatures indicative of atypical activity have been plotted against geophysical data from MC118 and areas of suspected venting identified for further study.

EXPERIMENTAL: MONITORING STATION SYSTEMS STATUS SUMMARY

Geophysical Sensor Systems

The geophysical sensor systems design has evolved since its conception, as described in earlier proposals and reports, primarily in response to changing circumstances and advancements in geophysical technology. Briefly, the original plan to monitor changes in the hydrate stability zone with a net of five 200m water-column vertical acoustic line arrays (VLAs) gave way to a plan for a single VLA tied into one leg of four horizontal line arrays (HLAs) laid out in a cross pattern on the seabed. The advantages of the newer design include better 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 wind-driven wave noise, as a passive acoustic energy source. Additionally, microseisms, known to occur frequently in the region, produced by ubiquitous salt movements as well as by deeper, basement-related seismic events, can be recorded and possibly linked to phenomena - such as pore fluid migration and large scale episodic fluid venting - observed at the study site.

Plans to access one or more boreholes for the installation of multi-sensor bore-hole vertical line arrays (BLA) (p- and s-wave, plus thermistor, pore fluid and pressure) have thus far proven elusive. Beginning in the spring of 2003, communications with the Joint Industries Project (JIP) gave hope to accessing a site in Atwater Valley. Regrettably, the 1300m water depth at the site proved too great a challenge for the various sensor technologies available to the Consortium, as well as funds available for the project. More recently, plans to core, log and emplace down-hole arrays at the observatory site, MC118, were aborted when a change in drilling vessels available to the JIP forced cancellation of planned operations at MC118. Although all attempts thus far for acquiring a borehole within our budget parameters have met with frustration, the Consortium continues to investigate borehole opportunities, optimistic that an affordable option will become available.

In the meantime, utilizing SFPs to emplace various sensor arrays has been successful. In spring, 2005, a gravity driven version of the SFP was used to emplace a 10m Thermistor Array (TA), (formerly referred to as the geophysical line array). The data logger for the TA was recovered on a Johnson SeaLink (JSL) Cruise of September 2006 with 5 months of interesting data. An improved version of the data logger is scheduled for deployment in 2009. A much deeper TA would be incorporated in the hoped-for future composite BLA.

Currently the water column VLA (designed for this project, built and tested successfully and modified from autonomous to station configuration) has been completed and is now awaiting installation along with the seabed HLA horizontal cross. The HLAs have been delayed due to manufacturing of certain special order, fiber-optic cables, but are now complete, with deployment scheduled for the next cruise with reasonably calm seas predicted. For the record, the water column, acoustic VLA in its various configurations, was funded entirely by DOE while funding for the more costly seabed HLA horizontal cross was divided among the three agencies: DOE with cabling and connections; NOAA with hydrophones; and MMS with data loggers.

Geochemical Sensor Systems

Evolution of geochemical sensor systems has occurred for reasons similar to those for progress and delays of the geophysical systems. A 200m water-column oceanographic line array (OLA) was planned to monitor hydrocarbon pore-fluids venting from surficial sediments in the vicinity of hydrate mounds and transiting the lower water column. As experience and an improved understanding of the hydrocarbon system and hydrography of the lower water column have emerged, a more comprehensive approach has been developed.

The OLA, DOE/NOAA, has been modified to a 60m length and designed to monitor the benthic boundary layer, hence the new designation Benthic Boundary Layer Array (BBLA). In addition, a small barrel-like, chimney sampler array (CSA), NOAA/NIUST, outfitted with sensors, was fabricated by STRC subcontractors and tested in shallow water. The prototype unit was deployed and tested at MC118 in September, 2006.

Further, the pore-fluid sampling array (PFA), was funded by DOE, and designed to sample and analyze pore-fluid chemistry of the shallow, near-seabed HSZ. This first PFA was completed in time for deployment during May 2005 cruise using a 10m SFP in much the same way as the TA was emplaced. The osmo-sampler retrievable section was recovered on the September 2006 JSL dive along with the TA data-logger. Recovered water samples have since been processed yielding valuable pore-fluid chemistry data representative of its location. The PFA design and its sampling success have prompted the fabrication of a second PFA and additional pore-fluid sampling devices to expand the aerial coverage of the pore-fluid investigations to additional areas – both laterally and vertically - of interest. Most recently, 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 navigation system (USBL)). Again, it is hoped that eventually a bore hole will provide a deployment site for a longer (150m) pore-fluid circulation array (PCA) with complementary sensors, as envisioned since the SFO's beginning.

Microbial Experiments

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. Studies focused on the relationships of microbes to the formation of hydrates were among the first undertaken by the Consortium and results of these research efforts include the discovery of the role of microbially-produced biosurfactants in hydrate association. The possibility of adding a microbial component to the station has long been discussed. In spring, 2005, the NIUST Director made competitive funding available specifically for researchers in microbiology to become involved in the mission of the SFO. Four projects were funded. All have been provided ship time (MMS) 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. Microbial collectors have been deployed and several sampling efforts have succeeded in beginning to elucidate the microbial activities at the observatory site. In this way, the SFO becomes a three-way research platform 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.

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 is now complete and scheduled for deployment at the earliest opportunity, 2009.
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 significantly extending the life of a conventional battery such as the AGM. Subsequently, a follow-up proposal was provided by MMS for a full-scale test of a bio-trickle charge system for this application. Bioconcepts reports the system is presently producing a more or less constant 8 volts (at low amperage); this system is scheduled for test deployment in 2009. 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 fitted with a wet-mateable communications link (WMCL). Most recently, however, this arrangement has been 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 lowered safely to the sea-floor, out of the reach of long-liners. This system is scheduled for deployment with the IDP on the first available cruise of 2009.
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's 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. Initial steps have been taken in development of this system: a) multipurpose suspension cable acquired, terminated and tested, successfully, using a drift camera to survey the carbonate mound at 850 to 875m depth at MC118, within the MMS restricted zone (for hydrate research); b) deployment and recovery of microbial experiments. Yet another task has been added to the SSD work order. Previously the various cable laying jobs; the 1000m fiber optic cable, connecting the IDP and pop-up buoy of the DRS, and the four 500m HLA cables of the horizontal cross, were to be conducted by the Multi-purpose Sled. Now however, with a better understanding of the seabed surface at the mound site, its rocky outcrops and biologic communities, obvious advantages will be gained by laying the cables from the SSD, via a reel towed above the seabed so as not to impact the bottom surface. The SSD will be the work-horse in deployment of the IDP and DRS systems with associated cable laying and in a subsequent deployment, underwater connection (to IDP), and laying of the HLA's and attached VLA, currently scheduled for March and June, 2009.

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 pay load capacity, making the vehicle ideal as a test platform for a variety of sensors. The 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. On the coming year's calendar is the modification (now complete), installation (AUV adapters nearing completion) and testing of the Woods Hole Oceanographic Institute's (WHOI) mass spectrometer 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 subbottom depths of 500 to 700m, navigation accuracy, noise reduction and reduction of survey time by a factor of four. Further AUV developments include a polarity-preserving/discriminating chirp sub-bottom profiler system that can 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.

CRUISE ACTIVITIES

For reports of cruise activities, see online reports at
http://www.olemiss.edu/depts/mmri/programs/ppt_list.html

Activities Report for Cruise GOM2-08-MC118 aboard the R/V Pelican to Mississippi Canyon Federal Lease Block 118 from May 31 to June 10, 2008. The purpose of the cruise was to install the Integrated Data/Power Unit and the Data Recovery System for the Seafloor Observatory, conduct a subbottom survey of the site and to deploy and/or recover instruments. Installation activities were successfully accomplished but only limited success was achieved with the other activities due to equipment and environmental issues.

Activities of a scientific research cruise to Mississippi Canyon Federal Lease Block 118 from April 22-28, 2008. The purpose of the cruise was to collect sediment samples using gravity and box coring devices, and to deploy a second Pore Fluid Array. Acoustic transponders were used in the sampling and deployment activities and provided a high degree of accuracy in these activities.

Activities of a scientific research cruise to Mississippi Canyon Federal Lease Block 118 from November 4-13, 2007. Operations included survey efforts using the station service device, exchange of the storm monitoring device, sea trials of mass spectrometer and microbial filter, and core collection.

Activities of a scientific research cruise to Mississippi Canyon Federal Lease Block 118 from July 2-8, 2007. The report describes and illustrates the second series of sea-trials for the Hydrates Research Consortium's Station Service Device or SSD, the remotely operated vehicle designed especially to support activities at the Hydrates Sea-floor Observatory at Mississippi Canyon 118.

This report covers the first of two cruises (second was June, 2007 but results are included here) to survey the site of the Hydrate Research Consortium's Sea-Floor Observatory in Mississippi Canyon Federal Lease Block 118, Northern Gulf of Mexico, using the CMRET's deep-towed Shallow Source – Deep Receiver seismic survey system, April 17-24, 2006.

Activities Report for Cruise GOM2-06-MC118 aboard the R/V *Pelican* covers the initial at-sea tests of the DeepSee Drift Camera at the site of the Sea-floor Observatory, Mississippi Canyon Federal Lease Block 118 Northern Gulf of Mexico, March 24-28, 2006.

Activities Report for Cruise GOM1-06-MC118 aboard the R/V *Pelican* is a report of initial efforts to survey the site of the hydrates Monitoring Station/Sea-floor Observatory by acquiring seismic reflection profiles across the mound in MC118 using the Surface-Source-Deep-Receiver (SSDR) technique, March 1-7, 2006.

Activities Report for Cruise GOM3-05-MC118 aboard the R/V *Pelican* includes activities of a scientific research cruise to Mississippi Canyon Federal Lease Block 118 from October 15-21, 2005. The purposes of this cruise were 1) to install, calibrate, test and put to use the ultra-short base-line (USBL) locating system, 2) to collect CTD (conductivity, temperature, depth) data in support of the design of a seismic survey of the block, and 3) to collect sediment and water samples to further characterize the sea floor and shallow subseafloor environments at MC118.

Activities Report for Cruise GOM2-05-MC118 aboard the R/V *Pelican* including the Deployment of the Initial Components of the Sea Floor Monitoring Station - The Pore-Fluid Array And The Geophysical Line Array - Via The Sea Floor Probe System And Collection Of Core Samples, Mississippi Canyon 118, May 15-19, 2005.

Activities Report for Cruise GOM1-05-MC118 aboard the R/V *Pelican* describes the activities of a scientific research cruise to Mississippi Canyon Federal Lease Block 118 from January 25-27, 2005. The primary tasks accomplished during the cruise include 1) deployment of Seafloor Probe, 2) sediment coring, and 3) acoustic evaluation of a bottom-founded pipeline.

RESULTS AND DISCUSSION

Results and discussion of those results that derive from cruise and meeting activities are reviewed in the summary section (previous). Results of specific investigations funded under this DOE –NETl cooperative agreement are covered in additional detail in Appendix B, *Final Reports from the Subcontractors*.

CONCLUSIONS

This report covers the accomplishments of the Hydrates Research Consortium and their efforts to establish a permanent seafloor observatory for investigations of the hydrate stability zone in the northern Gulf of Mexico. Cooperative Agreement DE-FC26-02NT41628, between the Department of Energy and the Center for Marine Resources and Environmental Technology, University of Mississippi went into effect in June, 2002 and was completed September 30, 2008. The efforts of the Hydrates Research Consortium are reviewed; at-sea activities reported; meeting and reporting responsibilities reviewed. All subcontractors have completed the work proposed for this cooperative agreement and have submitted final technical reports, final inventory reports and hazardous waste reports per DOE protocol. The status of the Observatory at MC118 is given, icluding summaries of the geophysical geochemical, microbial and support systems. An ROV and and AUV to service the station have been acquired by co-investigator agency, NOAA and put into surveying service. The NIUST AUV has been transferred to USM and physically located in Oxford, Mississippi where the CMRET team will be responsible for tending it. Additional recoveries and deployments of station components are anticipated for 2009-10.

Work to complete the Observatory continues under DOE-NETL cooperative agreement DE-FC26-06NT42877. Established under the visionary leadership of James Robert Woolsey, the Observatory will be completed and named in his honor. Although his untimely death in July, 2008, has resulted in additional challenges to the project, his example continues to inspire the Consortium to project completion.

REFERENCES

Please see Appendix C

ACRONYMS

4-C	four-component
AGM	Absorption Glass Mat battery system
AUV	autonomous underwater vehicle
BBLA	Benthic Boundary Layer Array
BHA = BLA	Borehole Line Array
BLA = BHA	Borehole Line Array
BCS	Barrodale Computing Services, Ltd.
CA	Cooperative Agreement
C&C	Chance and Chance
CMRET	Center for Marine Resources and Environmental Technology
CSA	Chimney Sampler Array
DOC	Department of Commerce
DOE	Department of Energy
DOI	Department of the Interior
DRS	Data Recovery System
EGL	Exploration Geophysics Laboratory
FY	Fiscal Year
GOM	Gulf of Mexico
GOM-HRC	Gulf of Mexico-Hydrates Research Consortium
HLA	horizontal line array
HRC	Hydrates Research Consortium
HSZ	Hydrate Stability Zone
IDP	integrated data power unit
I-O; I/O	Input-Output Corporation
JIP	Joint Industries Project
JSL	Johnson SeaLink
mbsf	meters below sea-floor
MC	Mississippi Canyon
MIR	Mid-Infrared Sensor Systems for Continuous Methane Monitoring
MMRI	Mississippi Mineral Resources Institute
MMS	Minerals Management Service
MS/SFO	monitoring station/sea-floor observatory
MSU	Mississippi State University
M/V	merchant vessel
NETL	National Energy Technology Laboratory
NIUST	National Institute for Undersea Science and Technology
NOAA	National Oceanographic and Atmospheric Administration
NURP	National Undersea Research Program
OBC	ocean-bottom cable
OLA	oceanographic line array
OBS	ocean bottom sensor
PFA (=PCA)	pore-fluid array
p-wave	compressional wave
ROV	remotely operated vehicle
R/V	Research Vessel
SDI	Specialty Devices, Inc.
SFO	Sea Floor Observatory
SFP	Sea Floor Probe

s-wave	shear wave
SSD	Station Service Device
SSDR	shallow-source/deep-receiver
SSS	Station Support System
STRC	Seabed Technology Research Center
UGa	University of Georgia
UM	University of Mississippi
US	United States
USBL	ultra-short base-line (navigation system)
USC	University of South Carolina
USF	University of South Florida
USGS	United States Geological Survey
USM	University of Southern Mississippi
VLA	vertical line array
VSP	vertical seismic profile
WMCL	wet-mateable communications link

APPENDIX A:

Trip Log from Seward Johnson/Johnson SeaLink Cruise, September, 2006

R/V Seward Johnson/Johnson Sea Link Cruise
Mississippi Canyon 118 Observatory
September 11 – 17, 2006
Center for Marine Resources and Environmental Technology
MMS/DOE

Trip Log

Scientific Crew:

Bob Woolsey, CMRET, Co-Chief Scientist
Chris Martens, UNC-DOE, Co-Chief Scientist
Jesse Hunt, MMS, Contract Inspector, Navigation Log
Paul Higley, SDI, SDI/STRC
Jeff Chanton, FSU, DOE
Laura Lapham, UNC, STRC
Kevin Martin, USM, STRC
Rich Camilli, WHOI, STRC
Norm Farr, UNC, STRC
Oscar Pizarro, WHOI, STRC
Howard Mendlovitz, UNC, STRC
Joanne Goudreau, WHOI, STRC
Karen Lloyd, UNC, STRC
Dan Albert, UNC, STRC
Roger Sassen, Texas A&M, DOE/STRC
Rudy Rogers, MSU, DOE/STRC
John Noakes, UGA, STRC
Mandy Joye, UGA, STRC
Ian McDonald, Texas A&M, STRC
Vladimir Samarkin, UGA, STRC
Keith Martin, UMiami, RSMAS, Marine Tech.
Elizabeth Bruce, UMiami/HBOI, Marine Tech.

NOTE: All times are Eastern Daylight Times

Tuesday, September 12, 2006

AM Dive 3566
Pilot: Phil Santos
Front Obs: Paul Higley
Crew: Allen Fuller
Rear Obs: Bob Woolsey

Purpose: Land in large N. crater, take punch cores, deploy sonar target, survy north and locate Pore Fluid Analyzer (PFA) and 2nd scientific package. Attempt to recover PFA.

(all times are EDT)

Sub on the bottom at 09:11, searched for large crater to deploy sonar target, but couldn't find it. Found a large crater about 600 ft. across with prominent walls. Found PFA and successfully retrieved it after 1.5 years on the bottom. Took 8 push cores and 6 Niskin bottle (water) samples.

No active seeps detected, but several areas of fresh ejection sites. It is surmised that Sunday's magnitude 6.0 earthquake may have released all free gas, and system hasn't recharged enough yet to begin seeping again.

PM Dive 3567
Pilot: Phil Santos
Front Obs: Mandy Joye
Rear Crew: Allen Fuller
Rear Obs: Kevin Martin

Purpose: To locate the site at the SW crater, deploy a hydrates collector near a gas seep, obtain push cores and Niskin water samples, survey and photograph the area.

Launched sub at 16:50 and permission to dive. The dive was late due to excessive draw down of batteries on morning dive. The sub arrived on the bottom at the SW crater and found 3 hydrate mounds, one of which leaked oil when a piece of hydrate was broken off. Numerous rocky ledges were observed which had gorgonians, and even pink coral. A sonar reflector was placed on the largest mound so we can return to it. The actuator arm on the sub began leaking hydraulic oil, so no push cores were taken. The Niskin bottles were tripped, and the hydrate collector was positioned adjacent to a gas seep. It was not leveled, and only one valve of the three was opened, so it will be leveled and the other valves opened during a later dive. Found numerous sites where very, very recent gas expulsion had taken place, but all was dormant except for the one good seep. We speculate that the magnitude 6 earthquake about 140 miles to the SE on Sunday may have de-gassed the area causing numerous expulsion events. Photos and video were taken around the area.

The hydrate collector deployed by Dr. Rudy Rogers may be the most important experiment on the cruise. It consists of a small elevated platform to trap gas, with 3 pipes leading into hyper-insulated chambers with high pressure valves on each end. Inside the chambers are

perforated plastic tubes, and the annular space is packed with 4 types of clays. The idea is to open both valves to allow the free flow of gas through each chamber over several month, then close both valves to maintain seafloor pressure, and retrieve the platform to determine which clay mineral best promotes the formation of hydrates.

Wednesday, September 13, 2006

Winds 13 kts at 310 to 320 degrees, seas 1 to 2 ft. The R/V Acadiana was on station with the Discovery Channel film crew prior to dive, but had to stand by until the sub was on the bottom before small boat transfer.

AM Dive 3568
Pilot: Craig Culligan
Front Obs: Rich Camilli
Crew: Frank Lombardo
Rear Obs: Oscar Pizarro

Purpose: Locate yesterday's site, test mass spectrometer, locate a site for the chimney lander, take push cores and water samples.

Launch was at 08:06, on bottom at 09:14. Searched for yesterday's site, but had trouble finding it. Sub navigation was erratic with fixes jumping all around. Found several features seen yesterday, but never located the hydrates collector put down yesterday. Found a large piece of hydrates, and more pink coral. Tested the mass spec., took 8 push cores and 2 water samples. Also placed a float on top of a small boulder at the top of a rise, and can see the radar reflector about 30 ft. away down slope at 030 degrees.

A film crew from Discovery Channel arrived and transferred over to the R/V Seward Johnson from the R/V Acadiana during the morning dive. They will be filming on board today and tomorrow.

Wednesday, September 13, 2006
(winds 320 degrees at 13 kts)

AM Dive 3568
Pilot: Craig Culligan
Front Obs: Rich Camilli
Crew: Frank Lombardo
Rear Obs: Oscar Pizarro

Purpose: Locate yesterday's PM position, test mass spectrometer, locate site to deploy chimney lander.

Launched sub at 08:06, and searched for yesterdays site where sampler was deployed. Sub navigation was very erratic. Found a good gas seep area, but not suitable for the chimney lander. The bottom is too irregular. In searching for the sampler deployed yesterday, found numerous hydrates outcrops and an area of pink coral. Found a radar

reflector left yesterday, but no luck at finding the sampler. Took 8 punch cores but had problem putting them in the quiver. Tight fit resulting in hydraulic action resulted in pushing water out the top and disrupting the "jello" consistency mud. Put a float on top of the adjacent rise. (Marker #7) The sub left the bottom at 11:25.

PM Dive 3569
Pilot: Don Liberatore
Front Obs: Roger Sassen
Crew: Frank Lombardo
Rear Obs: Nick Brown (Discovery Channel)

Purpose: Discovery Channel PR, locate hydrate collector (Rogers device) and open other 2 lower valves and reposition, deploy methane saturation peepers adjacent to hydrate, deploy Noakes microbiological generator, collect cores and water samples.

Sub was launched at 16:40 and was on bottom at 17:23. They located numerous small depressions, several gas seeps, and a number of hydrate chunks, some as large as 20 ft. long sticking up 4 ft. One appeared to be a bridge. Two Niskin bottles were tripped in the bubble stream over a gas seep, and Dr. Noakes microbiological growth experiment was installed over a gas seep. A methane saturation peeper was installed adjacent to a chunk of hydrates. They took 5 punch cores, but never found yesterday's apparatus. More sub navigation problems plagued the afternoon dive. The sub left the bottom at 19:54.

Thursday, September 14, 2006

AM Dive 3570
Pilot: Don Liberatore
Front Obs: Rich Camilli
Crew: Allen Fuller
Rear Obs: Oscar Pizarro

Purpose: Find a suitable site for the chimney lander, and search for the Pore Fluid Analyzer. Re-install the osmopump on the PFA probe. Test the mass spectrometer for real time readings.

The submersible was launched at 08:24 and reached bottom at 09:08 in 2877 ft. of water. They observed, videoed and collected red squid. They observed shell hash, bacterial mats, and mineralized mud vent chimney tubes and took samples. Tube cores and Niskin water samples were taken over a bacterial mat. **Mass spec. readings were almost off the scale for methane.** Push cores were taken in the mat, and gas bubbles came out of core holes. **The mass spec. showed elevated levels of methane, butane and propane.** The decision was made to place the large chimney lander at this location and a marker was set. The sub proceeded along the edge of the feature and found and videotaped a geophysical probe installed last year. The sub then proceeded along the edge and found the PFA probe, and successfully re-installed the osmopump collected on Tuesday.

Between dives, 13:00 to 17:00, the chimney lander with floats to an acoustic release was

deployed. Attempts were to position it on the bacterial mat observed on the morning dive. The afternoon dive will attempt to fine tune the position over the mat. Plans are to retrieve the lander on Saturday with an acoustic release from a weight and retrieve it at the surface. The lander was dropped from about 10 ft. from the ocean floor, and landed within 10 feet of the mat using the ships fathometer. The lander consists of a large diameter plastic pipe open on each end which contains a camera system and a series of strobes. An inverted funnel contains a methane sensor, oxygen sensor, conductivity, salinity and transmissivity sensors. Any detection of methane (gas bubble release) triggers the camera system and the strobes are triggered in sequence. Plans are to install the mass spectrometer to analyze the C2 through C5 gas content in the gas release.

PM Dive 3571
Pilot: Don Liberatore
Co-pilot: Phil Santos
Crew: Allen Fuller
Rear Obs: Norm Farr

Purpose: Relocate the chimney lander, detach camera system on tether from it and place in close proximity, reposition the lander over the bacterial mat sampled this morning. Attempt to relocate the geophysical array probe and retrieve data logger, collect water samples.

The submersible was launched at 17:25 and had a good hit on sonar from the floats. They arrived at the lander at 18:21 at a depth of 2890 ft. It appeared to have slid 15 to 20 ft. downslope, and was resting at an angle of 15 degrees. The bubble camera system was removed and placed upslope about 50 ft. away over a mineralized vent tube. The lander was then successfully relocated to within 10 ft. of where the cores were taken on the morning dive in the center of the bacterial mat. Niskin water samples were taken, then the sub proceeded to and found the geophysical probe array deployed last year in 2900 ft. of water. The data recorder and battery pack was successfully removed and retrieved. The sub left bottom at 19:45.

Friday, September 15, 2006
Winds calm, seas greasy flat

AM Dive 3572
Pilot: Phil Santos
Front Obs: Ian McDonald
Crew: Frank Lombardo
Rear Obs: Karen Lloyd

Purpose: Locate Rudy's hydrates generator, level it, and open the other 2 valves; Deploy Ian McDonald's time lapse camera, Deploy hydrates peepers, deploy osmolander, take push cores and water samples.

This is the same site in Tuesday morning's dive with the same pilot. The sub was launched at 08:11 and reached the seafloor at 08:54. Temperature was 5.54C, visibility 30 ft., and depth 2906 ft. They had a good sonar target upon arrival at the seafloor and

proceeded in that direction. They first located the pink coral observed Tuesday, then located Dr. Noakes' hydrate collecter and Marker 6. From there, they located Dr. Rudy Rogers' hydrates generator experiment, leveled it, and opened the other 2 lower valves. Dr. McDonald's time lapse camera was deployed along with 3 hydrates peepers. Laura Lapham's osmolander was deployed, then 8 cores and 6 niskin water samples were collected. The pilot observed that there appeared to be much more gas escaping from the seeps than on Tuesday. The sub received permission to leave the bottom at 11:17.

Important Note: Direct observations appear to support our suppositions about the amount of gas leaking. It appears that Sunday's Magnitude 6 earthquake 140 miles SE of this site shook the site enough to cause degassing and now that that the plumbing is recharging, much more gas is again escaping.

PM Dive 3573
Pilot: Phil Santos
Front Obs: Bob Woolsey
Crew: Frank Lombardo
Rear Obs: John Noakes

Purpose: Bob to reconnoiter the area to familiarize himself with it for Nov. ROV work. Will attempt to take hydrates samples with pressure container, deploy hydrates peepers, take push cores and water samples.

The sub was launched and received permission to dive at 17:36 and arrived on bottom at 17:54. The temperature was 5.52 C and visibility 35 ft. A large chunk of hydrate was collected, which turned out to be too large to fit in the high pressure vessel. Some pieces had to be broken off to close the lid. A large slab of hydrates about 20 to 25 ft. long and 4 to 5 feet thick was under-washed, forming a bridge. This slab also had ice worms in it. Gas was actively seeping out around the bridge. Not to far away was a spire of hydrate emerging from the seafloor about 4 to 5 feet high. Hydrate peepers were deployed, the valves on the osmolander were adjusted and aligned, and another marker (#10) was placed near the ice bridge. Tube cores and Niskin samples were taken. A couple of rocks were also collected.

Back on the vessels, the rocks and mud collected had strong gold fluorescence under blue light, indicating oil soaking.

Gas chromatograph data was finally obtained and nicely corresponded with the mass spectrometer data, indicating methane as well as higher hydrocarbons up to septane. This definitely indicates thermogenic as opposed to biogenic gas.

Saturday, September 16, 2006

AM Dive 3574
Pilot: Craig Caddigan
Front Obs: Howard Mendelovitz
Crew: Allen Fuller
Rear Obs: Norm Farr

Purpose: Put a grid in the lander and photograph with stereo camera and video, proceed to PFA and galvanic generator, check generator to time LED flashes, then to Site 5 at South Crater and obtain water samples.

The sub was launched and received permission to dive at 08:05 and arrived on bottom at 08:50. Water depth was 2892 ft., visibility 20-25 ft., temperature 5.59C, and currents were 0.2 kts. from 025 degrees. They placed a grid in the lander and shot video and stereographic photos of it. A water sample was taken, then they proceeded to the bubble experiment and retrieved it. Three punch cores were taken – 2 inside a bacterial mat and one just outside, then the sub proceeded east to the PFA site. After arriving at the PFA, photos and video were taken and the sub checked the galvanic generator to be sure the LED lights were flashing. They were confirmed to be flashing every 3 seconds. They then proceeded south west to the first crater observed on the first dive on Tuesday. They arrived, took photos and two water samples in the crater. The sub left bottom at 10:52

After the sub was recovered, the lander was released acoustically and floated to the surface. It was successfully retrieved.

Saturday, September 16, 2006

PM Dive 3575
Pilot: Craig Caddigan
Front Obs: Rich Camilli
Crew: Allen Fuller
Rear Obs: Oscar Pizarro
Purpose: Run the mass spectrometer over the features, obtain stereo photography over the features, take push cores and water samples and deploy another galvanic generator.

The sub was launched and given permission to dive at 15:44. They arrived on bottom near John Noakes' experiment at 16:20. They set down and observed gas bubbling up behind Noakes' experiment, then deployed the other galvanic generator experiment adjacent to it. They took photos of the site, then moved up slope and took 4 punch cores. Oil was bubbling out of the holes left by the cores. Two Niskin water samples were taken in the bubble stream. They had trouble with the mass spectrometer, and eventually had to shut it off. They proceeded around the area and took stereographic photos around the experiments, the hydrates ice bridge, and spar. More push cores and water sampes were taken and the sub left bottom at 18:46. Around 18:10, a pod of pilot whales accompanied by spinner dolphins were sight just north of the vessel. Identifications were tentative.

APPENDIX B: Final Reports from the Subcontractors

Gas Hydrate Sea Floor Observatory Vertical Line Array

FINAL REPORT

Subcontract to
DOE Award Number: DE-FC26-02NT41628

Paul Higley: Principal Investigator
Specialty Devices, Inc.
Wylie, Texas

November, 2008

Gas Hydrate Sea Floor Observatory Vertical Line Array

Abstract

The vertical acoustic line array (VLA) was developed as a stand alone acoustic array as part of the Gas Hydrates Research Program and was installed several times collecting data at different sites. Early data, while useful, suffered from a lack of real time communications to the surface needed to accurately time events between a surface sound source and the sea floor mounted array. A cable to shore would provide the needed communications and provide a data recovery route but proved financially prohibitive. Alternate seafloor to surface communications schemes were investigated and the stand alone VLAs were incorporated into a Sea Floor Observatory (SFO) with a fiber optic communications to the surface provided by an “M” shaped mooring buoy. A planned set of 4 VLA s were replaced by a single VLA and an Oceanographic Line Array (OLA) to be connected to the SFO. The OLA evolved into another array developed to initially function as a stand alone array and later to be integrated with the SFO. The SFO is intended to provide a long term means to study characteristics of gas hydrate deposits. This report addresses the development of the VLA, the integration into the SFO and the new technology developed along the way to make this possible.

Introduction

The design for the vertical array includes an array of 16 hydrophones spaced 12.5 meters apart and extending approximately 200 meters up from a point just above the sea floor. A data logger was designed for the earlier versions of the VLA and was self-timed to record during the arrival of the acoustic signal of interest. Communications to the data logger was via an acoustic modem and included command and control and some limited bandwidth data recovery. Timing accuracy was limited by the internal clock drift on short deployments or the accuracy of the acoustic modem clock reset capability on longer deployments, neither of which addressed the growing need for more accurate timing. Power was provided on the earlier VLAs by an array mounted pressure compensated battery pack. Recovery of the array with its battery pack and data logger was accomplished through activation on an acoustic release connecting the array to the anchor and glass floatation on the upper VLA. The design was intended to allow several days of data collection using a near surface towed sound source. Several versions of this array were built, deployed and used to acquire data.

Integration of these stand alone VLAs into the SFO provided means for longer term deployments, precise timing between surface source firing and bottom recording, and a method to recover larger data sets. The SFO is equipped with a real time communications link to the surface ship and a replaceable longer term, higher energy, power source which is installed on the sea floor. Modifications were required to interface the VLA data recorder to the SFO and to increase deployment durations from weeks to years, utilize the more accurate timing available from a system with real time communications to a surface ship, be powered up and down remotely by the SFO and accept commands from the surface and later the SFO sea floor controller, the IDP.

Interest within the Gas Hydrates consortium for measurements in gas hydrate areas including active methane vents of near sea floor boundary layer parameters lead to the conversion of one of the two VLAs into an Oceanographic Line Array (OLA). In a later effort

to have this array better equipped to study the boundary layer, the OLA was renamed the Benthic Boundary Layer Array (BBLA). The responsibility of the BBLA has been passed to a team of universities lead by WHOI.

The VLA and its highly modified Data Acquisition and Telemetry System (DATS) has been completed and updated to be deployed at MC118. Since the VLA extends well up into the water column and entanglement with the Station Service Device (SSD) ROV cables, particularly during the HLA deployments, the VLA will be deployed along one of the HLA legs and well out away from the IPD and center of the HLA. This VLA will be deployed after the HLA arrays are deployed.

Summary

New technology developed following the original VLA development was utilized in the design and construction of a new VLA. These improvements included cable design, modifications to software programs, addition of a remote real time "T0" timing command, faster data retrieval through a hardwired and fiber optic Ethernet capability and development of a ROV mateable underwater multi-conductor connector system. Software and hardware changes to the Data Acquisition and Telemetry System (DATS) recorders interfaced the DATS of the original VLA design to the SFO data retrieval system.

Experience gained in the previous deployments of the VLAs were applied to the design and deployment techniques of these arrays.

Experimental

The original VLA deployed in MC798 was later deployed at a site that exceeded the design depth. While some data was collected for this site, the deployment resulted in damage to the array and this array was not repairable. An engineering effort was initiated to improve the cable design and a cable was built for an application in Italy using this new design. Five deployments were performed in the Italy site without damage to the cable. This experience verified the improved design and was incorporated in the VLA for the SFO.

The acoustic modems on this deep deployment were repaired and will be used on the SFO IDP. Additional acoustic modems were purchased with a deeper depth rating, along with the appropriate surface communications units for the deeper modems.

Integration of the VLA to the Sea Floor Observatory

Real time communications from the surface ship to the SFO IDP was to be provided using radio telemetry to a surface buoy on the "M" mooring and a fiber optic cable to the seafloor mounted IDP. The "M" mooring was replaced by a newly designed Popup buoy due the potential damage to the "M" buoy by local fishing activities. The Popup buoy brings the fiber optic cable from the sea floor installed IDP to the surface. A hard wired cable connection will be used from the IDP to the VLA DATS. These extension cables require make and break under water connections with multiple conductors. These connections need to be ROV mateable. Presently available connectors were either limited to 4 conductors or difficult to install with an ROV. The costs for these connectors was also prohibitively expensive when ROV mateable. As a result, a new connector system was designed and installed in the TDATS system deployed in early 2005. This connector system is now the basis for all connections on the sea floor IDP installed system and will be used to connect the IDP to the VLA DATS.

The VLA DATS computer and software programs were modified to include three forms of communications to the termination of a sea floor fiber optic link. A “T0” timing pulse was needed for the coordination of the gun firing with the bottom VLA DATS. A serial command line provides control and house keeping functions and a high speed Ethernet communications capability was added for large volume data recovery from the VLA DATS. The development included hardware and software modifications to the VLA DATS computer.

VLA Positioning sensors

The positioning sensors including the compass and tilt sensors were completed. These sensors are to be used to define the offset of the acoustic sensors due to water currents during acquisition of geophysical data. The sensors and housings were completed and pressure tested. The pressure rating for these housing is twice that of any anticipated deployment. Similar heading and tilt sensors were also deployed on the Italy installations and functioned well.

Results and Discussion

Efforts included improving the design of the array connection, developing methods to lengthen the design life of components of the VLA, and investigation of power sources for the VLA and SFO energy requirements. Extending the deployed life of the SFO components to achieve five to ten year deployed life has been part of the efforts. Corrosion protection of most exposed metal components has been addressed by enclosing these components in neoprene jackets with an oil fill providing a barrier to sea water. Remaining metal components are being addressed with anodes and new coating methods to inhibit corrosion. The need to install the VLA at a location well remote from the IDP presented yet another challenge. The Ethernet communications planned between the IDP and all underwater data recording systems is not compatible with long remote locations. As a result SDI designed and built a Ethernet to DSL conversion capability that is now installed in the IDP and VLA DATS. This converts Ethernet data into DSL communication protocol and back to Ethernet in a manner that is seamless to the communications devices on both ends. This now allows extension of the Ethernet communications to approximately 1,000 meters.

Conclusion

The VLA development program started with evaluation of the early VLA deployments and development of methods to implement improvements. The demise of the VLA cable lead to changes in the construction of the cable intended to make this critical element more robust. These improvements were tested due to a fortunate opportunity to use similar application of this technology at a site in Italy. Alterations of the early VLA were made to allow integration of the VLA array into the SFO. As the SFO has evolved, new requirements of the VLA DATS and array have continued to arise. The present design of the VLA includes all these changes that have occurred along the way. The most recent modifications to the VLA are to allow installation at newly defined locations within the SFO installation. The Vertical Line Array now awaits deployment at the MC118 site following successful deployment of the HLA arrays.

CONSTRUCTION OF THE PROTOTYPE SEA FLOOR PROBE

Subcontract to
DOE Award Number: **DE- FC26-02NT41628**

Final Report covering the period

DECEMBER, 2004 – MAY, 2005

Submitted by
J. Robert Woolsey

JANUARY 17, 2006

DESIGN AND DEVELOPMENT OF THE SEA FLOOR PROBE

Abstract

The Sea Floor Probe (SFP) is a multiuse tool designed to effect sensor deployment into the shallow subsea-floor. Its penetrometer configuration has now been proven in a series of sea tests at MC118, January 2005. Its gravity coring capabilities were proven on this and a return trip to MC118 in May, 2005 when 3-7m cores were collected in the vicinity of a large carbonate mound structure known to have associated gas hydrates. Later in the May cruise two probes were deployed with the SFP: a pore-fluid sampler array and a geophysical thermistor array. The "box" from the pore-fluid array and the data-logger from the geophysical array will be collected at the earliest opportunity via remotely operated vehicle (ROV) or manned submersible.

Introduction

The concept of a Sea Floor Probe (SFP) has been a part the GOM Gas Hydrate Research Consortium plans for a Sea Floor Observatory since inception, but it has varied in design and mission due to changing program circumstances. Currently, in several configurations, it has become an important part of the overall observing system plan. Variances in design mainly related to changes in site location and opportunities for access to a borehole for installation of a multi-sensor down-hole array (altering original SFP requirements). In the fall of 2002 consultations with members of the GOM Joint Industry Program (JIP) gave hope for an opportunity to utilize one or more core-holes to be drilled in Atwater Valley Block 14 which could possibly serve a dual role for seabed sensor installation. The plan was expanded and in 2003 was advanced to include the design and development of a multi-sensor, borehole line array (Figure 1). However promising the plan, in 2004 it became increasingly apparent that the 1300m water depth at AV 14 was too problematic for the 1000m geochemical instrument depth limitations. Although hope remained high for an eventual opportunity to install a borehole array at a suitable hydrate site, in less than 1000m water depth, a return to the original SFP concept, however expanded, would be appropriate at least as a viable, interim measure. Factored into the design of the revised SFP plan was the recent experience with the mega coring technology of the French *R/V Marion Defresne*, which had consistently driven gravity core barrels to depths greater than 10m in the Mississippi Canyon area. Based on this experience, modifications to the SFP would include a simplified gravity drive, capable of array emplacement to approximately 10m. The system would provide valuable multi-sensor data at low cost, and aid in the development of the final bore-hole array design (Figure 2).

EXECUTIVE SUMMARY

Conceptual design and technology of the Sea Floor Probe (SFP) has evolved over the course of the project to accommodate changing circumstance; i.e., changes in site locations and opportunities for access to a borehole for installation of seabed sensors. As the project progressed, priority was given to the deployment of a multi-sensor borehole array to be installed in cooperation with the Joint Industry Program (JIP), utilizing for this purpose, one or more core-holes to be drilled in Atwater Valley Block 14. However promising this plan, it became increasingly apparent that the 1300m water depth at AV 14 would be insurmountable for the Geochemistry Team with their 1000m instrument depth limitation. Although hope remained high for an eventual opportunity to install a bore-hole array at a suitable hydrate site (in less than 1000m water depth), the original SFP concept

was revisited as a viable, low cost interim measure. Factored into the design of the revived SFP plan was the recent experience with the mega-coring technology of the French ship, *R/VMarion Defresne*, which had consistently succeeded in gravity-driving core barrels to depths greater than 10m in the Mississippi Canyon area. Based on this experience, modification to the SFP would include a simplified means for gravity drive, capable of array emplacement to approximately 10m. The system would provide valuable multi-sensor data at low cost, and aid in the development of the final bore-hole array design. The SFP concept was expanded throughout the project to include a; Penetrometer, 10m Gravity Coring System, Pore Fluid Array, and Thermister Geophysical Line Array.

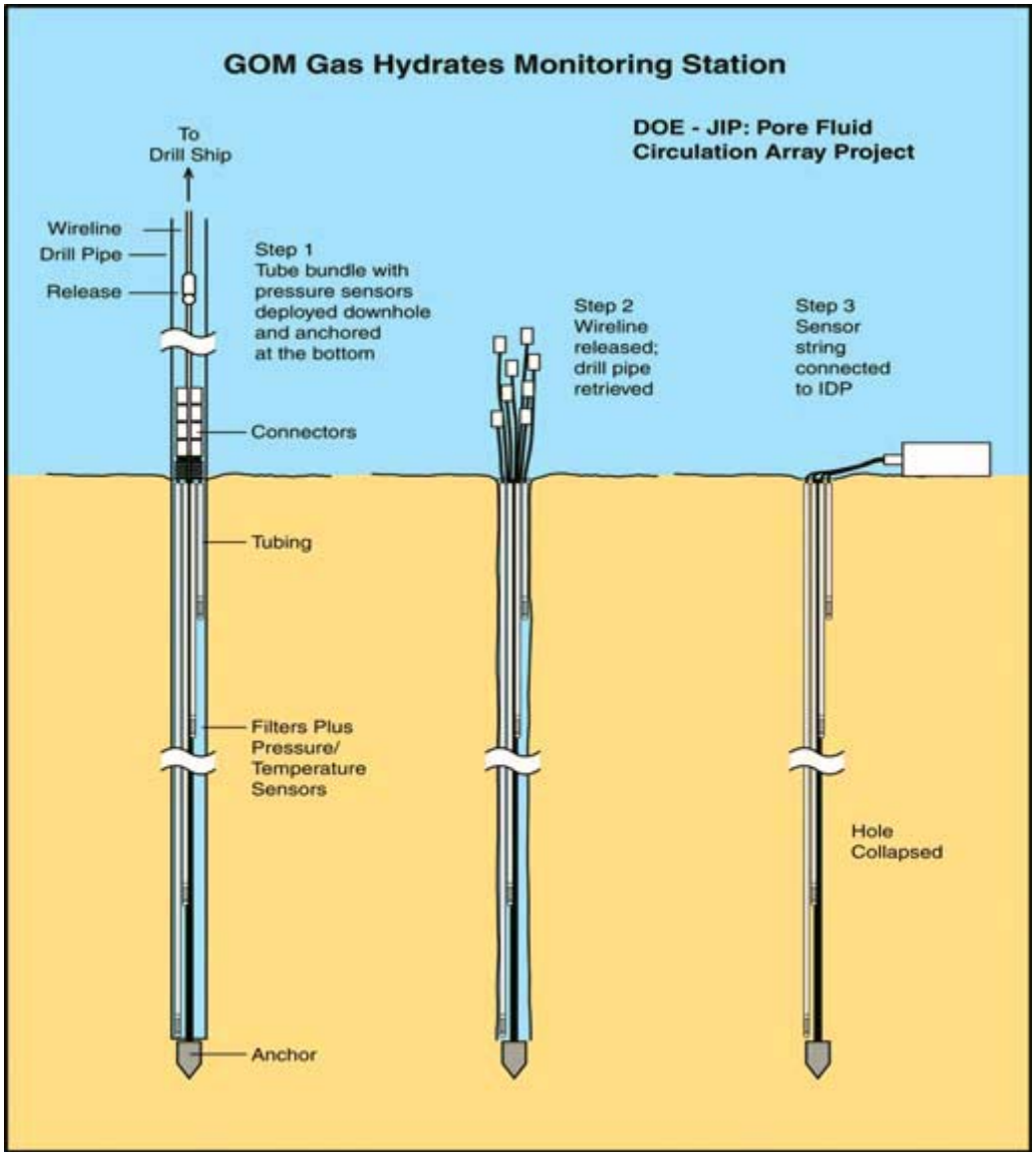


Figure 1

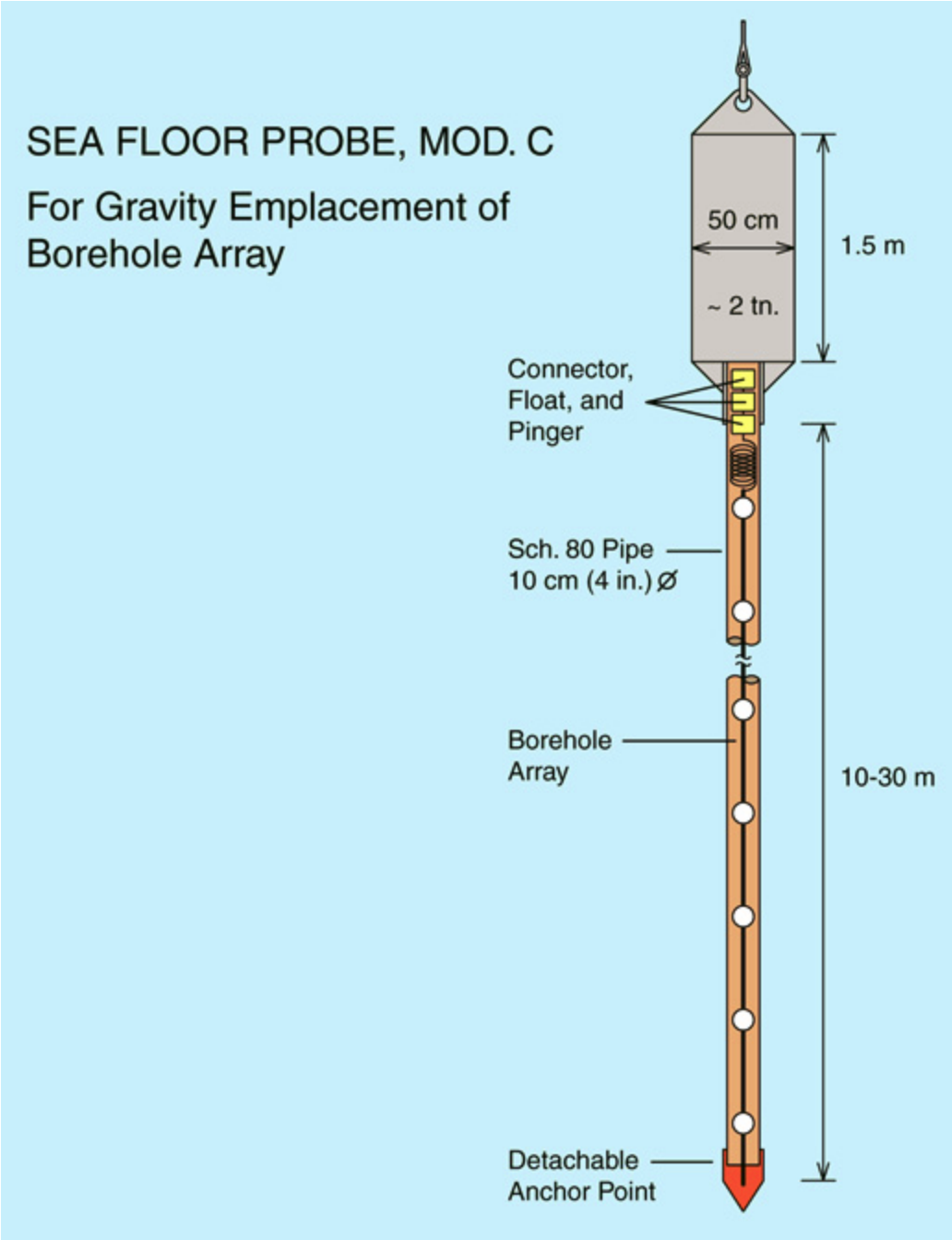


Figure 2

EXPERIMENTAL

Experimental work involving the Gravity SFP was established in two parts. First a SFP Penetrometer was constructed, more or less identical to the design shown in Figure 2, without the array and with a fixed point. The purpose of the penetrometer was to determine the average depth to which the instrumented SFP could be expected to penetrate into the bottom sediments at the study site. Once determined, a good estimate could be established for the depth of array emplacement which could in turn be used to evaluate the feasibility of the system for geophysical and geochemical applications. If an appropriate

depth could be achieved, the second task would involve the design and development of two sensor systems to be emplaced by the Gravity SFP. One, a thermister, geophysical line array (GLA), for monitoring thermal variations of the near- seafloor bottom sediments over time; the other, a pore fluid array (PFA), for monitoring the chemistry of pore fluids, including hydrocarbons, within the shallow sub-bottom sediments over time.

The basic multi-sensor SFP design, used for these latter purposes, would incorporate a channel beam fitted with a detachable point to deliver the array in the penetration drive (Figure 3). The channel beam would be fitted with a 1 ton concrete weight which can be detached from the beam by an acoustic release. The array cable is attached to the detachable point, strung through the channel beam, and connected to a recoverable instrument section fitted to the top of the concrete weight. Following impact and penetration into the sediment, the weight is released remotely and the channel beam retracted. The recoverable instrument section is designed to be recovered remotely and exchanged using an underwater vehicle, manned or remotely operated vehicle (ROV).

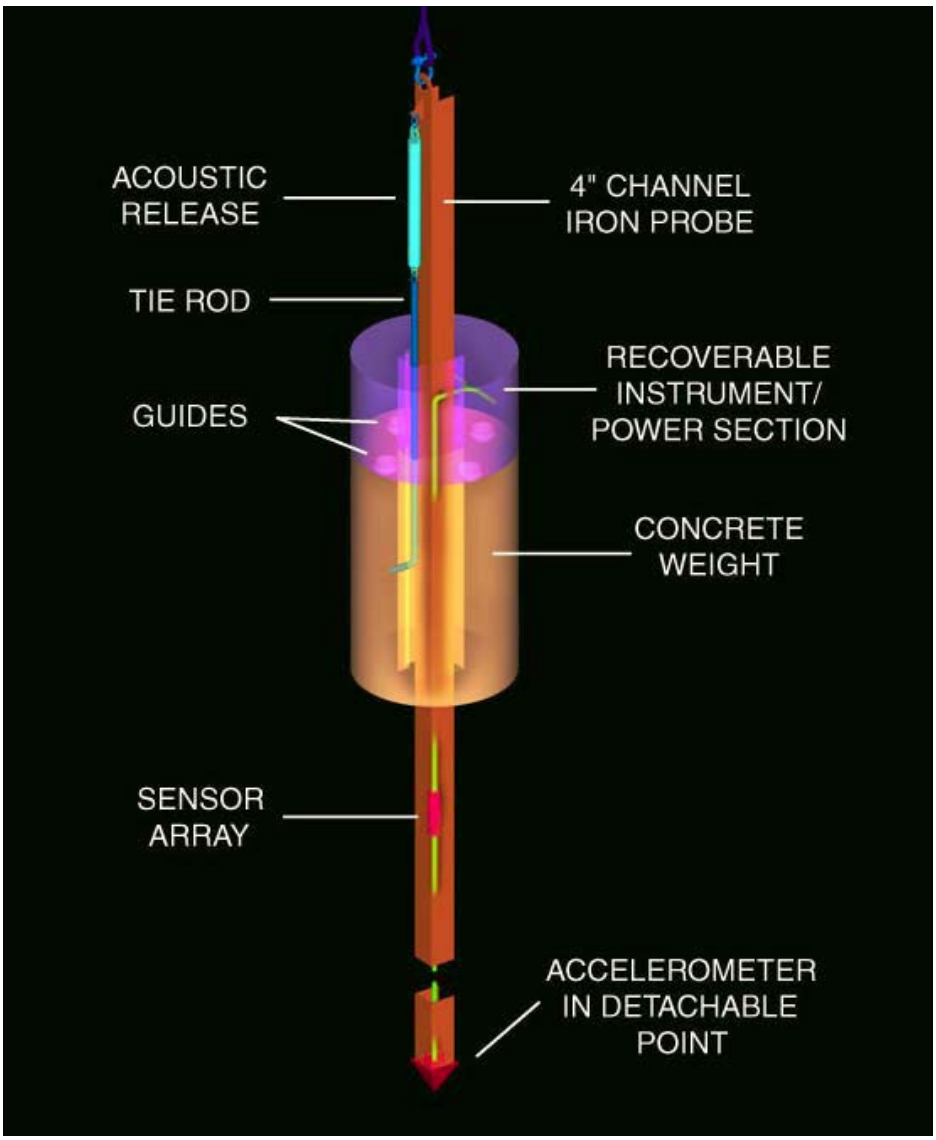


Figure 3. Conceptual Multi-Sensor SFP Design

Results

Deployment

Two cruises were conducted to Mississippi Canyon Block 118 (MC118) in winter, January 26-28, and spring, May 16-19, 2005 on board the *R/V Pelican*. Work involved the deployment of several versions of the Gravity SFP. The winter cruise was devoted to the determination of an average expected depth of penetration for the study area using the SFP Penetrometer (Figure 4).

Figure 4: Gravity SFP Penetrometer

Gravity Core and Pore Fluid Array

The spring Cruise involved the deployment of the Pore Fluid Array (PFA) and the prototype thermister Geophysical Line Array (GLA). Prior to deployment of these two systems, core samples were collected to establish a suitable location. Twelve sites were cored with either the SFP 10m, or the ship's 3m Gravity Coring Systems. Cores recovered were examined on deck to check for evidence of hydrates and gas, (Figures 5 & 6). Positive

indications were observed in areas corresponding to the northwestern periphery of the mound as determined by recently acquired AUV Multibeam, sidescan, and chirp data as well as visual observations made during a 2002 MMS Johnson Sea Link dive**.** Subsamples from the cores were collected for additional chemical, geological, and microbial analyses.

Figures 5 and 6. Section of sediment core with evidence of possible gas hydrate dissociation (left) and split core with section of gas expansion (right).

The Pore Fluid Array (PFA) was designed to provide continuous sampling of sediment interstitial fluids at several depths below the seabed. The PFA collects these samples by means of an osmotic fluid pump and coiled tube storage device mounted in a container on the top of the SFP weight. The container is arranged in such a way as to enable removal and replacement by underwater vehicle.

The PFA was installed using the 10m, Gravity SFP. This device is designed to drive a steel box beam into the seafloor, fitted with fluid acquisition ports and associated tubing. An osmotic pump brings these fluids to the coiled tube collecting/storage device. Specialty Devices, Inc. (SDI) constructed an underwater vehicle compatible, eight port, fluid coupler and a mating assembly which houses the osmotic pumps and master control shut-off valve. The fluid coupler and housing were designed to survive the installation process and be recoverable via underwater vehicle. The housing and coupler are also designed to be reinstalled by a small remote vehicle to extend the potential sampling duration. Recovery and reinstallation will enable continued long-term monitoring of pore fluid chemistry by Jeff Chanton and Laura Lapham, Florida State University and University of North Carolina, Chapel Hill, respectively, (Figures 7 and 8).

Installation was performed by CMRET personnel and was accomplished by lowering the SFP/PFA using the ship trawl winch (Figure 8). The winch was operated at a maximum speed of approximately 90 m/minute. When the device was driven into the sea floor, an acoustic release was activated to free the trawl cable from the SFP. A second acoustic release remained on the SFP/PFA for use in locating the sea floor position of the array. This second release was activated and recovered following triangulation and recording of the location.

Figures 7 and 8. Recoverable osmo-pumps and sample storage units (left) and deployment of the Pore Fluid Array (right).

Thermister Geophysical Line Array

The prototype thermister geophysical line array (GLA) consisted of an array of temperature sensors with inline micro-controllers and an underwater vehicle recoverable DATS data logger and power supply (Figure 9). This deployment (Figures 10 and 11) served to test several new designs to be used in the geophysical study area of the Sea Floor Observatory. These designs are intended to allow servicing by small remote vehicles, reducing the costs associated with building and maintaining the Sea Floor Observatory geophysical section and extend the operational life of its components.

This deployed instrument array is similar to the deep bore-hole array design for installation through a 3.6” drill stem, planned for a later JIP bore-hole deployment. The goal of this installation was to test the design of components for the bore-hole system in addition to the continuous acquisition of high resolution near-seafloor sediment temperatures for the purpose of monitoring the thermal gradient over time. The acquisition of both acoustic data from the solid/gas phase discontinuity at the base of the hydrate stability zone (noted by a polarity reversal), and thermal gradient data over time will, hopefully, enable the monitoring of vertical migrations of the base of the hydrate stability zone and related consequences. The prototype array consisted of two remote in-line temperature sensors and an in-line temperature acquisition module. The array is intended to provide long life with no required maintenance. The sensors and acquisition module were housed in anodized aluminum housings encased in neoprene bladders designed to prevent sea water contact with the pressure housings. This technique is intended to extend the useable life of the sensors and electronics to 5 to 10 years. Also included in this array installation is a new ROV mateable design for connectors and a remote vehicle recoverable/replaceable instrument housing.

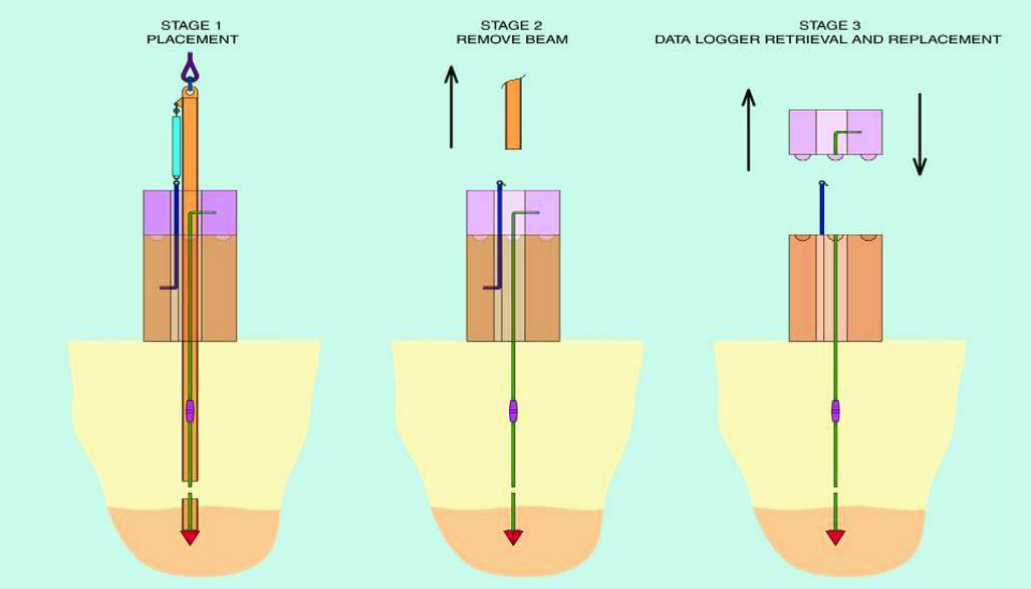


Figure 9. Conceptual drawing of GLA installation and DATS retrieval and replacement.

Figures 10 and 11. Prototype Thermister GLA with ROV replaceable DATS (left), GLA readied for deployment (right).

Positioning

The positions of these arrays were triangulated from slant range and ship position information following deployment. The Benthos acoustic transponder release and corresponding model 210 deck box provided the slant range. HYPACK navigation software coupled to the ship GPS positioning system was used to provide the Benthos surface

transducer location. Slant range and position information was entered into SDI's "Angulate" program to resolve bottom transponder position and depth. Three slant range positions are used in the calculation with additional ranges used to verify the computed location. Positioning on future cruises will be accomplished using a recently acquired Ultra Short Base Line (USBL) system.

The resulting positions for the seabed locations for these arrays and for the cores used to determine the array placements are provided below and presented on the location map, Figure 12.

Array	Latitude	Longitude	UTM X (Easterly) (Zone 16)	UTM Y (Northerly)
Pore fluid	28° 51.47121	88° 29.5199	354472.3	3193151.8
Geophysical	28° 51.384413	88° 29.554113	354414.6	3192992.2

CORE #	LATITUDE	LONGITUDE	TOTAL LENGTH	Water depth
MC118-505-1	28° 51.264′	88° 29.952′	231cm	903m
MC118-505-2	28° 51.337′	88° 29.635′	175.5cm	895m (wire)
MC118-505-3	28° 51.305′	88° 29.653′	337cm	908m
MC118-505-4	28° 51.461′	88° 29.490′	186cm	897.6m
MC118-505-5	28° 51.482′	88° 29.470′	211cm	887m
MC118-505-6	28° 51.432′	88° 29.490′	156cm	892.6m
MC118-505-7	28° 51.342′	88° 29.574′	228cm	895.3m
MC118-505-8	28° 51.353′	88° 29.586′	142cm	894m
MC118-505-9	28° 51.448′	88° 29.503′	724.5cm	877m
MC118-505-10	28° 51.488′	88° 29.503′	371cm	894m
MC118-505-11	28° 51.456′	88° 29.491′	~ 200cm	880m (wire)
MC118-505-12	28° 51.510′	88° 29.520′	~ 400cm	890m

Cores (gravity) collected during May cruise, 2005.

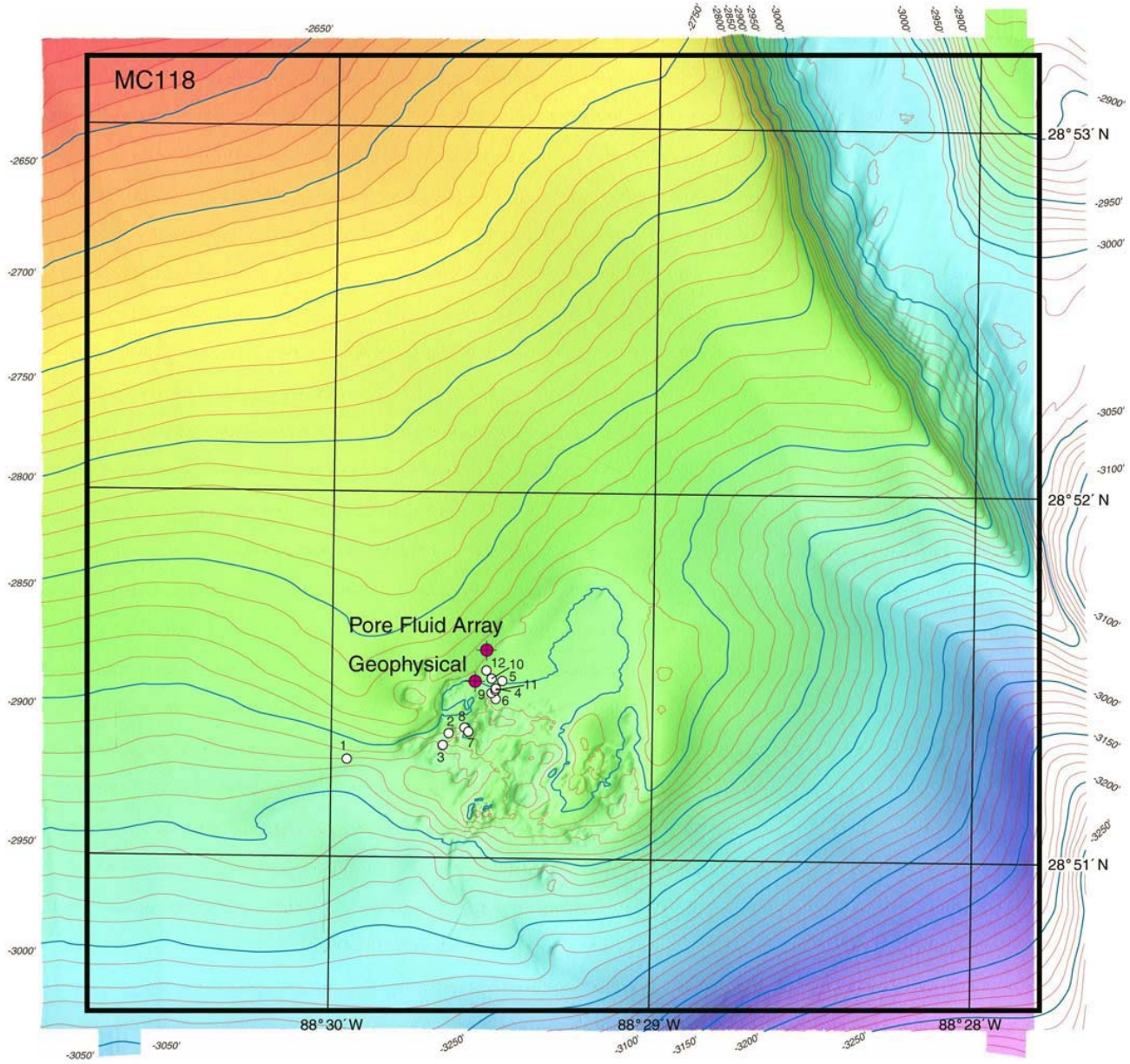


Figure 12. Mississippi Canyon 118. Cores 1-12, recovered in May, 2005, appear as open circles. The two probes deployed on the same cruise are labeled and appear as filled circles

Final Report

Gulf of Mexico Monitoring Station: Acoustic Systems for Monitoring Gas Hydrates

Jerald W. Caruthers and Ralph R. Goodman

University of Southern Mississippi
Department of Marine Science

Subcontract to
DOE Award Number: DE-FC26-02NT41628

December, 2005

Gulf of Mexico Monitoring Station: Acoustic Systems for Monitoring Gas Hydrates

The work conducted under this project for FY2004 centered on trying to understand the nature of the gas-hydrate bubbles emitted from the seafloor at depths of 500 to 1000 m, and design a sonar system to match the expected bubble characteristics. During the year TV images were analyzed to determine expected bubble diameters, raise rates, and density. The bubble radii ranged from about 500 to 5000 microns (mm) and the rise rates were in the expected range of 20 to 30 cm/sec. The expected density of bubbles was a bit more variable depending on the particular vent and probably the local bottom temperature and could not be accurately estimated.

A bubble at resonance is a very effective scatterer and absorber of sound. A given bubble with radius a_r, in microns, will resonate at a frequency f_r, in kilohertz, given by

$$f_r = 3270(1 + 0.1\sqrt{z}) / a_r$$

where z is depth in meters. Based on the expected radii and depths to be investigated suggested a range of frequencies from about 2.4 to24 kHz in order to obtain resonant scattering from the bubbles, and thereby determine their distribution over their range of radii.

Most of the recent work on this project involved specifying the design of a measurement system. Two candidate systems were investigated: (1) A measurement system including an acoustic transmitter and a series of hydrophones on an arc of a circle about a meter in diameter was investigated. In final design, it was expected to cover the resonance frequency range. A prototype system was built and tested in a tank by the Naval Research Laboratory. This design appeared to be difficult to realize in hardware for deep operations. (2) The second system was to be based on three Neptune Science T70 transduces that we had in hand from previous Office of Naval Research funding. These transducers operate at 12 kHz (the middle of the expected resonance-frequency range) and each have two rows of five elements. The system was planed to be in a planar-block arrangement of five by six elements and be approximately 0.72 by 0.46 m in size on their face. Beampattern and beam steering algorithms were computed to determine the capability of the system to monitor the 3D volume of a gas-hydrates vent.

Due the lack of Department of Energy funding for FY2005, plans to construct this system were abandoned. A version of the system will be built with DURIP (Defense University Research Instrument Program) funding through ONR. This Department of Defense configuration of the system, however, will be a towed, wide-swath, subbottom profiler, and not configured or available for gas-hydrates work. The basic planar array and electronic components will be the same as the previously planned DOE configuration.

Construction and Testing of an Electromagnetic Bubble Detector and Counter

Start Date: 01/01/02
End Date: 11/30/2004

Subcontract to
DOE Award Number: DE-FC26-02NT41628

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Final Report

October 24, 2005

Abstract

In order to characterize the activity at the hydrate sites, it is necessary to quantify the volume of gas being released into the water column, the temporal variability of this release, and the sizes of bubbles being generated. This project involved the design and construction of a bubble detector based on a technique which is used widely in the ocean to measure the conductivity of the water. The conductivity sensor was able to measure bubbles because they lower the conductivity of the water in which they are entrained and this signal was recorded as the bubbles rise through the sensor. Although this type of sensor has seen widespread use, there were concerns regarding its responsiveness and inherent sensitivity. To address these concerns, the sensor was tested rigorously in the laboratory using a calibrated volume of air that served as a standard. In most cases, the error between the actual gas volume and that detected by the system was less than 5%. The system was field tested over an area were natural methane is seeping from the seafloor near Cape Lookout in North Carolina with excellent results. Future plans call for the system to be deployed over a deep methane seep in the Gulf of Mexico to evaluate the potential for hydrate formation inside the funnel and to compare its results with those of other techniques.

Introduction

Hydrocarbon seeps are locations where gas bubbles (vents) naturally from the marine sediment. The gas at these seeps is formed either thermogenically under high temperature and pressure or by microbial respiration. Large quantities of gas hydrates are formed in marine sediments mainly along continental margins and in the permafrost in polar regions. Gas hydrates can be comprised of several gases, such as, ethane, propane, and carbon dioxide, however, methane (~99.9%) is the most prevalent gas (Kvenvolden, 1988). At locations where the thermodynamic conditions are not met or are interrupted, the gas is released directly from the sediment into the water. The small bubbles dissipate in the water column but large bubbles have the potential to reach the atmosphere; highly active seeps can actually be observed by bubbling at the surface.

Kvenvolden (2002) estimates that between 500-24,000 Gt of methane are associated with gas hydrates. Even if the estimates were just 10,000 Gt, this is still twice as large as fossil fuel reservoirs, which contain 5,000 Gt of carbon. This makes gas hydrates currently the largest reservoir of organic carbon in the global carbon cycle. However, the role of gas hydrates in the global organic carbon cycle is not completely understood. MacDonald et al. (1994) propose that gas hydrates work as a pressure release system. They state that the accumulation of gas hydrates traps oil and free gases, which are released from below the hydrates when the "plug" of gas hydrates is dislodged due to excess buoyancy force or the rise in water temperature.

A great deal of interest for information on the extent of the gas release from hydrates and hydrocarbon seeps has been brought forward in recent years. Leifer et al. (2000) conducted a study that showed greater than 108 times more methane in the water column around hydrocarbon seeps than atmospheric equilibrium values in the Santa Barbara Channel (SBC), indicating that the release of gas plays an important role in the marine environment. However, due to the lack of a reliable technique, only estimates exist for the quantity of gas released into the environment. Several papers (Max and Miles, 1999; Dickens, 2003) have stated that both regional and global estimates of gas output vary significantly and that it is necessary to find the total flux of gas from venting hydrates.

This suggests a need for comprehensive surveys and the development of an accurate but simple technique to quantify gas release. This study hopes to bridge that gap by incorporating an extensively used concept in oceanography, conductivity, to quantify the gas release.

Background

Gas hydrates are formed, at low temperatures and high pressure, from the incorporation of gas and water into a solid cage-like configuration, known as a clathrate (Zaptsepina and Buffett, 1998). A saturated clathrate structure of methane contains 5 ¾ molecules of water for every molecule of methane present. In theory, due to expansion factors, 1 m^3 of pure methane hydrate contains ~ 164 m^3 of methane gas at standard conditions (Kvenvolden, 1993).

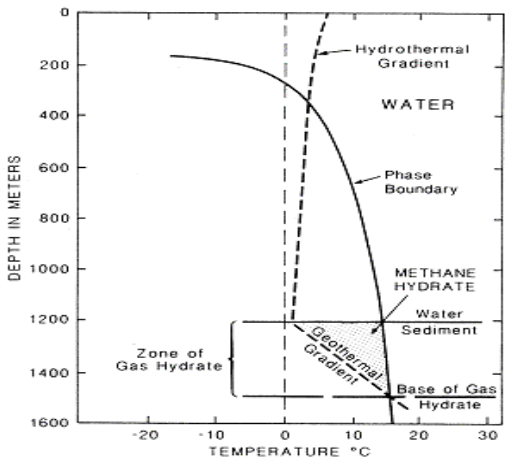

Figure 1. Examples of depth-temperature zones for hydrate stability; outer continental margin adapted from Kvenvolden (1988).

Hydrate formation is normally confined to continental margins due to the adequate supplies of organic matter to generate the gas; even though temperature and pressure conditions required to form gas hydrates occur elsewhere in the ocean (Hyndman and Davis, 1992). The free gas (gas not associated with any other substituent) under excess pressure will react with ice or liquid water to form hydrates (Enns et al., 1965). Furthermore, the temperature and pressure conditions suitable for hydrate stability in the seafloor are dependent upon the composition of the gas and the presence of salt and other constituents in the surrounding seawater (Zatsepina and Buffett, 1998). The physical properties and surface chemistry of deep marine sediments may also affect the thermodynamic state, growth kinetics, and spatial distribution of hydrates (Clennell et al., 1999). In oceanic sediments gas hydrates occur when the bottom temperature approaches 0oC and the depth of the water exceeds 300m; the lower limit is determined by the geothermal gradient (Figure 1) (Kvenvolden and Lorenson, 2001). Wherever the geothermal gradient is interrupted, either by a decrease in pressure or an increase in temperature or salinity, the hydrate dissociates, releasing gas into the surrounding environment (Dickens, 2003).

The Gulf of Mexico (GOM) is one area where the presence of gas hydrates has been well-documented (MacDonald et al., 1994; Sassen et al., 2003; Brooks et al., 1984; Leifer and MacDonald, 2003). In the GOM, Leifer and MacDonald (2003) observed three separate seepages with total gas flux of 62.3 $x10^{-3}$ mol s^{-1}; however, rates at each of the vents were completely different, with one venting ~7 times more gas than the others. Bubble radii ranged from 1 to 2 mm for the small bubbles and larger bubbles up to 2 cm with bubbles with average radii of 5.5 mm. They also observed that the larger bubbles more closely resemble spheres and broke apart into smaller bubbles almost instantly. Furthermore, they noted that the larger bubbles were more contaminated with oil, a condition that may have led to the spherical shape. Upwelling velocities were calculated to be 1-15 cm s^{-1}.

There are also locations in the marine environment where gas hydrates are never

formed because the conditions needed are not ideal; yet, substantial gas is formed and vented from the sediment. These seeps are usually located shallower than gas hydrates therefore more observations exists. One well-documented area of hydrocarbon seeps is in the SBC (Hornafius et al., 1999; Leifer et al., 2000). The SBC seeps are shallow (20-70m) and are probably the most active seeps, with an estimated 1.5x105 m^3d^{-1} gas release with a bubble radius of 1-15 mm (Hornafius et al., 1999). At the surface of the SBC, upwelling rates were observed to be 30-100 cm s^{-1} (Leifer et al., 2000).

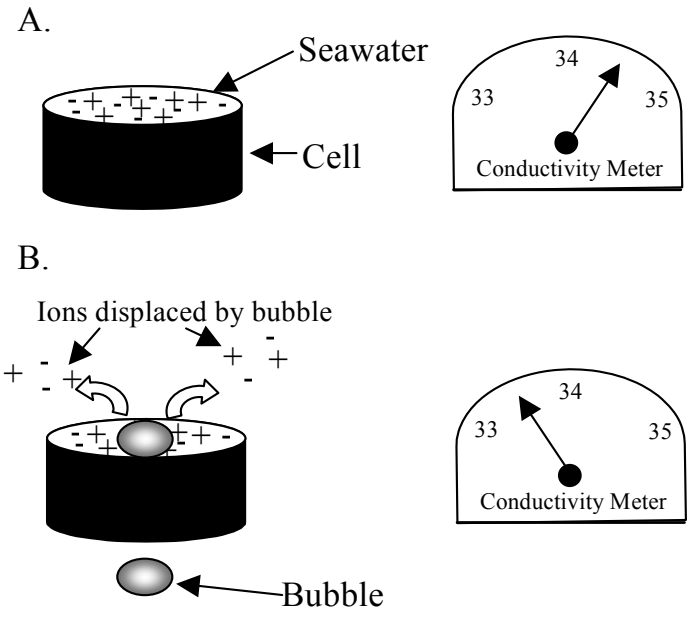

Figure 2. A dramatization of the purposed concept. A) Conductivity cell in seawater. B) Bubble in the cell displacing seawater ions causing a reduction in conductivity.

There have been a few different techniques used to estimate the gas flux from hydrocarbon seeps and hydrates. One of these techniques is the use of acoustical sonar (Hornafius et al., 1999). Sonar observations of bubble size are useful for large-scale observation but may lack the resolution to observe the smaller bubbles. Sonar also lacks the capabilities for long-term studies. Another technique being used is imaging (Leifer and MacDonald, 2003). This technique is applicable for observing all bubbles sizes; however, due to memory constraints has a limited application time, usually several hours. Leifer and MacDonald (2003) also note that errors occur when the plumes are too large and encompass a large portion of the camera's field of view. In addition, they state that errors can occur if a bubble is not in the narrow plane of focus. Other techniques have included a rotating wheel (MacDonald et al., 1994) and a tipping bucket (Roberts et al., 1999). These methods have to be coupled with other sensors creating a large and bulky sensor package to deploy. The technique being proposed, using an electromagnetic sensor, would allow for a simple and small sensor package and for long term monitoring of gas emissions.

The proposed technique utilizes a fundamental concept in oceanography, conductivity. Conductivity is the capability for a material to pass an electrical current. Therefore, in this application, the ion in solution carries an induced electrical current, meaning the greater number of ions the higher the conductivity and vice versa. In oceanography, this concept has been used to infer salinity using the law of constant proportions. The development of this technique will take it one step further. Using the concept that a rising bubble acts like a large void in the seawater that removes a quantity of ions within the conductivity cell as it passed through creating a drop in conductivity (Figure 2). After the bubble exits the cell, the surrounding seawater will replenish the cell with ions returning conductivity to the original value. Furthermore, the drop in conductivity should be proportional to the volume of the bubble.

Experimental

An RBR XR-420-CT Conductivity and Temperature sensor was used as the experimental inductive conductivity cell. This particular CT is a one-off sensor with a pigtail connected to the sensor before the factory A-D converter allowing direct access to the

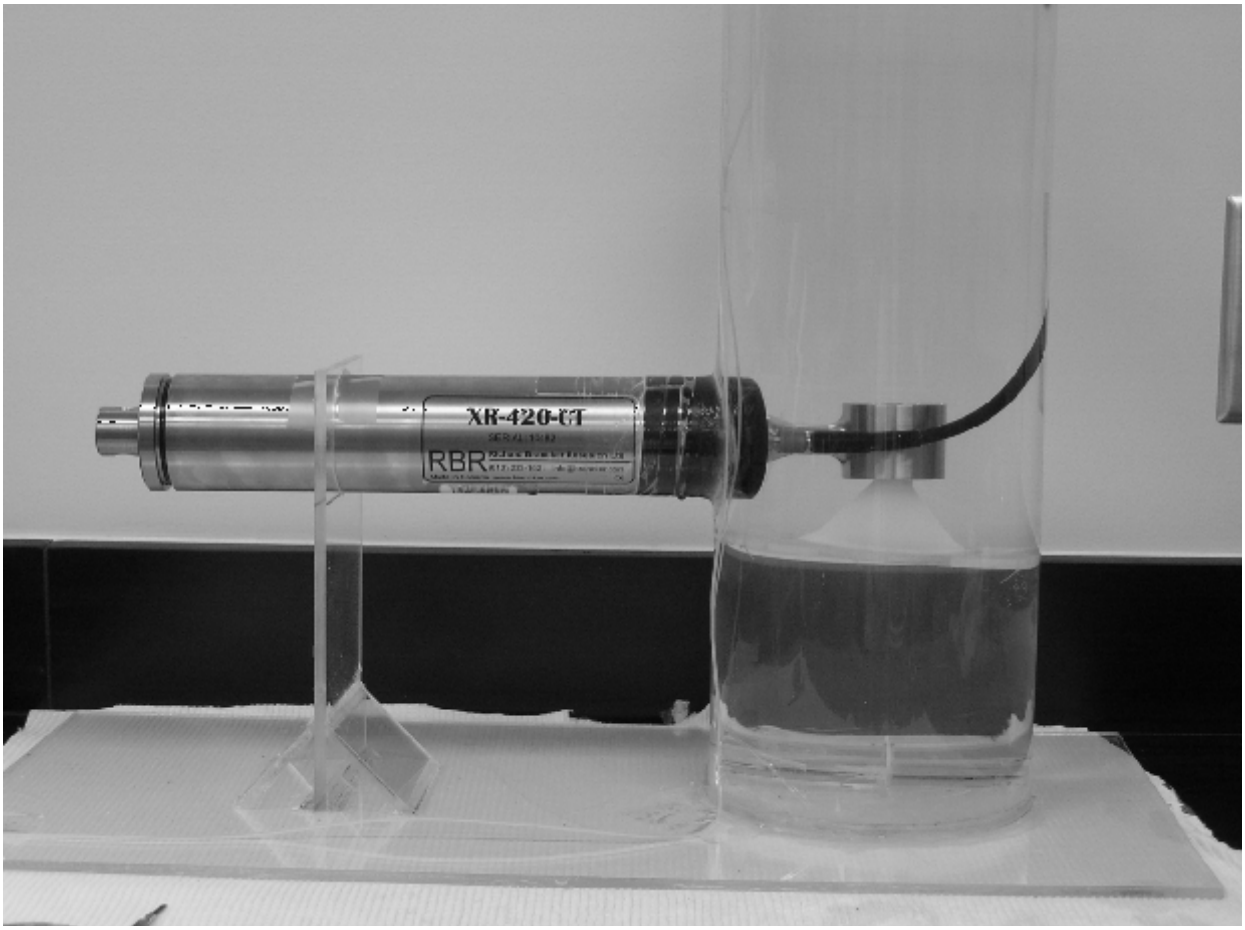

Figure 3. Laboratory test tank with Brancker conductivity sensor installed.

unfiltered analogue signal. The reason for accessing the analogue signal directly is that the factory A-D converter does not sample at a high enough speed (1Hz). The signal from the sensor was supplied to a Tattletale Model 8 data logger with a 12-bit A-D converter with maximum sampling speed of 100kHz. High sampling rate was necessary in order to capture the bubble as many times as possible within the cell.

A test tank (figure 3) was constructed using clear 6-inch PVC pipe and Plexiglas. The tank was maintained at a salinity of 35 using table salt and temperature of ~20oC (room temperature). An air hose was inserted into the tank to create the bubbles, and by varying the orifice size at the submerged end, different bubble sizes were created. Bubbling rates were controlled by varying the air pressure into the air hose using a regulator. A series of bubbling rates and bubble sizes were generated to find the limits of the sensor. A funnel was placed at the bottom of the sensor to ensure the bubbles pass through the cell.

The complete analogue signal of voltage changes (i.e. conductivity changes) for each bubble size was compiled for statistical analysis. Once the data were compiled, they were graphed in MATLAB and/or Excel and comparisons were developed. Using Matlab1

a mathematical correlation between bubble size and conductivity change was developed. The complete mathematics behind this correlation are still being developed as part of Martin's thesis research, but preliminary observations show that curve fitting for each bubble may be necessary.

Bubble size verification was determined by a set of different techniques. The first technique that was used is volume displacement. A 10 ml graduated cylinder was placed on top of the conductivity cell to eliminate the need for a hydrostatic pressure correction. The number of bubbles required to displace a given volume of water (different volumes depending on bubble size) was counted. The volume of an individual bubble will then be calculated by:

$$V_{bub} = V_d/B_n$$

Where V_d is the volume displaced and B_n is the number of bubbles required to displace that volume. The second technique were by optical means. Pictures were taken of the bubbles using a digital camera. Behind the bubbles, a meter stick were placed allowing for direct determination of bubble diameter. Volume was calculated using the volume of a sphere equation ($V_{bub}= 4/3\pi r^3$).

Once the sensor system was calibrated in the laboratory, it was taken to the field for an in situ evaluation. For these tests, the deployment setup incorporated a simple triangular pyramid made out of ¼" acrylic sheeting. The bottom opening was 45x45x45cm, tapering to a 14mm opening at the top, with sides sloping at 70 degrees. It was found that above 65 degree slope bubbles tend not cling to sides of funnels. The CT attached to the top and was supported by a saw horse type frame. The funnel and frame where places on a sheet of plywood to avoid sinking into the bottom. A bottle was then placed at the top of the setup to collect gas to later truth the results calculated. The Tattletale data logger and batteries were housed in an aluminum pressure housing built to withstand a 6,000m immersion so that it can be used for deployments at hydrate sites as well as for these shallow water tests.

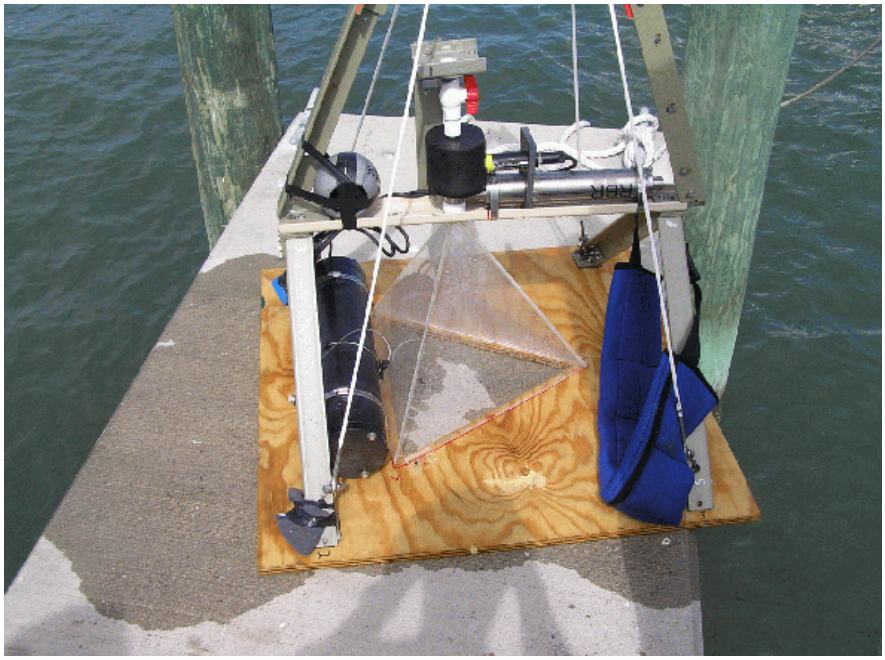

Figure 4. System configuration for in situ testing, including funnel and pressure case.

Results and Discussion

Laboratory tests:

Using the hardware described above, bubbles were introduced into the sensor, producing the data shown in figure 5. Conductivity (on the Y axis) decreases each time a bubble passes through the orifice. This result clearly shows that samples are being acquired at a sufficiently rapid rate to allow for more than adequate characterization of each bubble. The noise in the baseline signal is inherent in the sensor, requiring the construction of a simple low-pass filter (simple R-C circuit) to reduce the noise level without compromising sensitivity.

Thirteen different size orifices were utilized, with each orifice creating a different size bubble. Volumes for these bubbles, ranging from 20ml to 957ml, were then calculated using volume displacement (figure 6). Each of these bubble volumes were streamed through the cell and were sampled at 500Hz and 1kHz. These runs were duplicated in waters of salinity 40-15 (changing by 5) to observe, if any, the effect of salinity on the results. Data files were also created with a known volume of gas but different size bubbles, to help truth the mathematics that will be developed as part of Martin's thesis.

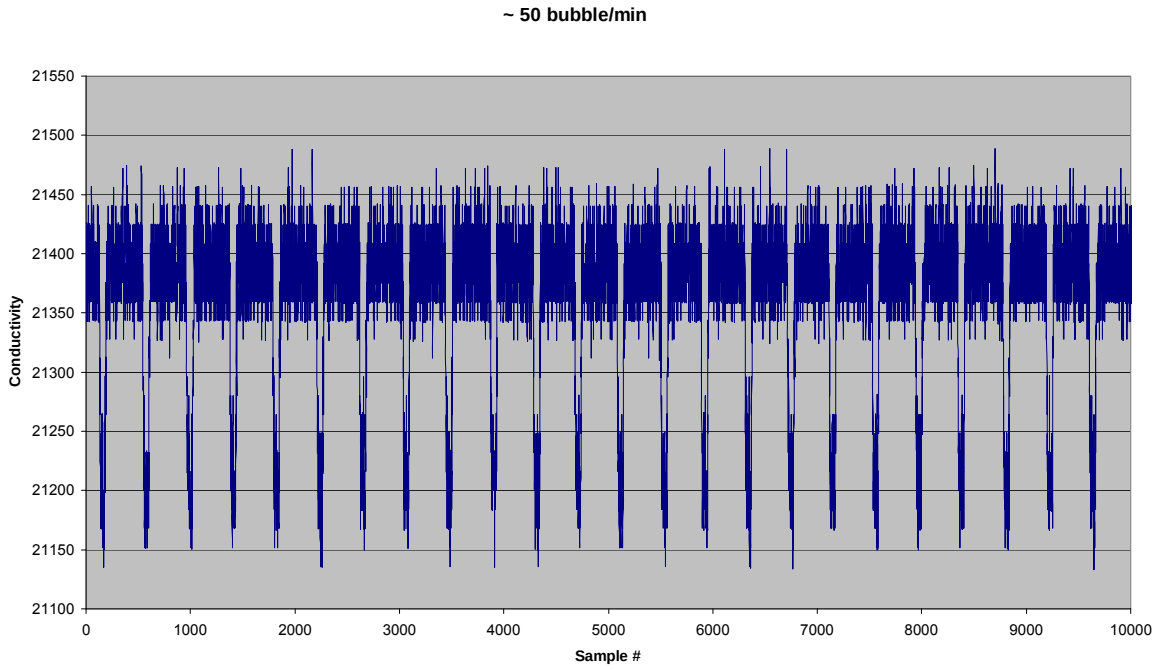

Figure 5. Bubbles passing through the sensor are detected as spikes of reduced conductivity lasting for a fraction of a second. In this experiment, samples were acquired at the loggers maximum rate of approximately 1kHz.

Figure 6. Response of the system to varying bubble sizes

North Carolina cape lookout bight deployment:

To assure that the in situ setup was working properly, it was tested at the dock using divers and measured volumes of air. The system was suspended from the UNC Marine Institute pier and divers injected known volumes of air at the under the funnel which were then captured in the bottle. Volumes were then compared and the data shown in figure 7 were obtained. All decreases in the conductivity (y axis in arbitrary units) on the graph are bubble signals.

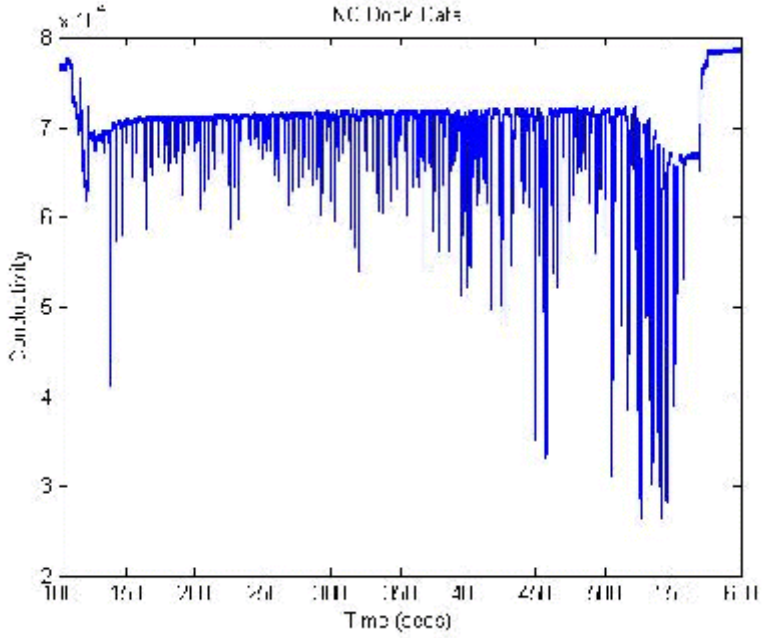

Figure 7. Record of air captured by the system while suspended from the dock.

After setup was found to be working, it was deployed at Cape Lookout Bight, NC where methane bubbles from the seafloor naturally. Here the sensor was placed on the bottom, 30 feet deep, for 2-3 hours, during a low tide cycle, to observe how the CT responded to natural bubbling. The funnel worked well with 120 ml of gas being captured in the reservoir bottle at the top. The data obtain from that are depicted in figure 8.

Figure 8. This graph shows the fluctuation in conductivity as the tide changes, yet the bubble signals can still be seen as decreases from the conductivity trend. After the low tide was complete, the time when the most bubbling occurs, the system was relocated to shallow water where more known volumes of gas were bubbled through the sensor for more calibration testing.

Conclusions

These experiments have successfully demonstrated that the concept of using a conductivity sensor to measure bubble flux is valid. The laboratory tests proved that the

volumes measured are accurate and repeatable and the field tests provided data that will be used to better understand the system and its response to such highly variable conditions. The project and data will continue to be developed by Martin as part of his Master's thesis and the system and its design details will be made available to other investigators as required.

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Project: DE-FC26-02NT41628

(DOE, Subcontract to University of Mississippi)

Mid-Infrared Sensor Systems for Continuous Methane Monitoring in Seawater

Methane detection using attenuated total reflection (ATR) spectroscopy.

Final Technical Report

Research Activities December 01, 2004 – November 30, 2005

Boris Mizaikoff (PI), Gary Dobbs

December 13, 2005

DISCLAIMER

ABSTRACT/SUMMARY

This final technical report will summarize progress towards development of deep-sea detection and monitoring systems for methane and gas hydrates based on mid-infrared (MIR) attenuated total reflection (ATR) spectroscopy during the periods from December 01, 2004 – November 31, 2005. Representative figures from the reported project period are provided in the appendix; complete details from previous project periods can be found in the progress reports.

- A brief summary of the significant works performed in previous project periods, April 01, 2001 through November 30, 2004, is provided.
- Experimental investigations of IR-ATR signal generation were performed to facilitate precise insight into 'active' sensing regions along planar ATR waveguides.
    - Experimental results reveal discrete sensing regions along multi-reflection waveguides providing valuable knowledge for optimizing construction designs of deep-sea IR-ATR sensing probes.
- Complimentary spectral ray tracing simulations establish a virtual environment for rational development and evaluation of deep-sea probe configurations.
    - Spectral ray tracing simulations facilitate efficient evaluation of light guiding optics and sensor transducers. Resulting, an optimal selection and arrangement of optical components for deep-sea sensing probes and optics platform for 'SphereIR' can be established.
- Modifications to the previously reported pressure vessel for simulated deep-sea measurements expand experimental capabilities for synthetic hydrate formation and spectroscopic investigations of hydrate formation and dissociation via fiber-optic evanescent field spectroscopy.
    - Development of a custom high-pressure viewport and custom high-pressure fiber-optic feed-throughs were successfully implemented to confirm synthetic hydrate formation and evaluate this spectroscopic techniques ability to monitor hydrate formation and decompsosition.
- Initial investigations reveal the capability of IR-ATR fiber-optic sensors for *in-situ* monitoring applications of gas hydrate formation and dissociation.
    - State-specific changes to the infrared spectra of water provide the ability to monitor *in-situ* formation and dissociation of gas hydrates.

Ongoing investigations to distinguish state-specific infrared absorption features of liquid water, ice, and the three hydrate structures (I, II, and H) are currently underway and will be concluded early in 2006. Based upon current progress, we anticipate the final construction and first field tests of a miniaturized multi-component IR sensor system capable of *in-situ*, deep-sea methane detection and

passive monitoring of gas hydrate formation and dissociation by natural processes in deep-sea environments during continuation of this project in 2005/2006.

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LIST OF GRAPHICAL MATERIALS

FINAL TECHNICAL REPORT

Summary of Work from April 01, 2001 through November 30, 2004

Our contribution to the Gulf of Mexico Hydrates Research Consortium (GOMHRC) is the development of spectroscopic sensors for the determination of hydrocarbon concentrations (with focus on methane) in the liquid phase and in the gas phase. Most recently, the feasibility for *in-situ* monitoring of gas hydrate formation and dissociation via IR-ATR spectroscopy has been established. Deployment of these sensors will be an integral part of the station, continuously providing information on the measured parameters during long-term observation periods.

Our progress in the framework of this project demonstrated the feasibility for detection of dissolved methane via IR-ATR spectroscopy in a laboratory environment including evaluation of potential spectroscopic interferences by salt ions in year 1.[1] Significant strides in the development of a miniaturized deep-sea mid-infrared spectrometer ('sphere-IR') were completed in year 2 by establishing data evaluation strategies[2-5], selection and testing of the fundamental instrument components including a Stirling-cooled MCT detector ideal for extended maintenance free deployment, and design considerations for an improved deep-sea sensor system from past experience of the PI's research group.[6-11] During year 3, computer assisted drawings (CAD) developed in year 2 for the primary instrument components facilitated the complete design and construction of the electrical compartment for 'SphereIR'. Design and fabrication of fasteners for primary optical components for 'SphereIR' were also completed in year 3. Finalization of the optics compartment will follow successful construction and testing of optimized deep-sea sensing probes in year 5 of this project. Investigations of a novel fiber-optic/planar waveguide sensing probe were initiated at the end of year 3. Experimental measurements revealed the capability to successfully couple radiation into the planar sensing transducer via fiber-optics. This approach is expected to ensure robust performance in deep-sea conditions. This work was also extended into year 4 with details provided in this report. Furthermore, initial experimental investigations into pressure influences on water diffusion into polymer extraction membranes were also performed during year 3. No significant spectral changes were observed at pressures correlating to ocean depths of approx. 70m, warranting improvements to the experimental apparatus for more thorough evaluation of pressure equivalents of 1,000+ meters of operational depth. Complete details on previous work can be found in the annual and semiannual progress reports for the duration of our involvement with this project.

Experimental Investigations into IR-ATR Signal Generation along Planar Waveguides

As stated in previous reports, the mission critical aspect in developing viable submersible optical sensors is the engineering of optical chemical sensor probes for interfacing the encased spectrometer with the marine environment. Thus, it is of paramount importance to optimize the probe design for ensuring delivery of radiation to the transducer surface, maximizing signal transduction, and effectively guiding the generated signal to the detection module. To optimize design and construction of deep-sea IR-ATR sensing probes, it is of fundamental importance to have specific insight into light propagation inside the waveguide structure and resulting signal generation. Specific knowledge of these parameters ensures rational development for optimal operation by minimizing interferences from construction materials and radiation losses resulting from mounting the sensing transducer in a pressure proof housing.

To obtain this information, a novel experimental procedure was conceptualized to interrogate the signal generation along the sensing surface of a typical 72 x 10 x 6 mm ZnSe horizontal ATR crystal.[12] For a 72 x 10 x 6 mm trapezoidal crystal geometry, six individual reflection regions should be present along the measurement surface. Therefore, it was hypothesized that by consecutively depositing small, discrete residues at fixed intervals along the measurement surface, one could accurately identify individual 'active' sensing regions at the waveguide surface. To perform this experiment, 0.75 μL deposits of polystyrene-co-butadiene (PSCB) were deposited at 3 mm intervals along the waveguide surface while infrared spectra were collected after each sequential addition. A representative IR-ATR spectrum of PSCB is provided in **Figure 1** with highlighted absorption features utilized in analytical evaluation. In 'active' sensing regions, strong PSCB spectral features are observed as opposed to 'inactive' sensing regions where no PSCB spectral features can be identified as displayed in **Figure 2**. The deposition frequency (based on a modified version of the Nyquist theorem) provided the ability to extract the specific locations of individual sensing regions for four of the six internal reflection elements and extrapolation of the two unidentified sensing regions. **Figure 3** displays an optical image of polymer deposits along the planar waveguide (A), signal intensity for each residue at each deposit location (B), and a surface plot of extrapolated individual sensing regions.

The precise identification of individual sensing regions determined from these experiments provides specific information regarding the position of light coupled into the planar waveguide as well as the path of radiation propagation through the internal reflection element. Furthermore, the absorption data can be utilized to extrapolate other important optical parameters including the propagated cone of radiation and diameter of light coupling into the reflection element with the aid of complimentary spectral ray tracing analysis by emulating experimental measurements. Therefore, ray tracing procedures were developed and performed for this specific purpose and will be discussed in the following section...

Spectral Ray Tracing Analysis of IR-ATR Signal Generation along Planar Waveguides

Ray tracing software generally provides the capacity to simulate virtually any optical configuration, optical component, and many radiation parameters. Additionally, the spectral ray tracing software utilized in these experiments, SPRAY (W. Theiss, Aachen, Germany), provides the ability to incorporate simulated infrared absorbers for emulating analytical spectroscopic measurements. Thus, it was hypothesized and successfully demonstrated that this software could be utilized to produce identical analytical information collected during experimental measurements by matching the experimental radiation parameters in the simulation. The power of this approach is highlighted through the blind trial-and-error approach for extrapolating the radiation cone angle and size of radiation impinging upon the in-coupling facet of the IRE without *a priori* knowledge of such parameters (verified experimentally after simulation trials). Furthermore, the successful application of this virtual platform provides an excellent tool for optimizing optical configurations and probe designs for 'SphereIR' in a cost efficient manner.

For ray tracing analysis, a simple 5-component model was devised simulating the experimental configuration in real dimensions. The simulated set-up models the in-coupled radiation as a circular light source, and was configured such that the internal reflection angle ($\theta_{int,}$) equals the beveled HATR in-coupling facet angle (45°). The position of the circular light source at the beveled 45º in-coupling facet was off-set from the central axis of the modeled 72 x 10 x 6 mm HATR element to closely emulate the experimental conditions. A closed cylinder with a diam. of 2.5 mm was implemented with an IR absorption band at 1443 cm^{-1}, thereby simulating the spectral response of deposited PSCB residues. A 72 x 10 mm rectangular screen for imaging the radiation distribution along the measurement surface of the HATR element was also integrated in the model. Furthermore, a 40 x 42.4 mm rectangular detector was modeled and positioned parallel to the beveled exit facet of the crystal. All photons transmitted through the ATR element were therefore collected at this simulated detector element generating infrared absorption spectra of simulated PSCB deposits. The application of a large simulated detector provides the capability of evaluating signal generation of residues for virtually any combination of in-coupled light source radius, radiation cone angle, and in-coupling position. Additionally, this model does not require precise dimensional modeling of optical components or their configuration for a particular experimental set-up, as normalized simulation data will only be comparable to normalized experimental data if the simulated radiation path, in-coupled light source radius, and radiation cone angle resemble the through-coupled radiation (detected radiation) for the experimental studies. However, precise dimensional modeling for developmental applications is required.

Procedures performed during experimental measurements were precisely followed during spectral ray tracing analysis. Many combinations of in-coupled cone angles ranging from 1° – 16° and light source radii from 0.00215 cm – 0.25

cm were evaluated. From all simulations, the combinations with a 0.1278 cm ± 0.042 cm light source radii with a constant cone angle of 2° (CCA), and combinations of a constant light source radius of 0.1278 cm with cone angles of 2° ± 1° (CLSR) most closely emulate the experimental results generated in this study. **Figure 4** displays an overlay of normalized integrated peak values for averaged simulation trials with averaged and normalized experimental data. It is clear that the simulation platform was very capable of emulating experimental results indicated by total residual error values (sum-of-squares) of 0.110 for CLSR and 0.123 for CCA combinations. Cone angle values were later confirmed by additional experimental measurements resulting in a range of 1.9° to 2.9°. Furthermore, estimated sizes for individual sensing regions (**Figure 5**) in the experimental studies were calculated using both experimental and simulation results.

In addition to emulating experimental measurements, the ray tracing analysis was utilized to visualize the influence of radiation parameters on the actual sizes of 'active' sensing regions. **Figure 6** displays the 'active' sensing regions along a 72 x 10 x 6 mm planar waveguide with select cone angles ranging from 2° – 16° and a light source radius of 0.1278 cm. The importance of optimizing the selection and configuration of optical components for the development of sensing probes and the optics compartment for 'SphereIR' is accented in these results. Clearly, smaller radiation cone angles are desired to minimize interferences from sensor probe materials and losses due to mounting the transducer in a pressure proof housing.

In the specific context of this project, this simulation platform accurately mimics experimental signal generation for IR-ATR experiments enabling optimization of optical configurations for 'SphereIR' and evaluation of deep-sea IR probe designs in a virtual environment. Resulting, a solid basis for predicting the performance and signal generation for deep-sea IR evanescent field probes is established facilitating the rational design and fabrication of a viable submersible mid-infrared sensing platform 'SphereIR' as our contribution to the GOMHRC. Additionally, this approach significantly reduces developmental costs associated with trial-and-error procedures (time and money). For, complete details on spectral ray tracing results presented here, please see the attached .pdf of the revised submitted manuscript to Applied Spectroscopy. An additional manuscript is currently in preparation for the Journal of Optical Engineering further expanding the discussion on simulation applications for predictive evaluation of sensor transducers. A .pdf of the submitted manuscript will be forwarded to Carol Lutken upon submission of the manuscript anticipated Jan./Feb. of 2006.

In-situ Monitoring of Gas Hydrates

A variety of analytical tools have been successfully utilized to interrogate hydrate structures despite the low temperatures and high pressures needed to synthetically form gas hydrates in well-controlled laboratory environments. Currently, nuclear magnetic resonance (NMR)[13, 14], Raman[15-21] and Fourier

transform infrared (FT-IR) spectroscopy[22-24], along with X-ray diffraction[20, 25], gas chromatography[25], and neutron diffraction[14] have provided a wealth of information on gas hydrates. In addition to fundamental studies, a great need exists for the capability to monitor *in-situ* hydrate formation and dissociation in both environmental and industrial settings. However, as a result of the harsh environments in which hydrates occur, almost every laboratory analytical tool used to evaluate hydrates cannot logistically be extended to real-world monitoring applications.

To date, Raman spectroscopy has shown excellent *in-situ* monitoring capabilities of hydrate formation.[15-21] When a host gas is 'caged' in hydrate lattice structures, the molecules become vibrationally, rotationally, and translationally restricted compared to the 'free' or 'dissolved' gas. As a result, the fundamental vibrational and rotational energies of the host gas vary significantly between the 'dissolved' and 'caged' molecules. Therefore, the formation of hydrates can be monitored as a result of changes in the Raman spectra for the host gas as the central peak positions shift corresponding to the difference of vibrational and rotational energies of the 'dissolved' and 'caged' molecules. As a result, Raman spectroscopy can be used to indirectly distinguish liquid water from different clathrate structures by monitoring the host gas absorption features. In addition to Raman spectroscopy, FT-IR spectroscopy has the potential for monitoring hydrate formation and dissociation by spectroscopically evaluating variations in the molecular rotational and vibrational energies for either the host gas and/or water structure.

FT-IR spectroscopy has had limited application in hydrate research primarily as a result of the strong absorption of water, which limits the practicality for standard transmission measurements. Devlin and co-workers have minimized bulk water absorption by vacuum and vapor depositing films of clathrate hydrates thereby accessing the clathrate structures; however, this approach cannot be extended to real-world, oceanic or industrial applications.[22, 23] Recently, H. Oyama and colleagues performed the first infrared attenuated total reflection (IR-ATR) measurements of gas hydrates for CO_2.[24] ATR circumvents limitations of conventional transmission-absorption measurements as a result of reduced analytical volumes located along the surface of ATR waveguides. However, details of the setup utilized by Oyama and colleagues were not publicized other than the use of a high-pressure ATR probe rendering the reproduction of those results difficult. Additionally, the report focused only on the spectral absorbance of CO_2 while neglecting the primary component and strongest infrared signal of hydrates, water.

In addition to the possibility of evaluating the 'dissolved' or 'caged' host gas vibrational and rotational energies, FT-IR ATR measurements provide the capability of probing state-specific spectroscopic changes in water vibrational and librational (lattice vibration) bands. Liquid water has a unique infrared absorption spectra (**Figure 7**) containing a large O-H stretch in the spectral

region of 3100-3600 cm^{-1}, H-O-H bend mode from 1500-1700 cm^{-1}, and a broad combination peak at 2115 cm^{-1} (combination of the bend and libration bands). As liquid water changes to ice, the intensity of the H-O-H bending mode decreases sharply while the combination bend and libration band shifts to higher energies.[26] In addition to changes in peak intensities and locations, the band widths (as full width half maximum) also change during this process allowing multiple strategies for evaluating IR-ATR spectra. Because ice and hydrate structures have nominal similarities, it was hypothesized that IR-ATR could be utilized to monitor *in-situ* hydrate formation and dissociation by monitoring the infrared absorption features of water.

Development of Pressure Vessel and Testing for Synthetic Formation of Gas Hydrates

Hinging on the potential use of IR-ATR techniques for monitoring hydrate formation and dissociation, several modifications to our custom pressure vessel for simulating deep-sea environments were necessary. For successful ATR measurements, it was necessary to achieve hydrate conditions while coupling an infrared transparent silver halide fiber into the apparatus for benchmark laboratory ATR measurements (**Figure 8**). To visually verify hydrate formation, a custom designed high-pressure viewport was constructed for the pressure vessel (**Figure 9**). The viewport utilizes a 1/8" thick, 1" dia. sapphire window pressure rated to 865 psi with a 3-fold safety factor. Additionally, custom Teflon ferrules were fabricated to couple a silver halide fiber (700 μm dia.) into the pressure vessel and pressure proofed to at least 750 psig (**Figure 10**).

Once the pressure vessel was tested with all components necessary for spectroscopic measurements, initial hydrate tests were carried out to verify the capability of forming hydrates. First tests were carried out for methane hydrates requiring pressure up to 700 psig and a temperature range of 1 to 3 °C inside the vessel. A 290 ppm aqueous solution of sodium dodecyl sulfate (SDS) was utilized to reduce methane hydrate induction times to less than 1 hour similar to reports by Rogers and colleagues for ethane and natural gas hydrates.[27] A standard webcam was placed in front of the optical viewport to safely observe the progression of hydrate formation and dissociation. **Figure 11** provides optical images collected throughout the first successful methane hydrate trial.

In addition to a decrease in system pressure, which is indicative of gas hydrate formation, a small sample of remaining solid structure present inside the pressure vessel was removed for *ex-situ* FT-IR transmission analysis after the cell was depressurized rapidly while maintaining a constant temperature. The solid structure that was removed from the pressure vessel was audibly degassing suggesting the encasement of gaseous methane. This was verified *via* IR transmission measurements of methane's two fundamental infrared absorption bands located at 3020 cm^{-1} and 1305 cm^{-1} as gas was released from the melting structure. **Figure 12** provides the results of open path IR transmission spectra from a Bruker 66 spectrometer as the solid structure was allowed to melt

(approx. liquid volume 20 mL) inside the enclosed sample compartment providing evidence that methane hydrate was indeed formed.

In-situ Monitoring of Gas Hydrates via Fiberoptic Evanescent Field Spectroscopy

Following confirmation of hydrate formation in the pressure cell, a silver halide fiber was coupled through the cell and setup for *in-situ* measurements (**Figure 13**). Prior to hydrate formation the system was pressurized to record the infrared spectrum of water to determine if any spectral changes would be induced from pressure effects. **Figure 14** clearly displays no measurable pressure-related changes in the water spectrum from 0 to 700 psig. Currently, the large O-H band in the 3000 cm^{-1} region cannot be used for analytical evaluation. Further advances in the fiber-optic coupling technique or the use of deuterated water will provide the capability of assessing this absorption feature.

The first fiber-optic spectroscopic hydrate measurements were taken for ethane hydrates as its formation conditions (300 psig and 3-5 °C) are milder than those for methane hydrate (600 psig and 1-4 °C). Additionally, ethane hydrate induction times are typically shorter than for methane hydrate. Furthermore, gaseous ethane is encased in the large cage of structure I hydrate, which has greater structural differences than the small cage when compared to the lattice structure of ice. **Figure 15** displays selected regions of infrared spectra collected throughout the formation process of ethane hydrate.

As hypothesized, throughout the hydrate formation process, the combination band initially at 2110-2115 cm^{-1} shifts towards higher frequencies and the intensity of H-O-H bend at 1650 cm^{-1} decreases sharply. The combination bend and libration band shifts dramatically throughout the hydrate process after an initial peak shift to approximately 2128 cm^{-1} as a result of temperature induced reorganization of water at approximately 4 °C to a final observed peak position at approximately 2198 cm^{-1}. The gradual shift of this maximum peak amplitude provides an excellent marker for the progress of hydrate formation as the peak location is dependent upon the ratio of liquid:solid structure interrogated along the fiber-optic transducer. Furthermore, to display the capability of this sensing approach to monitor the dissociation of hydrate, spectroscopic measurements reveal that this spectral shift is reversible. **Figure 16** displays the behavior of the combination bend and libration band throughout both hydrate formation and dissociation.
In **Figure 16**, the final peak maximum returns to 2120 cm^{-1} during the time spectroscopic measurements were collected for dissociation. It is known that after the formation of ice (or hydrate), some residual structural memory in the aqueous solution is acquired and it could account for this observation. Further investigations are ongoing to evaluate the capability of this procedure to detect and verify this phenomenon from the bulk aqueous solution subsequent to hydrate formation trials.

For monitoring applications, the change of peak location for the combination band indicates the progression of hydrate formation or hydrate decomposition. **Figure 17** provides four plots of the pressure, temperature, and analyzed spectroscopic results throughout the measurement series of both ethane hydrate formation and dissociation. Upon hydrate induction the system pressure drops as gaseous ethane becomes encased in the hydrate structure (**Figure 17, pressure plot**). The overall system pressure fluctuates throughout hydrate formation as the ethane source was regulated to control the rate of formation through the manipulation of the ethane backing pressure. Additionally, the system temperature fluctuates throughout the formation process as energy from the latent heat of formation for ethane hydrate is released (**Figure 17, temperature plot**). In addition to visual confirmation, these two parameters are commonly used to identify and verify the formation of hydrate in laboratory environments. The analyzed spectroscopic data provides much greater detail of the formation process compared to the fluctuating pressure and temperature data (**Figure 17, peak and FWHM plots**). This results as the ratio of liquid:hydrate mass decreases throughout hydrate formation and the peak location of the combination band being dependant upon the ratio of liquid:hydrate mass in the analytically probed volume of the sensing transducer. Furthermore, the spectroscopic data provides superior information to pressure and temperature data throughout the decomposition process. As hydrate thermally decomposes at a constant pressure (excess ethane from degassing hydrate is removed from the system during this process via a pressure-regulating release valve) with the system temperature passively equilibrating to ambient conditions, there are no apparent pressure or temperature indicators to follow this process. This is clearly displayed when collectively comparing all four plots in **Figure 17**. In addition to the combination bend and libration band, analysis of the H-O-H bend mode at 1640 cm^{-1} can be used as an indicator of hydrate formation and dissociation. Inspection of the peak intensity of this band reveals analogous information to peak location data obtained for the combination bend and libration band (**Figure 18**). In **Figure 18**, the peak intensity of the H-O-H band tracks the peak position data for the combination band very well. However, the band intensity is dependant upon the amount of water interaction with the fiber (solid and/or liquid); therefore, further quantitative analysis of the H-O-H bend intensity is warranted with control experiments.

The analyzed spectroscopic data provides a great deal of information about the bulk material inside the pressure chamber during hydrate formation and dissociation processes. Firstly, the combination bend and libration mode gradually shifts to higher frequencies throughout hydrate formation and gradually shifts to lower frequencies during the dissociation process. This is a result of the changing ratio of liquid:solid interaction at the transducer surface which visual, temperature, and pressure data cannot reliably provide. In fact, visual observation alone could be misleading during hydrate formation as one may see bulk hydrate structure which has significant amounts of liquid trapped as

interstitial water inside the bulk structure. In fact, we observed this during these measurements. Within six minutes of catastrophic hydrate formation, the optical viewport was blocked by bulk hydrate mass preventing visual verification of continued hydrate growth (**Figure 19**). Over the next 100 minutes, significant hydrate formation continued by monitoring spectroscopic and pressure data. This most likely indicates significant amounts of both interstitial and residual bulk water being converted to solid hydrate and displaying advantages of this analytical technique. In real-world situations, pressure data will not fluctuate rendering substantial limitations when following hydrate formation solely based on visual observation. Furthermore, it is common to monitor the total gas volume introduced into the sample chamber during synthetic hydrate formation to determine the rate of interstitial water conversion.[27] However, this is again impractical for most real-world, environmental or industrial applications.

During the first measurements, we anticipated the capability of identifying the host gas as it was incorporated into the hydrate structure. Unfortunately, that was not observed in the initial measurements. However, we anticipate this will be possible as our experimental apparatus will be improved as our experience with this system increases. Additionally, we are also developing novel planar waveguide sensor probes that should provide the capability of detecting the host gas as displayed by Oyama and colleagues with the use of an ATR probe in their experiments.[24] Further investigations are currently underway to thoroughly evaluate the spectroscopic features of gas hydrates in addition to the possibility of identifying different hydrate structures based on the peak locations of pure hydrate structures as we hypothesize the vibrational and librational energies to be structure specific.

Finally, because the initial hydrate measurements only evaluated the spectroscopic changes of water, investigations of ice formation are currently ongoing. The formation of ice leads to similar changes in the spectroscopic data as hydrate formation. Therefore, the capability of distinguishing ice from hydrate becomes important in addition to identifying different hydrate structures. **Figure 20** provides initial measurements that we have collected on ice formation in the pressure vessel. Because similar spectroscopic changes are observed during ice formation as in hydrate formation, it will be difficult in multi-phase systems to discern ice from hydrate without host gas information. However, in oceanic environments the potential for ice formation is significantly decreased as pressure, salinity, and temperature favor hydrate formation. Improvements to analytical procedures including evaluation of different sensing probes have great potential for providing host gas information that will further improve the assessment of hydrate formation and structures using IR-ATR spectroscopy.

FIGURES

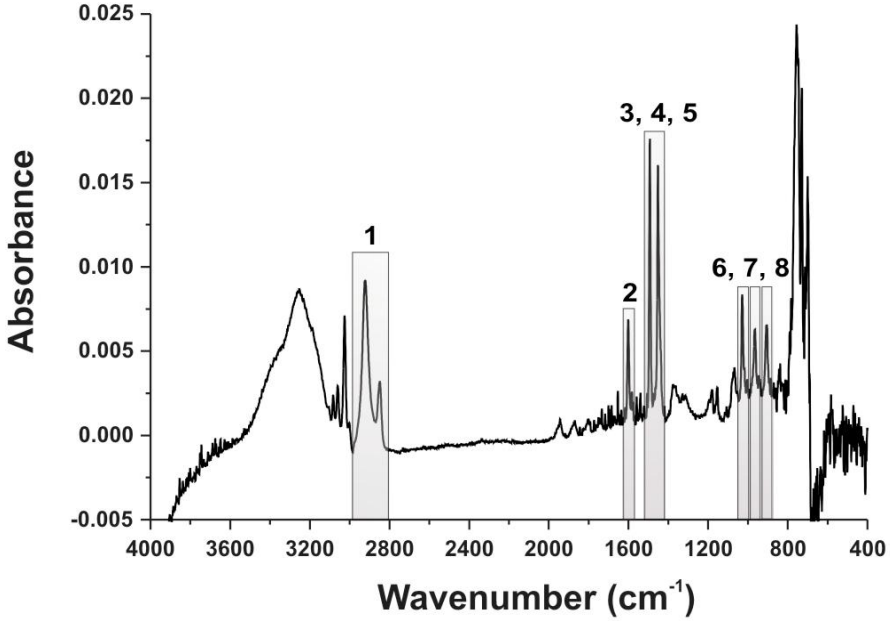

Figure 1: **Representative FT-IR ATR absorbance spectrum of PSCB with highlighted spectral regions utilized during data evaluation.**

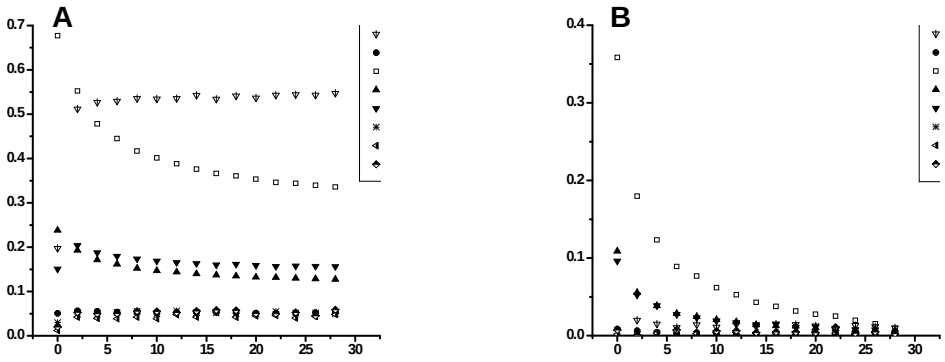

Figure 2: **(A) Exemplary representation of infrared absorption for a PSCB deposit at an active sensing region resulting in positive integrated peak values vs. time. (B) Exemplary representation of PSCB absorption for a deposit at an inactive region (no internal reflection) resulting in near zero integrated peak values. Stabilized IPVs are observed after approx. 25 min as the majority of solvent has evaporated leaving behind PSCB residues.**

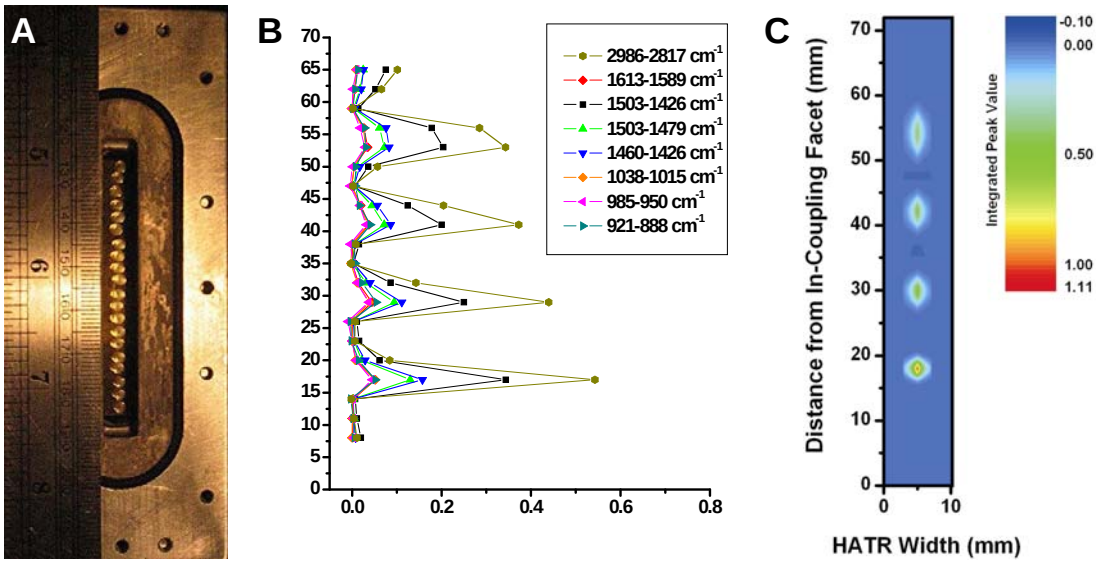

Figure 3: **(A) Optical image of PSCB deposits at a ZnSe HATR crystal surface mounted in a topless flow cell. (B) Absorption intensity (represented as IPVs) of PSCB vs. distance from the in-coupling facet of the HATR crystal.* (C) Surface map projecting the absorbance intensity of PSCB residues along the measurement surface of a HATR crystal displaying discrete 'active' sensing regions along the crystal surface. (*Lines are for assisting visual inspection.**

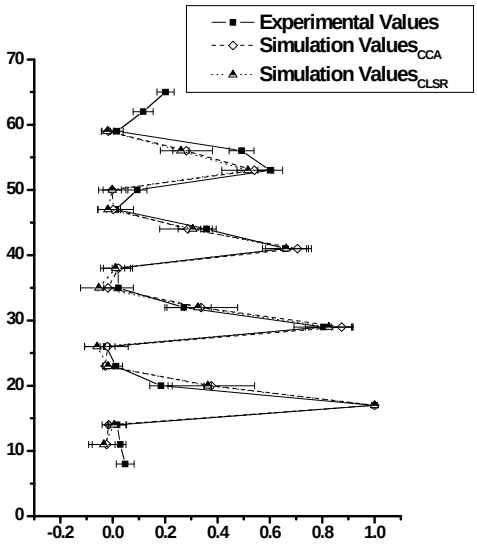

Figure 4: **Averages of normalized IPVs for experimental and simulation data*,** with respect to the measurement location plotted versus distance from the in-coupling facet of the horizontal ATR crystal (error bars are ± 1 standard deviation).*** (*Simulation Values$_{CCA}$ represent averaged IPVs for data obtained with combinations of a 0.1278 cm ± 0.042 cm light source radii with a constant cone angle (CCA) of 2°. **Simulation Values$_{CLSR}$ represent averaged IPVs for data obtained with combinations of a constant light source radius (CLSR) of 0.1278 cm with cone angles of 2° ± 1°. ***Lines are for assisting visual inspection.)**

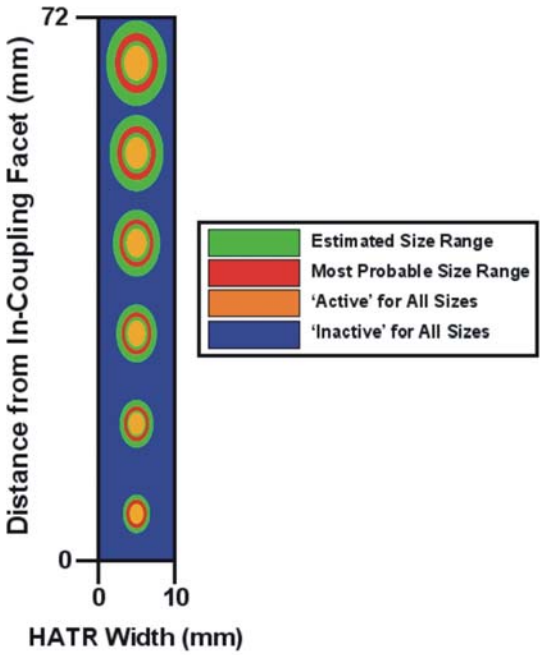

Figure 5: **Elliptical surface projections of (i) the range of dimensions of 'active' sensing regions shaded in green, (ii) the range of most probable dimensions of 'active' sensing regions shaded in red, (iii) always 'active' regions for the estimated range of dimensions of sensing regions shaded in orange, and (iv) always 'inactive' regions for the estimated range of dimensions of sensing regions shaded in blue.**

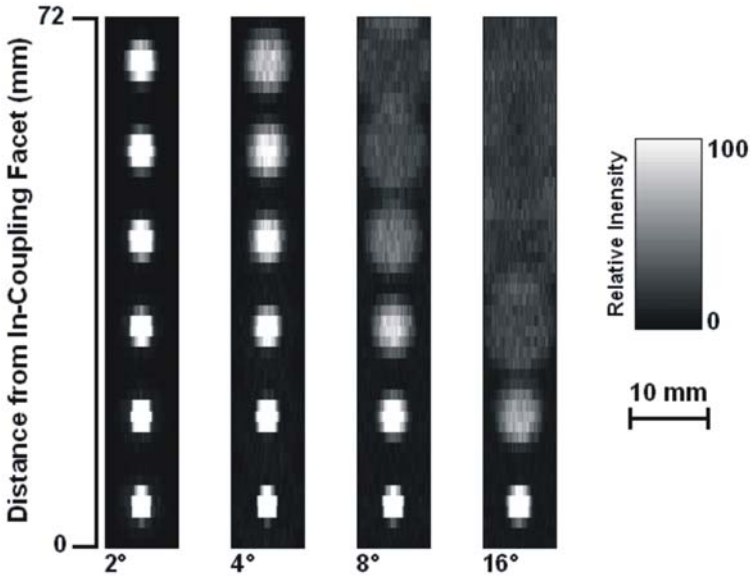

Figure 6: **Simulated radiation density maps displaying internal reflection regions and the changes in radiation distribution along the sensing surface of a HATR crystal with increasing radiation cone angles from left to right (2º, 4°, 8°, and 16°). The simulations were generated with a source radius of 0.1278 cm.**

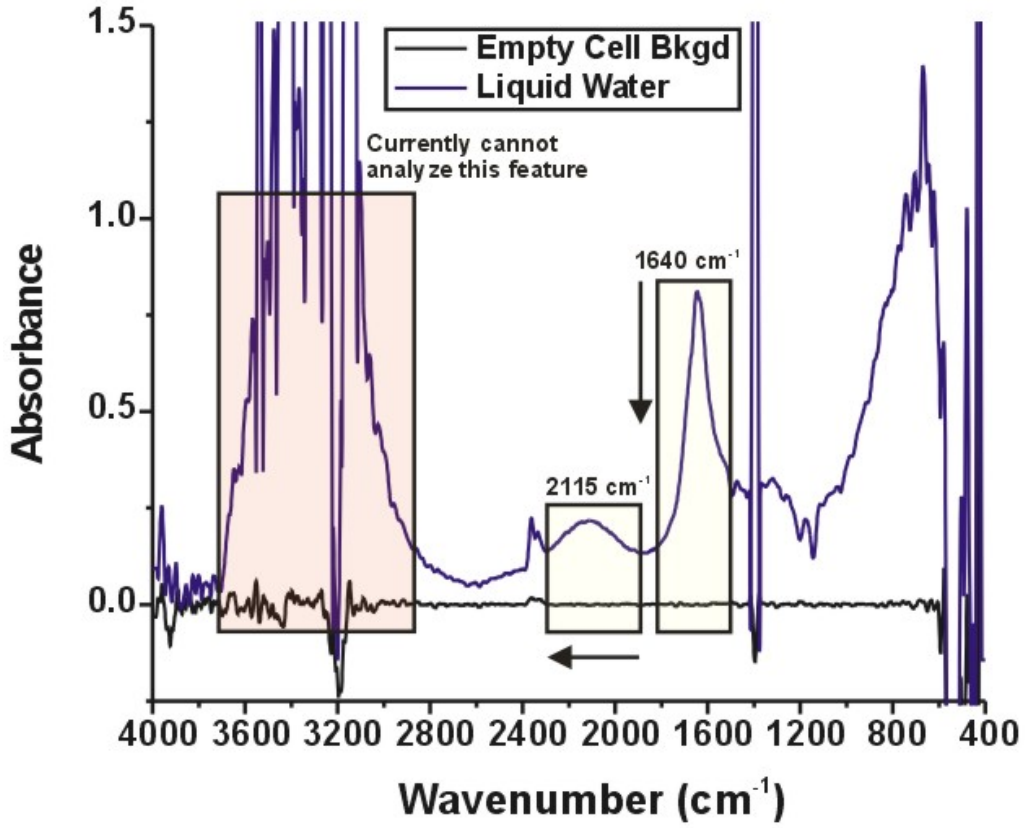

Figure 7: **IR-ATR spectrum of liquid water taken with a silver halide fiber coupled into the custom pressure vessel. (There is considerable noise in the broad O-H peak which currently excludes this region from being used in data analysis.) Arrows indicate changes in the water spectrum during ice/hydrate formation.**

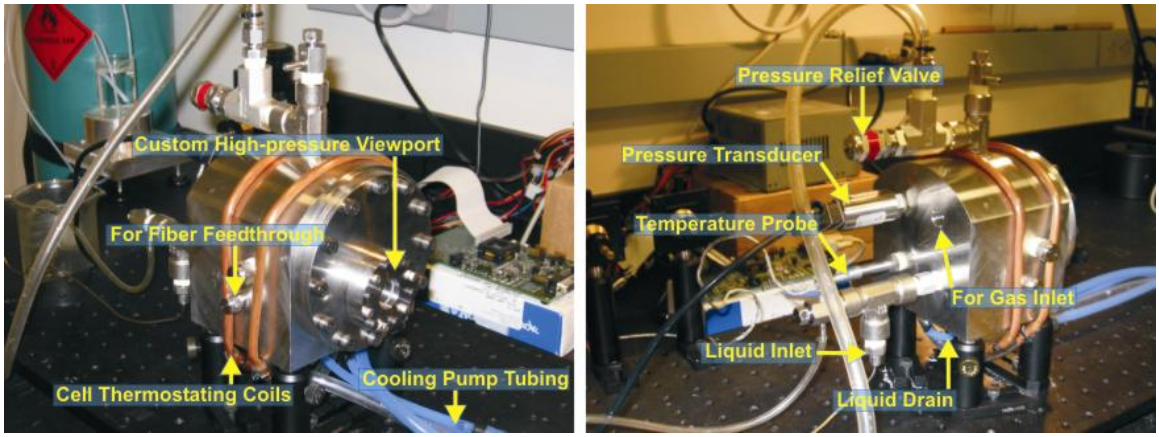

Figure 8: **Custom pressure vessel for synthetic formation of gas hydrates capable of achieving pressures > 750 psig. (Left) Front view of the custom pressure vessel. (Right) Rear view of the custom pressure vessel.**

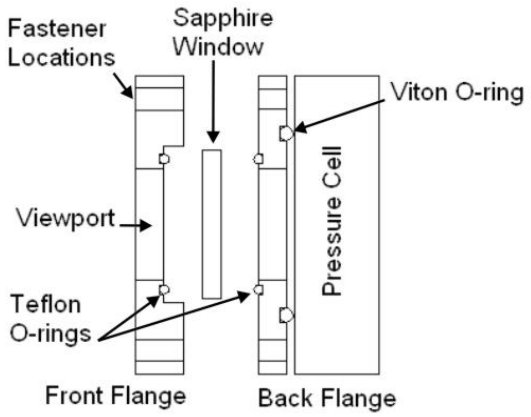

Figure 9: **CAD scheme of the custom high-pressure viewport design.**

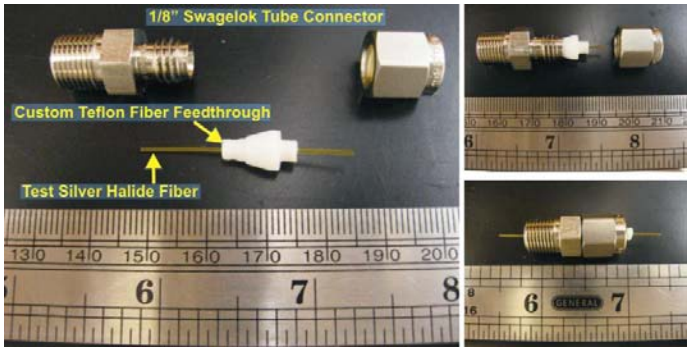

Figure 10: **(Left) Custom designed Teflon ferrule for coupling infrared transparent silver halide fibers into the pressure vessel for high-pressure measurements. (Right) Additional Images displaying assembly of the high-pressure fiber-optic feedthrough.**

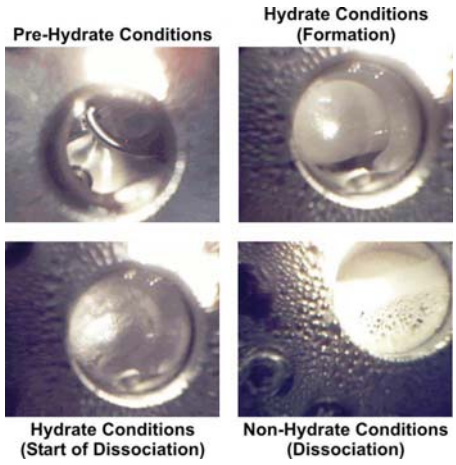

Figure 11: **(Top Left) Pre-hydrate conditions inside the pressure vessel filled with liquid water. (Top Right) Hydrate conditions inside the pressure vessel with bulk methane hydrate visible through the sapphire window. (Bottom Left) Start of hydrate dissociation as the phase boundary is being crossed by decreasing the pressure. (Bottom Right) Non-hydrate conditions with hydrate structure dissociating and degassing methane indicated by bubbling of the surfactant solution.**

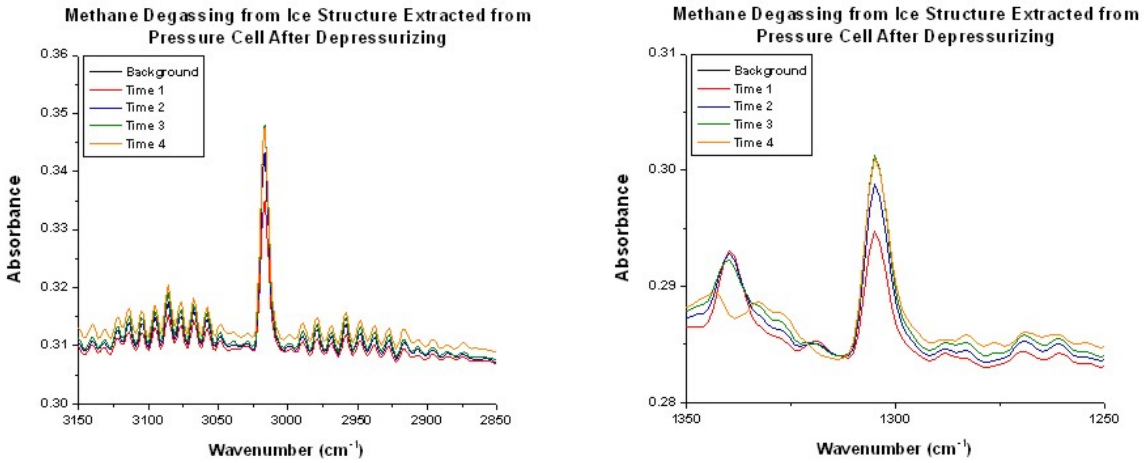

Figure 12: **FT-IR transmission spectra collected as solid hydrate extracted from the pressure vessel melted inside the sample compartment of a Bruker spectrometer. (Left) Methane absorption observed at 3020 cm^{-1}. (Right) Methane absorption observed at 1305 cm^{-1}.**

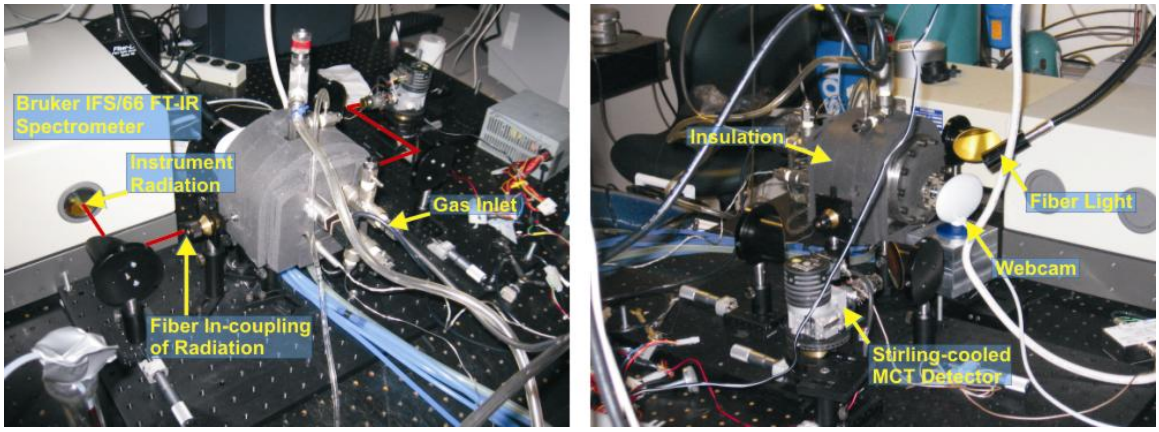

Figure 13: **Fiber-optic measurement setup for in-situ monitoring of hydrate formation and dissociation. (Left) Rear view of measurement setup. (Right) Front view of the measurement setup.**

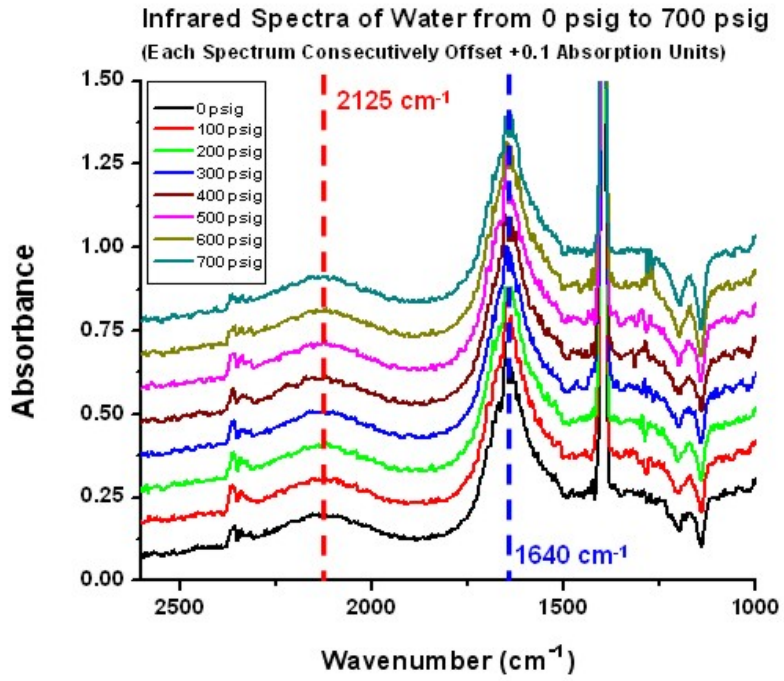

Figure 14: **Infrared water spectra from 0 psig to 700 psig.**

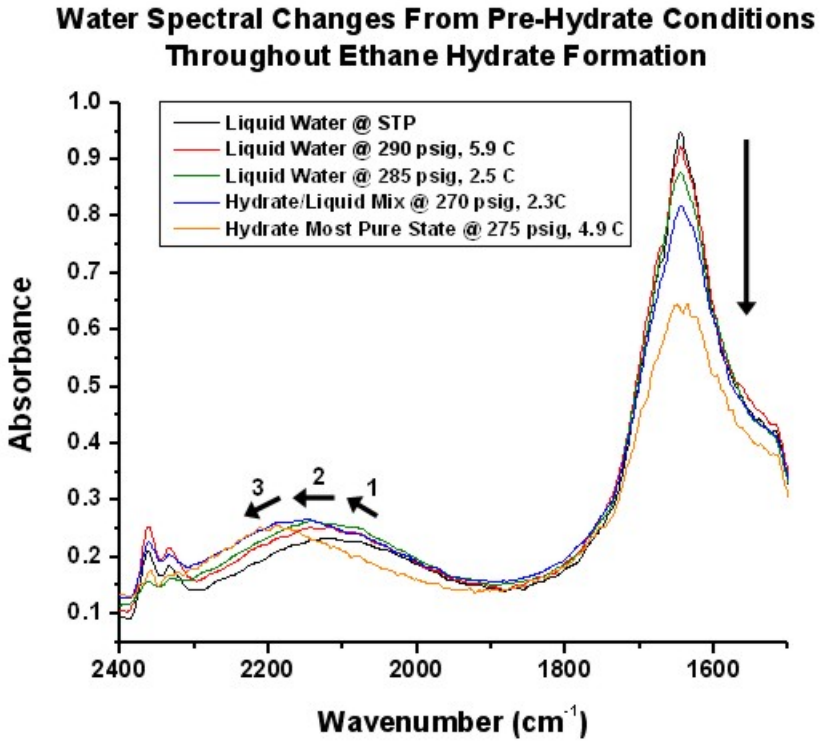

Figure 15: **Selected spectra taken throughout ethane hydrate formation in the region of 2400-1500 cm^{-1}.**

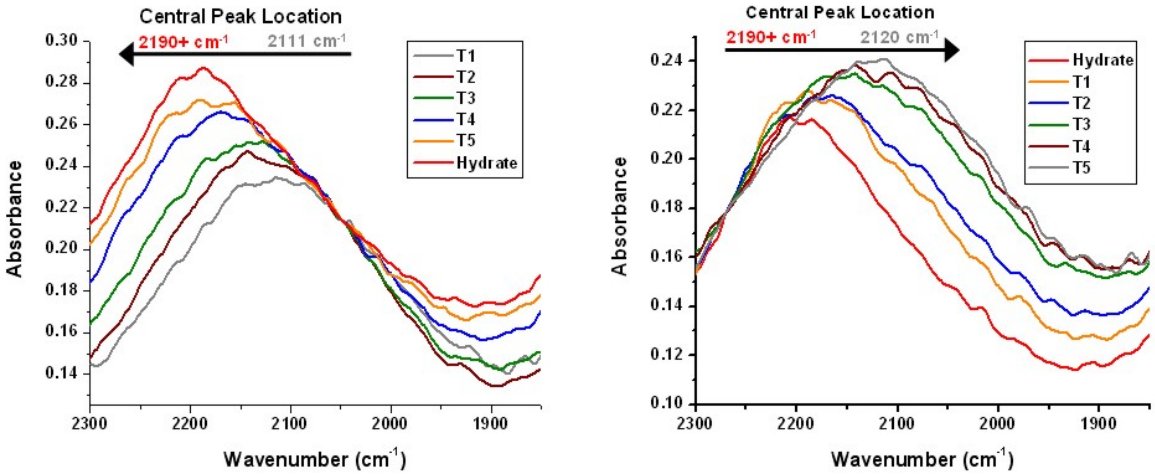

Figure 16: **Spectral shifting of the combination bend and libration band of water throughout (Left) formation and (Right) dissociation.**

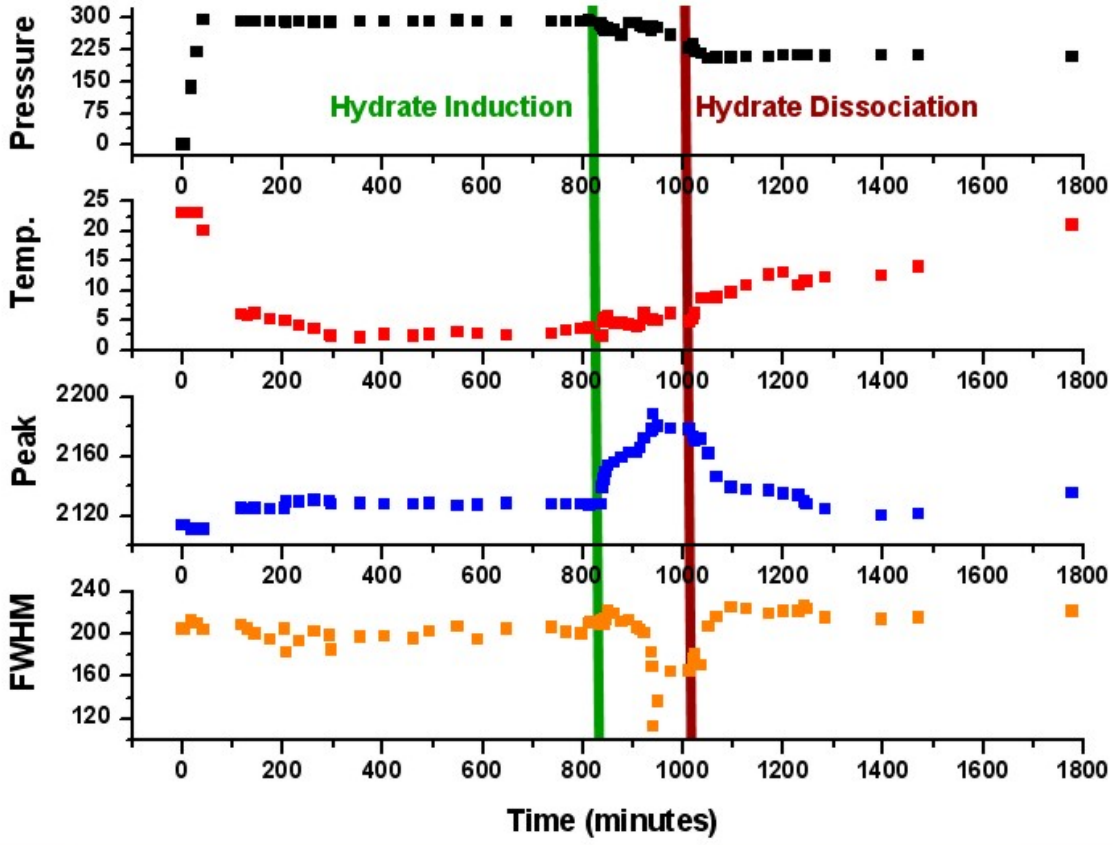

Figure 17: **Pressure (psig), temperature (°C), and spectroscopic results from first fiber-optic in-situ measurements of ethane hydrate formation. Analyzed spectral information is for the combination bend and libration band initially located at approx. 2115 cm^{-1} and the full width at half maximum of the absorption band.**

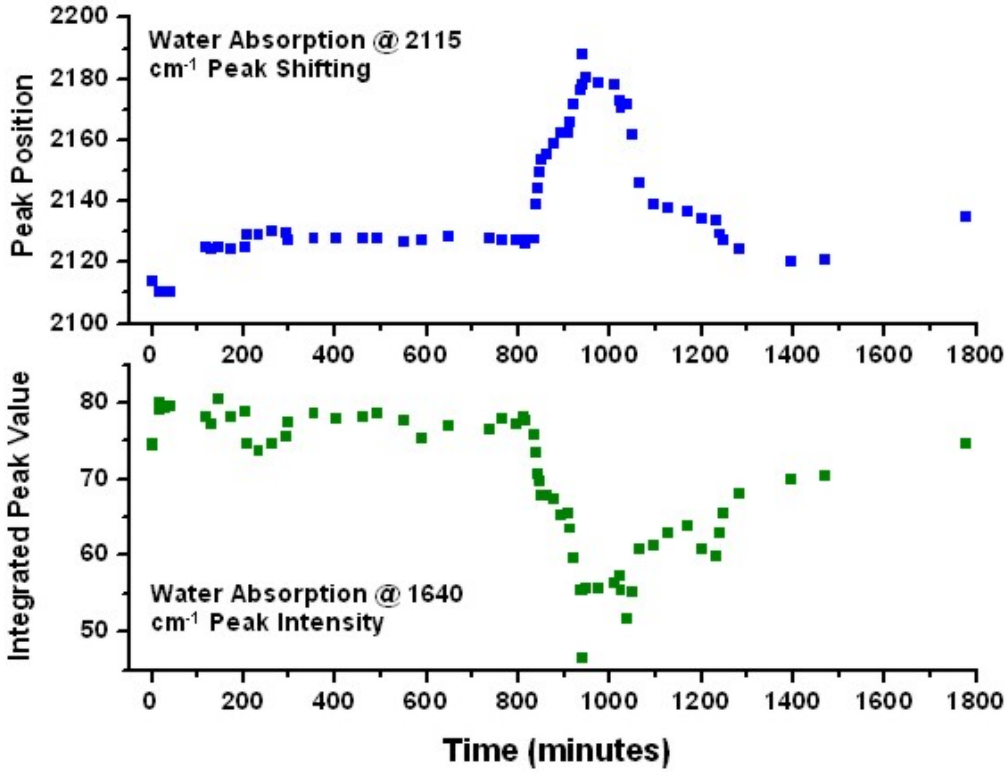

Figure 18: **Analyzed spectroscopic data comparison of the peak position for the combination bend and libration band at 2115 cm^{-1} and the intensity of the H-O-H bend band at 1640 cm^{-1}.**

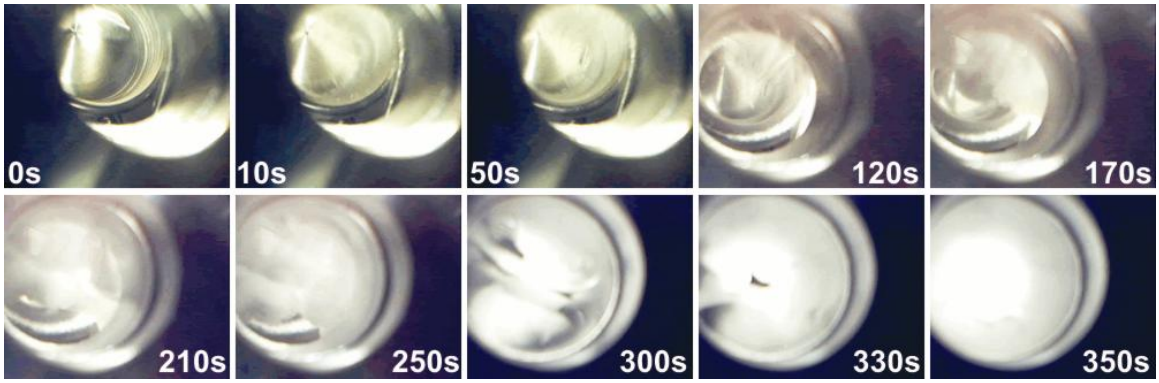

Figure 19: **Selected webcam captures beginning with the first image prior to ethane hydrate induction (0s) until the optical viewport was fully obstructed with bulk hydrate mass 350s after hydrate induction during in-situ spectroscopic measurements.**

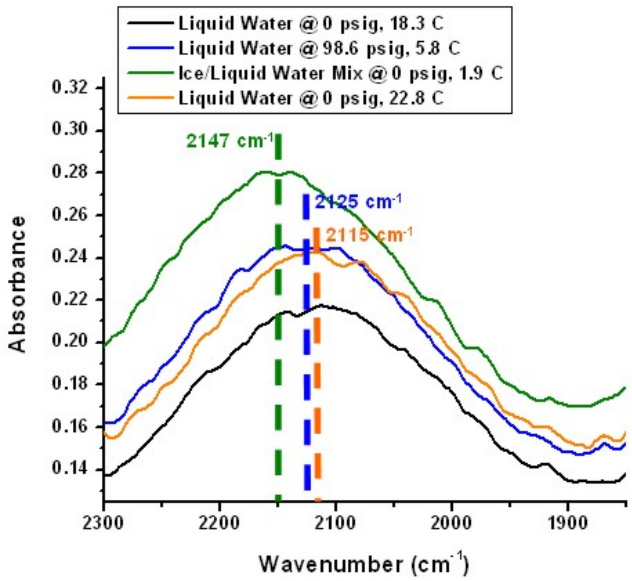

Figure 20: **Initial results from 2300 cm^{-1} – 1800 cm^{-1} for ice formation in the pressure vessel**

ABBREVIATIONS

MIR	mid-infrared
ATR	attenuated total reflection
IR-ATR	infrared attenuated total reflection (spectroscopy)
IR	infrared
FT-IR	Fourier transforms infrared (spectroscopy)
PSCB	polystyrene-co-butadiene
IPV/IPVs	integrated peak value/values
HATR	horizontal attenuated total reflection (waveguides)
CCA	constant cone angle of radiation
CLSR	constant light source radius
CAD	Computer Assisted Design
ASL	Applied Sensors Laboratory
ZnSe	Zinc Selinide
MCT	Mercury Cadmium Telluride (detector element)
GOMHRC	Gulf of Mexico Hydrates Research Consortium

SCIENTIFIC CONTRIBUTIONS

Oral Presentations:

"Update on the Design and Construction of a Mid-Infrared Spectroscopic Sensor for Methane in Seawater", **Gary T. Dobbs** and Boris Mizaikoff, Semiannual Meeting of the Gulf of Mexico Hydrates Research Consortium, 02-05, Oxford, MS (oral presentation).

"IR-ATR Deep-Sea Sensing Interfaces: Optimizing Probe Designs through Experimental and Spectral Ray Tracing Analysis of Evanescent Field Interactions", **Gary T. Dobbs** and Boris Mizaikoff, SPIE Optics in the Southeast Conference, 10-05, Atlanta, GA (oral presentation).

"First results of *In-Situ* Mid-Infrared Fiberoptic Evanescent Wave Detection of Ethane Hydrate Formation/Dissociation", **Gary T. Dobbs** and Boris Mizaikoff, Semiannual Meeting of the Gulf of Mexico Hydrates Research Consortium, 11-05, Oxford, MS (oral presentation).

Manuscripts:

Gary T. Dobbs and Boris Mizaikoff, Shining New Light at Old Principles: Localization of Evanescent Field Interactions at IR-ATR Sensing Interfaces, Revised Manuscript Submission 12-05, Applied Spectroscopy (Journal Article).

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SEISMO-ACOUSTIC CHARACTERIZATION OF SEA FLOOR PROPERTIES AND PROCESSES AT THE HYDRATE MONITORING STATION

Subcontract to
DOE Award Number: DE-FC26-02NT41628

Final Report covering the period

December 2003 – November 2004

Submitted by

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April 2005

ABSTRACT

Work has continued on the final development of the electronic part of an acoustic logging system designed for investigating fine-scale temporal changes in sea floor acoustic reflection responses, both at the sediment water interface and in the surficial sediment layer. The hardware has now been built and extensively tested, and commissioning is complete.

Testing along the way involved laboratory simulations and shallow water sea trials, using the acoustic logging system alongside `off the shelf` shallow water transducers (5kHz and 33kHz) for signal transmit and receive. Subject to further funding, future efforts will be concentrated on optimizing transducer specifications and packaging for deep water operations at the Gulf of Mexico Gas Hydrate Monitoring Station.

CONTENTS

1. INTRODUCTION

The intention within this DOE funded project has been to design and construct an electronic instrument able to operate a fixed station, acoustic logging device that will ultimately be deployed at the Gas Hydrates Monitoring Station. The primary requirement is for an instrument that is able to be pre-programmed for remote operation whilst under long-term deployment in the deep water environment of the Gulf of Mexico. The development work is being carried out under a collaborative agreement between the University of Wales Bangor and Scimar Engineering Ltd. (as subcontractor to the University).

2. EXECUTIVE SUMMARY

The rationale underpinning the research development and experimental trials in this DOE funded project is recognition of the value of the acoustic reflection signature for monitoring physical changes at the sediment water interface and within the subsurface sediment structure. To this end, a research prototype acoustic system previously developed for an EU project is being further developed in readiness for deployment at the Gulf of Mexico Gas Hydrates Monitoring Station.

While the project did suffer some delays along the way (initial delays with the issue of the contract and some unforeseen developmental problems), the main project deliverable (a laboratory-tested, electronic instrument designed to remotely log high-resolution acoustic reflection signatures, supplied in the form of a working board set ready for insertion in a pressure tube) is now complete.

3. EXPERIMENTAL DEVELOPMENTS

Work undertaken on hardware development and operational software has resulted in an instrument with the following specification:

- Two channel impulsive transmitter, capable of putting 400V clamped voltage spikes onto one of two transmitters
- Two channel selectable receiver, with selectable gain of 6, 18, 30, 42, 54, 66, 78 db of gain, 8 pole high pass filter with selectable knee frequency in 500 Hz steps to 255 kHz, 16 bit A-D conversion with selectable sampling rates to 320 kHz, 512 kBytes of RAM and 128 Mbyte (expandable to 1 Gbyte) of FLASH memory.
- Four channel temperature and pressure sensing auxiliary functions, and battery supply voltage monitoring.
- Fully integrated switched mode power supplies requiring single wide-range DC input, 9-30V DC, allowing use of very high capacity alkaline battery packs.
- Board set mounted in a custom housing ready for pressure tube mounting, and with bench test lead set, and host computer program for data stripping and manual mode control.
- Autonomous and umbilical controlled modes are possible. Virtually all parameters (pulse length, sampling rate, record length, TX and RX channel selection, gain, filter setting, recording dead time) are software selectable and can either be controlled from a surface umbilical (or used in a bench mode for testing) or set into a 4 deep configuration stack so that mixed mode autonomous operation is possible with almost infinite parameter variability.

- Data stored in FLASH ram can be replayed over the umbilical or by physical removal and reading in a standard PC card reader (MCC format). A PC utility to strip the data directly out of the FLASH memory will be supplied

During the final build, all system components were extensively tested prior to the final instrument commissioning.

4. RESULTS AND DISCUSSION

The challenges of the system development can best be described in two parts: the design stage and the implementation and testing stage.

The seabed autonomous operation of the instrument offered several elements that had to be combined, making this device quite different to many sonars, and definitely at this stage making it a scientific rather than `run of the mill` instrument.

The instrument has a highly programmable structure so that parameters can be changed in response to field experience (e.g., knowledge of the exact nature of the signals to be received, optimization of the measurement process).

For future deployment at the Hydrates Monitoring Station, it is proposed that the electronic instrument be interfaced with transmitting and receiving transducers on a fixed frame. The whole will be deployed on the seabed with a recommended 2 m (approx.) clearance between the transducers and the sediment surface. Given the short water path travel time, the electronic system has been designed to produce a very short duration clamped source and very fast settling time. It will provide for high accuracy, high frequency and high resolution (16 bit) data recording, with filter responses with little ringing, optimized for impulsive signals. The instrument will allow very high volume and secure data recording. In addition, power management will provide for optimal bottom battery life.

It should perhaps at this final stage be pointed out that aspects of the project proved far harder than originally expected and that the development team experienced some severe problems along the way meaning that overall bench development time was at least twice that originally estimated. There was no single major problem, the problems that absorbed the time were essentially three, the first of these perhaps a bit surprising:

(i). Because of the ability now to realize circuit elements in simulation, and the accuracy and ease with which simulated designs can now be brought from paper to PCB and then to the bench, virtually all of the circuit elements when tested separately early on, worked first time. This sounds like a major advance, but the effect was that these circuit elements were adopted far faster than would have

been possible a few years ago. However, the simulations have limits to the number of parameters that can be varied: when these circuit elements were put under software control problems emerged that the simulation would never have seen.

(ii). The major problem was that the sheer number of usefully variable parameters made this into a far more complex device than its size might suggest. By far the biggest single use of time was in debugging the vast number of variations that the system allows. An element of this that is common to all modern electronics development at component level is that IC manufacturers' data sheets tell you what you must know, and what they want you to know. However, all complex ICs have parameters that the manufacturers may want to hide, or at least not publicize, and parameter variations that they do not know about. The debugging process has to discover all such non-declared parameters.

(iii). It proved remarkably difficult to emulate the real acoustic world in the lab, and thus tests in real water with real batteries are needed. Very minor assumptions that were made to build a lab test rig were found not to be compatible with real testing, and so real-world testing has proved very time absorbing simply because test parameters have to be selected, and sometimes hardware modification has been needed, to make things work.

However, despite the above and the associated time over-runs, the final device met every element of the original specification.

5. CONCLUSIONS

The chosen electronic instrument design integrated many state of the art technologies, and tests have shown the data recording and source quality to be excellent. The project objectives have been fully realized, with the instrument meeting the hopes set at the outset.

Subject to the successful outcome of a follow-up proposal, future efforts will be concentrated on optimizing transducer specifications and packaging for deep water operations.

Support of Gulf of Mexico Hydrate Research Consortium: Activities to Support Establishment of Seafloor Monitoring Station

Applications of VSP Technology for Evaluation of Deep-Water Gas Hydrate Systems

FINAL REPORT

Reporting Period Start Date: January 1, 2006

Reporting Period End Date: December 31, 2007

Principal Investigator (Author): Bob A. Hardage

Date Issued: July 28, 2008

Subcontract to
DOE Cooperative Agreement No. DE-FC26-02NT41628

Task 6: Seismo-acoustic characterization of seafloor properties and processes at the hydrate monitoring station

Submitting Organization:
Bureau of Economic Geology
John A. and Katherine G. Jackson School of Geosciences
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Disclaimer

Abstract

In support of this project, work at the Bureau of Economic Geology focused on expanding the software needed to create compressional (P-P) and converted-shear (P-SV) images and compressional (P) and shear (S) attributes from 4-component ocean-bottom-sensor (4C OBS) data. These images and attributes are needed to estimate and quantify hydrate concentration across the seafloor observatory site in Block MC118. This report documents the sensor-calibration procedure that was used to do the wavefield separation that is required to do the P-P and P-SV imaging and illustrates the quality of images that can be created. The data used in this demonstration are not from Block MC118 but are from a similar water depth.

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Introduction

New 4C OBS data-processing software developed by Bureau scientists has been developed so that we can now use large-offset data to determine operators that calibrate hydrophone and geophone responses. P-P images of strata immediately below the seafloor are significantly improved when these sensor-calibrated data are used in the imaging process.

In this final report, we illustrate how we create sensor-calibrated 4C OBS data and how we convert these data into high-resolution images of deep-water, near-seafloor geology. The 4C OBC data used in this demonstration of our data-processing code were acquired in approximately 800 meters of water, similar to the water depths across Block MC118.

Executive Summary

Researchers at the Exploration Geophysics Laboratory (EGL) at the Bureau of Economic Geology were subcontracted to create deliverables for Work Task 6, *Seismo-acoustic characterization of seafloor properties and processes at the hydrate monitoring station*. The task assigned to EGL was to process and interpret seafloor-sensor seismic data acquired across the monitoring station in Block MC118, in addition to any VSP data that may be acquired. Particular emphasis at EGL was placed on developing data-processing code that would analyze 4C OBS P-wave and S-wave data acquired with receivers positioned on the seafloor and with seismic sources positioned at the sea surface. EGL scientists used project monies to partially fund their development of a software code that creates high-resolution P-P and P-SV images of near-seafloor geology from 4C OBS seismic data. We show in this final report the quality of images that can be created with the code that has been created.

Experimental

Experimental activity during this project focused on developing and testing software that allows sensor-calibrated 4C OBS data to be used to make improved P-P and P-SV images of near-seafloor geology. All experimental activity was confined to laboratory-based software analysis and seismic data processing.

Results and Discussion

Our research has led to the development of a unique strategy for processing deep-water 4C OBC data that results in high-resolution images of near-seafloor geology. Our procedure for constructing these near-seafloor images abandons the conventional common-midpoint (CMP) binning technique used for P-P data and the common-conversion-point (CCP) binning procedure that is used for P-SV data and utilizes only common-receiver trace gathers along

a line of profile. Our data-processing technique has been described in *The Leading Edge* by Backus and others (2006). This paper received an excellent peer-review accolade by being named *Best Paper in The Leading Edge* for the publication year 2006.

Hydrophone Data

In order to explain the fundamentals of the unique data-processing procedure we implemented to create P-P and P-SV images from 4C OBS data, it is best to first illustrate the type of data that are recorded by 4C seafloor sensors. We start by first illustrating the response of one of the seafloor hydrophones used in the 4C sensor packages that acquired the data we processed. A typical trace gather of data acquired by a seafloor-based hydrophone is displayed as Figure 1, with the data adjusted to a reduced-time format in which the arrival time of the downgoing direct arrival is defined as T = 0. Principal features of the data are labeled on the figure. Several air-gun bubbles are obvious as flat events parallel to the direct arrival, and numerous P-P reflection events appear as “smiles.”

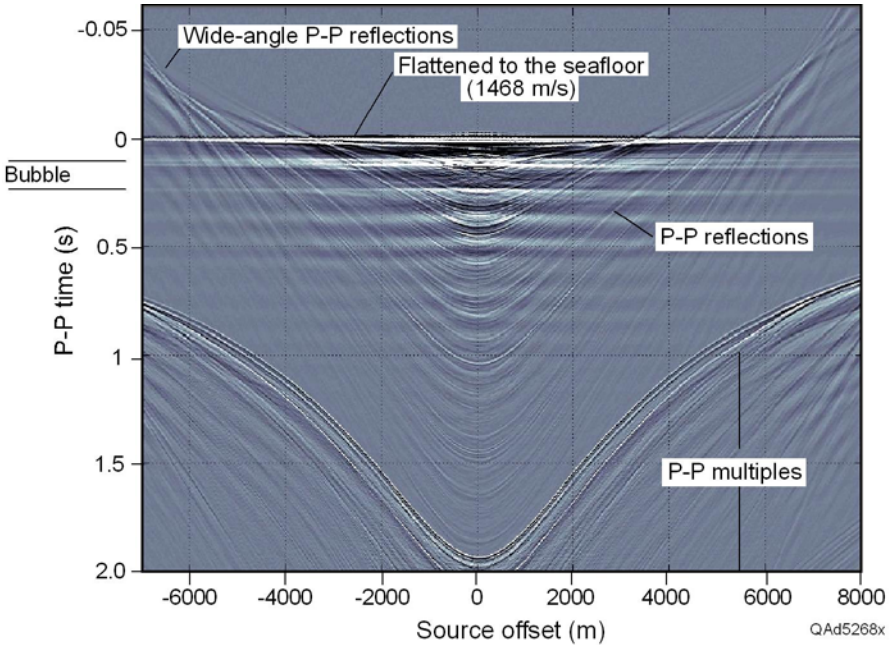


Figure 1. Common-hydrophone trace gather constructed at a seafloor receiver station.

Wide-angle reflection data arriving at large offsets before the direct arrival represent isolated pure up-traveling energy that is useful for sensor-response calibration. Hydrophone and geophone data must be added to isolate the downgoing P-P wavefield and then must be subtracted to create upgoing P-P and P-SV wavefields. These estimations of upgoing and downgoing wavefields are more accurate when these arithmetic combinations of hydrophone and geophone data involve calibrated receiver responses.

Vertical-Geophone Data

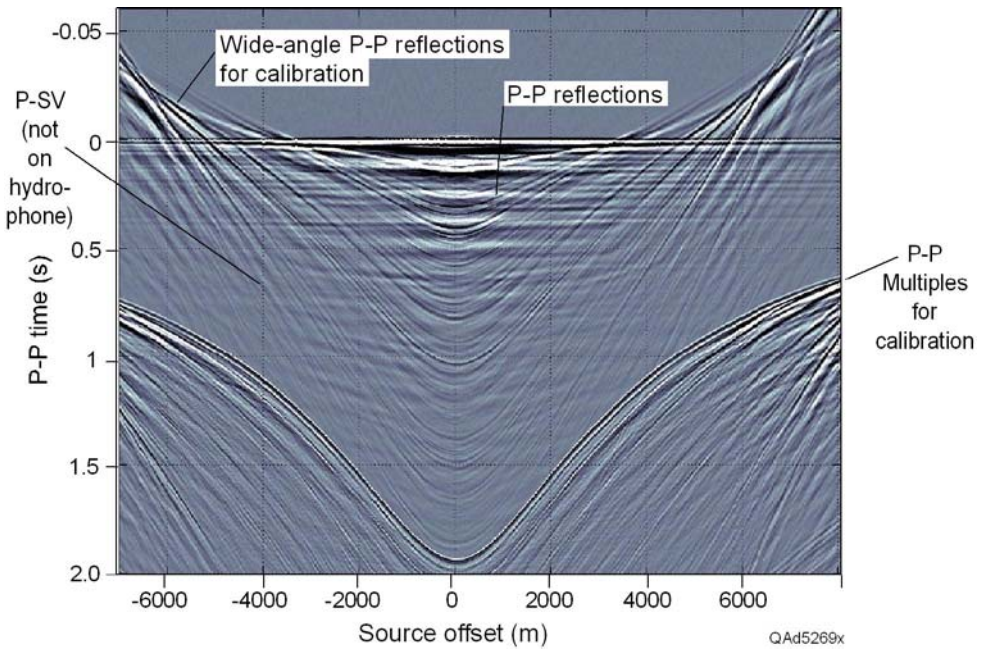
The common-receiver trace gather for the vertical geophone (**Z** geophone) positioned at the same receiver station as the preceding hydrophone data is displayed as Figure 2. The direct arrival, water-column multiples, primary P-P reflections, and wide-angle reflection events are similar to those seen in the hydrophone trace gather in Figure 1. However, there are important differences between the hydrophone and vertical-geophone data:

1. Air-gun bubbles are weaker on the vertical-geophone data (Fig. 2) than on the hydrophone data (Fig. 1) because direct and reflected waves interfere constructively in the hydrophone response but destructively in the vertical-geophone response.
2. The vertical-geophone response contains P-SV reflections in addition to P-P reflections. These P-SV reflection events appear as low-curvature (almost flat) events in a reduced-time display. Several of these reflections are highlighted in color to better illustrate how they appear in the common-receiver gathers that we create.

Horizontal Inline-Geophone Data

The common-receiver trace gather of data recorded by the horizontal inline-geophone (**X** geophone) at this receiver station is illustrated in Figure 3. The raw, unprocessed data are displayed in panel **a**. Panel **b** shows the data after the polarity of the negative-offset traces is reversed. The polarity of negative-offset data acquired with a horizontal inline-geophone should be opposite to the polarity of positive-offset data. These particular data do not conform to this principle. Here, positive-offset data and negative-offset data do indeed have opposite polarity for reflections that extend to depth $\mathbf{Z_1}$ below the seafloor. However, below depth Z_1, the data have a phase shift that causes a simple polarity change of a negative-offset reflection event to not align with its positive-offset equivalent. The anomalous phase behavior embedded in the data below depth Z_1 is caused by geology, not by the receiver. The most likely cause of the anomalous phase shift below coordinate Z_1 is local reflector dip, which causes the polarity reversal to occur at an offset coordinate that is shifted away from the zero-offset coordinate.

(a)



(b)

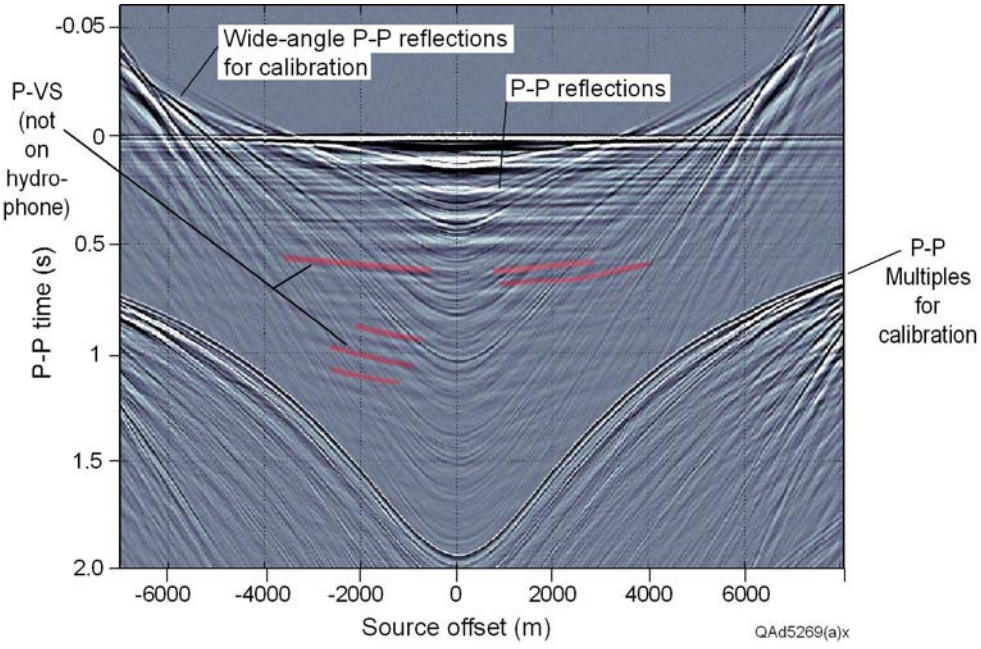
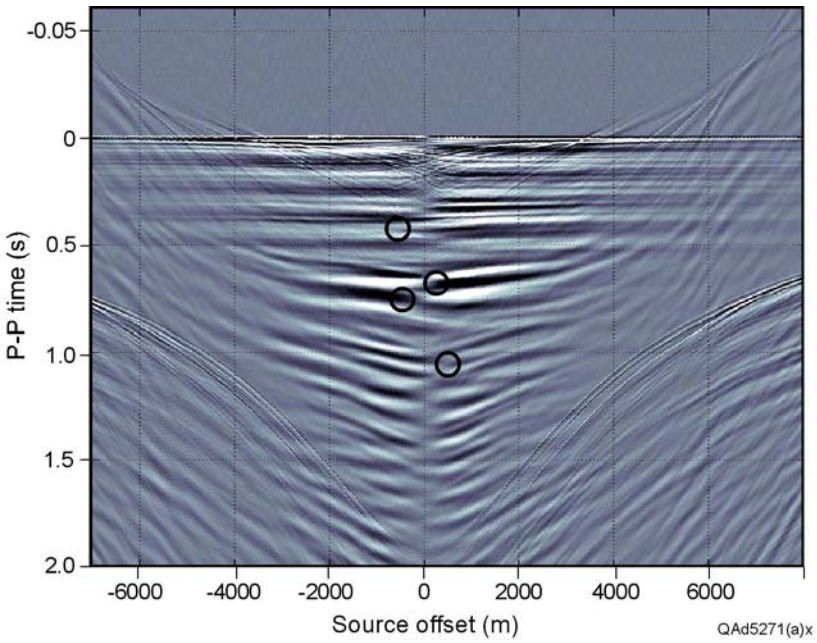


Figure 2. (a) Common-receiver trace gather for the vertical geophone positioned at the same receiver station as the hydrophone data in Figure 1. (b) Same data with P-SV reflections emphasized.

(a)



(b)

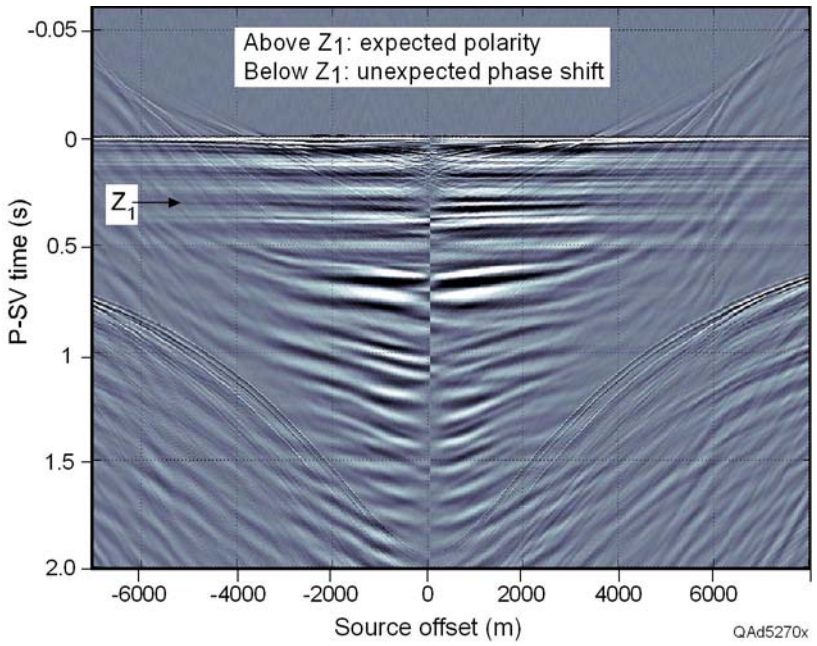


Figure 3. Common-receiver gather for the horizontal X-geophone. (a) Data as recorded. (b) Data after reversing the polarity of negative-offset traces. Reflections below depth Z_1 have a different phase shift than do reflections generated above Z_1 because of local reflector dip. Reflector dip at depth Z_1 (and deeper?) causes polarity reversals to occur at offsets that are positioned either left or right of zero offset. Examples of some of these polarity reversals are circled in a.

Receiver Calibration

Construction of downgoing and upgoing wavefields is a key step in EGL's strategy for making P-P and P-SV images of deep-water near-seafloor geology. To construct these downgoing and upgoing modes, data acquired by hydrophone and geophone sensors have to be added to create the downgoing P wavefield and then subtracted to create upgoing P and SV wavefields. If the responses of the hydrophone, vertical geophone, and horizontal geophones are not calibrated to each other, data recorded by these sensors may not combine to create optimal-quality definitions of these downgoing and upgoing wavefields.

It is important that a long-offset geometry be involved in the data acquisition because wide-angle data that arrive before the direct arrival contain only upgoing reflections and are ideal for calculating sensor-to-sensor calibration operators. The wide-angle data windows for the common-hydrophone gather constructed at this example receiver station (Fig. 1) are shown in the left two panels of Figure 4. The top center panel shows the hydrophone response estimated from the wide-angle reflections recorded by the vertical geophone (Z). The bottom center panel shows the hydrophone response calculated from the wide-angle reflections recorded by the horizontal inline-geophone (X). The right panels illustrate the difference between the hydrophone data and each of the estimated hydrophone responses. The differences are approximately zero, confirming that each sensor-to-sensor calibration operator does a good job of converting one sensor response to its companion-sensor response. Examples of other sensor-to-sensor calibration operators are plotted in Figure 5. An important finding is that these operators appear to be independent of offset, as demonstrated by the consistency of the operators shown in the offset-dependent panels on the left of this figure. Consequently, a single sensor-calibration operator can be used for the complete offset range of a common-receiver gather.

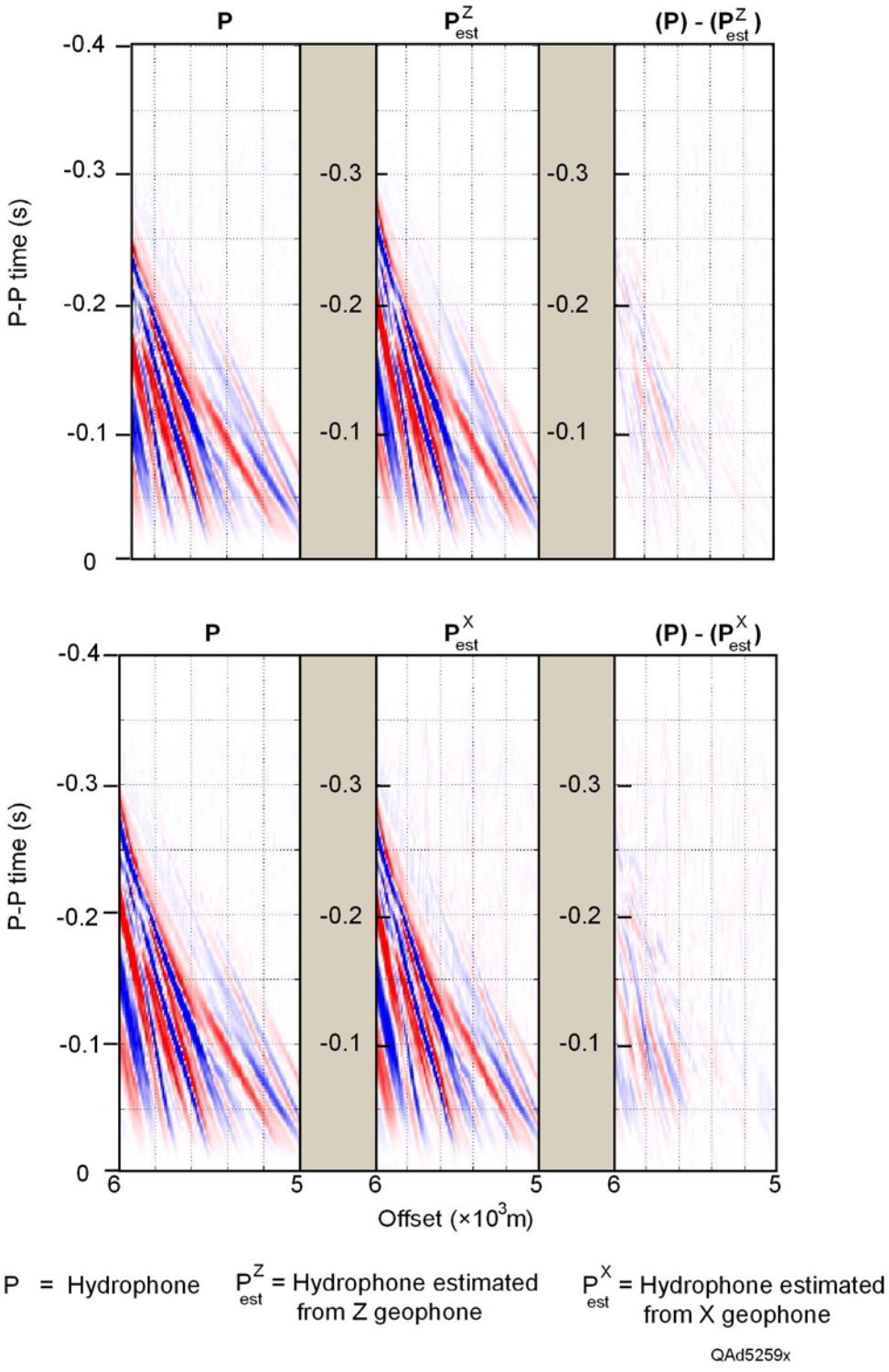


Figure 4. Wide-angle reflections used to calculate sensor-to-sensor calibration operators. These data windows are the events labeled "*wide-angle reflections*" in Figures 1 and 2 that extend above the T = 0 time datum; the time coordinates are therefore negative. These displays show that operators determined from these isolated reflections can convert either vertical-geophone data (top) or horizontal inline-geophone data (bottom) to hydrophone data.

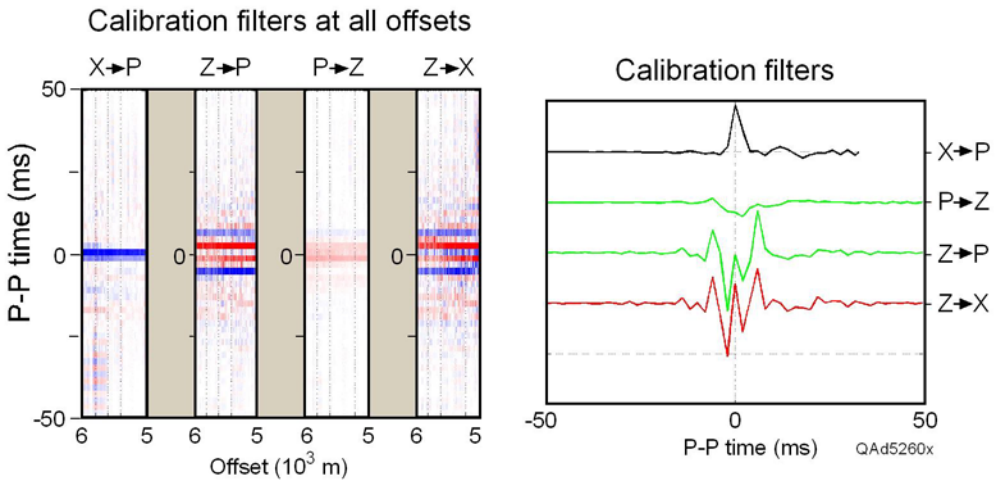


Figure 5. Examples of operators determined from wide-angle reflections that allow hydrophone (P), vertical-geophone (Z), and horizontal inline-geophone (X) data to be transformed from one sensor response to the other. (Left) Operators are independent of offset. This offset range is the same as that displayed in Figure 4. (Right) Expanded views of operators calculated at one specific offset.

Calibrated vs. Uncalibrated Data

How important is it that hydrophone (P), vertical-geophone (Z), and horizontal-geophone (X) sensors be calibrated before P, Z, and X wavefields are combined to create downgoing and upgoing P-P and P-SV wavefields? Many data processors ignore sensor calibration and simply add and subtract P, Z, and X wavefields, using time-invariant scaling factors. The 4C OBC data shown here allow P-P and P-SV images to be made with either calibrated-sensor or uncalibrated-sensor data and provide the opportunity to determine the value of each imaging strategy. Portions of the P-P image along one test line are illustrated in Figure 6. The top displays illustrate geology that extends to only 200 ms below the seafloor. The bottom displays focus on the geology that exists between 200 and 500 ms below the seafloor.

These images show that sensor calibration improves imaging only for the shallowest geology that extends to 50 ms below the seafloor. Below 50 ms, calibrated-sensor data and uncalibrated-sensor data produce equivalent images. We have found this same data behavior when we do calibrated-sensor analysis of 4C OBC data in the North Sea and in the Gulf of Mexico. P-P image quality is improved only for the first ~50 ms of P-P image space. However, we have also found that this improvement in P-P imaging in this shallow window immediately below the seafloor is important for accurate depth registration of P-P and P-SV images.

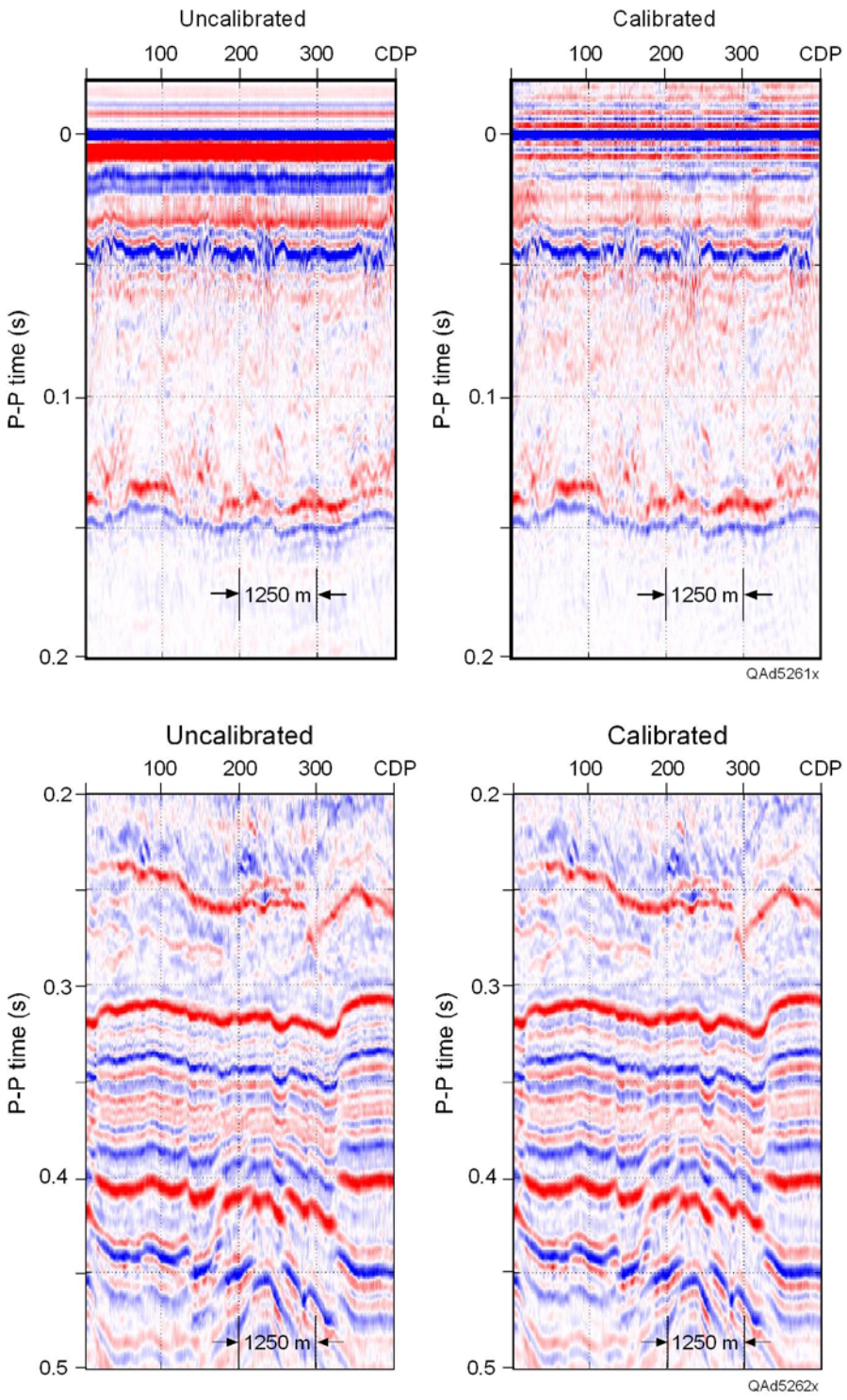


Figure 6. Comparisons of P-P images made with (right) and without (left) calibrated P and Z sensors. Calibrated data produce a superior image of the shallowest geology (top 50 ms, upper right). There are no significant differences between the calibrated-sensor and uncalibrated-sensor images at deeper depths (bottom displays). The improved P-P image in the first 50 ms of image space is important for P-P to P-SV image registration.

Images of Near-Seafloor Geology

P-P Image

EGL's strategy for extracting downgoing and upgoing P-P modes from 4C OBC seismic data and then calculating sub-seafloor P-P reflectivity from the ratio of "up" divided by "down" is summarized in Backus and others (2006). Our strategy produces P-P and P-SV images that are datumed relative to a flat seafloor that is positioned at image time T = 0. The P-P image of near-seafloor geology along the first cable lay of Line A (our demonstration profile of 4C OBC data) produced by our wavefield ratio procedure is compared to the image produced by the contractor that processed the data in Figure 7. To allow an easier and more accurate comparison of these images, the contractor image has been shifted to cause the water bottom reflection to be a flat event positioned at T = 0. This time shift was calculated at each CDP using the water depth value found in the trace header for that CDP coordinate and a constant water velocity of V_P = 1468 m/s. Inspection of the time-shifted contractor image shows the water bottom is not perfectly aligned with the T = 0 coordinate. We speculate that the seafloor is not a flat event in the contractor image after the data are static-shifted to remove the water column because of the technique that the contractor used to mute the direct arrival. When contractors mute direct arrivals in deep-water OBC data, portions of the seafloor reflection, together with portions of the shallowest sub-seafloor reflections, are often muted also. The amount of waveform muting usually varies along a profile. In contrast, EGL's imaging strategy requires no muting of the direct arrivals and retains the full waveform character of the seafloor and near-seafloor reflections.

Both images in Figure 7 seem to define the same reflecting interfaces. However, the EGL image, which involves a VSP-type deconvolution, has better resolution. Structural differences between the two images over station intervals 300 to 400 are mostly caused by the imprecise shifting of the contractor image to a seafloor datum. These static-induced structural differences are not an important issue in this discussion. Our reason for attempting to compare the data with a common seafloor datum is to better demonstrate the quality and resolution of the EGL image. Also, the contractor image is a post-migration image; whereas, the EGL image is not migrated. For shallow geology near the seafloor, there should not be a large difference between migrated and unmigrated data.

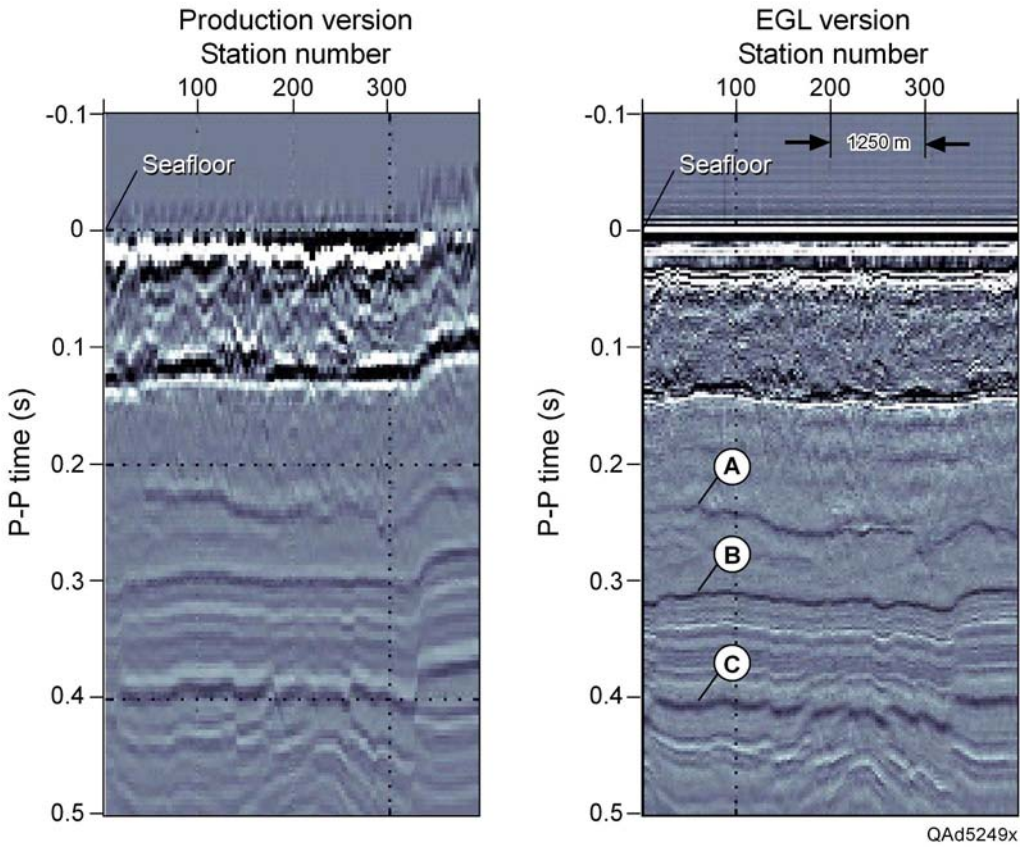


Figure 7. Comparison of contractor P-P image (left) and EGL P-P image (right) along the first one-third of Line A. The contractor image is shifted to a seafloor datum using water-depth values along the profile and a water velocity of 1468 m/s, but these static shifts do not create a flat seafloor event with a consistent waveshape. Reflections **A**, **B**, and **C** are key interfaces to the company that acquired the seismic data.

Our objective was to create an accurate definition of near-seafloor geology that extended to ~500 ms (P-P image time) below the seafloor. The upper 200-ms portion of this P-P data window along cable lay 1 is shown in Figure 8. The lithofacies, P-wave velocities, and stratigraphic layering labeled on the EGL image in this figure will be explained in later sections of this report. Much of layer **1** identified on the EGL P-P image does not appear in the contractor P-P image. As a result, shifting the contractor image to a seafloor datum causes the bold reflection at the base of layer **2** to be ~20 ms earlier than where the event appears in the EGL image.

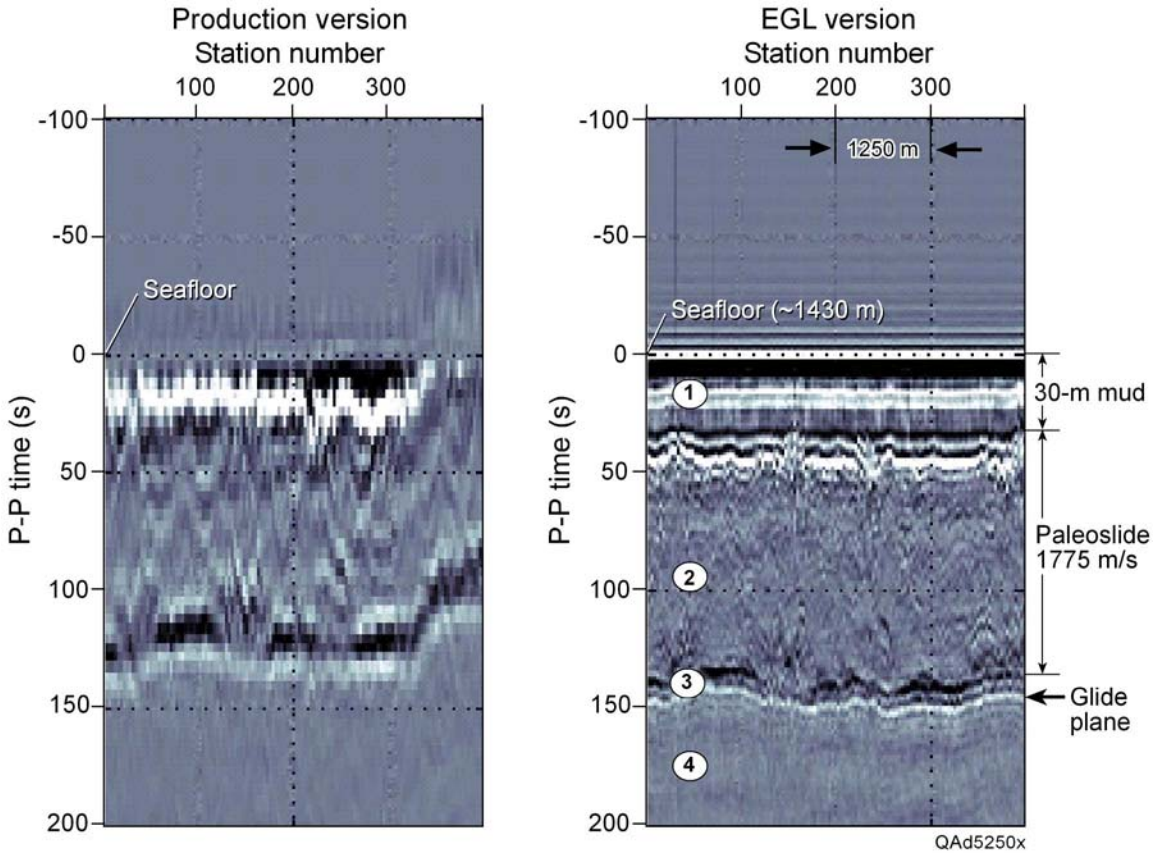


Figure 8. Zoom views of contractor (top) and EGL (bottom) P-P images along the first cable lay. The shift of the contractor image to a flat seafloor is not precise but is sufficient for image comparison. Numbers **1** through **4** on the EGL image identify the principal near-seafloor layers. The interpretations **Paleoslide** and **Glide plane** were offered by the oil company that acquired the data.

P-SV Image

Illustrated in Figure 9 is an example of P-SV sub-seafloor reflectivity calculated at one receiver station from the common-receiver gathers of P (hydrophone) and X (inline horizontal geophone) data acquired at that station. This reflectivity was obtained by separating downgoing P-P and upgoing P-SV wavefields and then calculating the ratio “P-SV upgoing” divided by “P-P downgoing” as described by Backus and others (2006). Panels a and b of Figure 9 are the P-SV reflectivity without any moveout corrections applied to the data. We refer to this P-SV reflectivity as a “brute” estimation of reflectivity. The data in panels c and d have been adjusted for offset-dependent moveout.

(a)

(b)

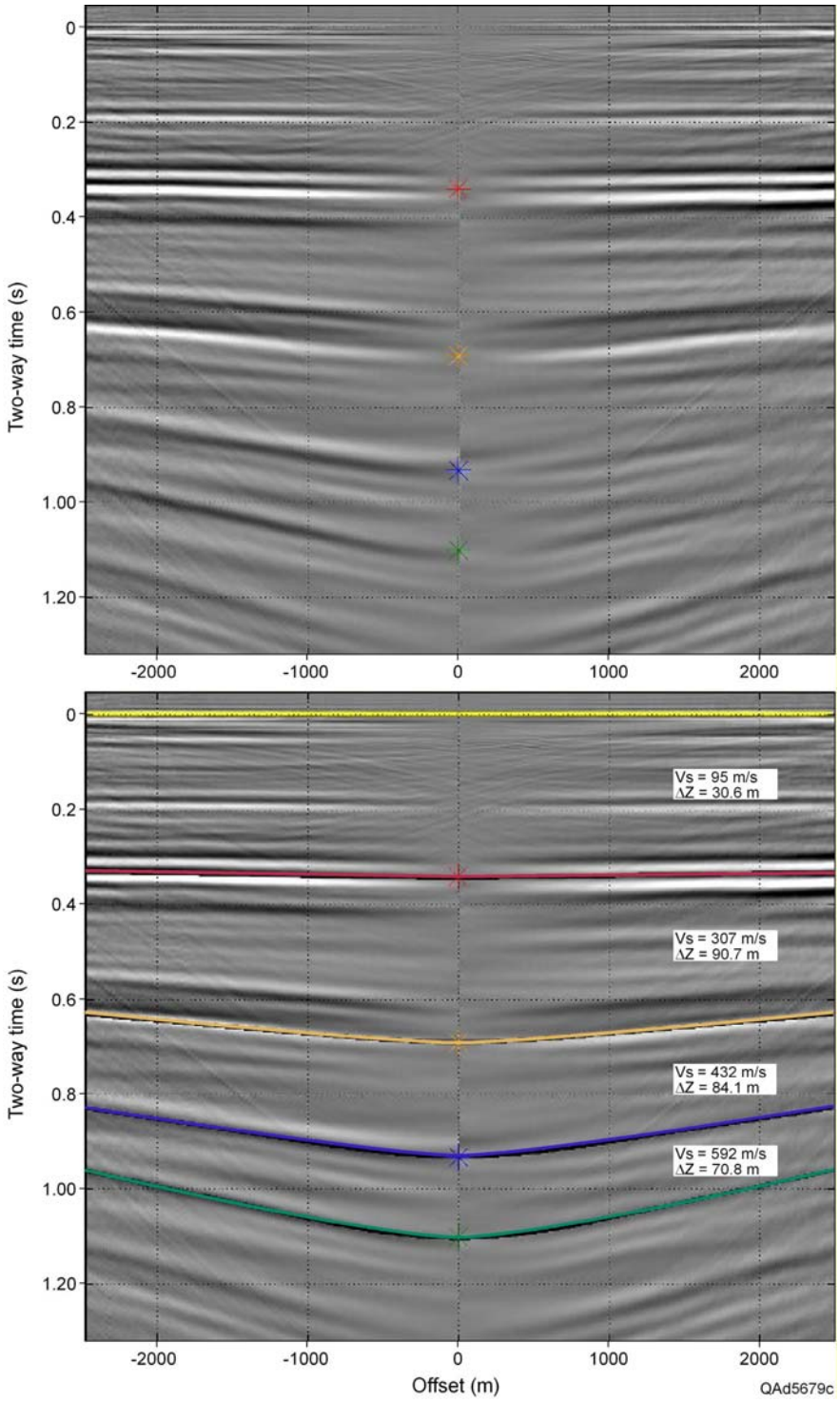


Figure 9. P-SV reflectivity determined at one receiver station. No velocity moveout (NMO) corrections have been applied to the data in panels (a) and (b).

(c)

(d)

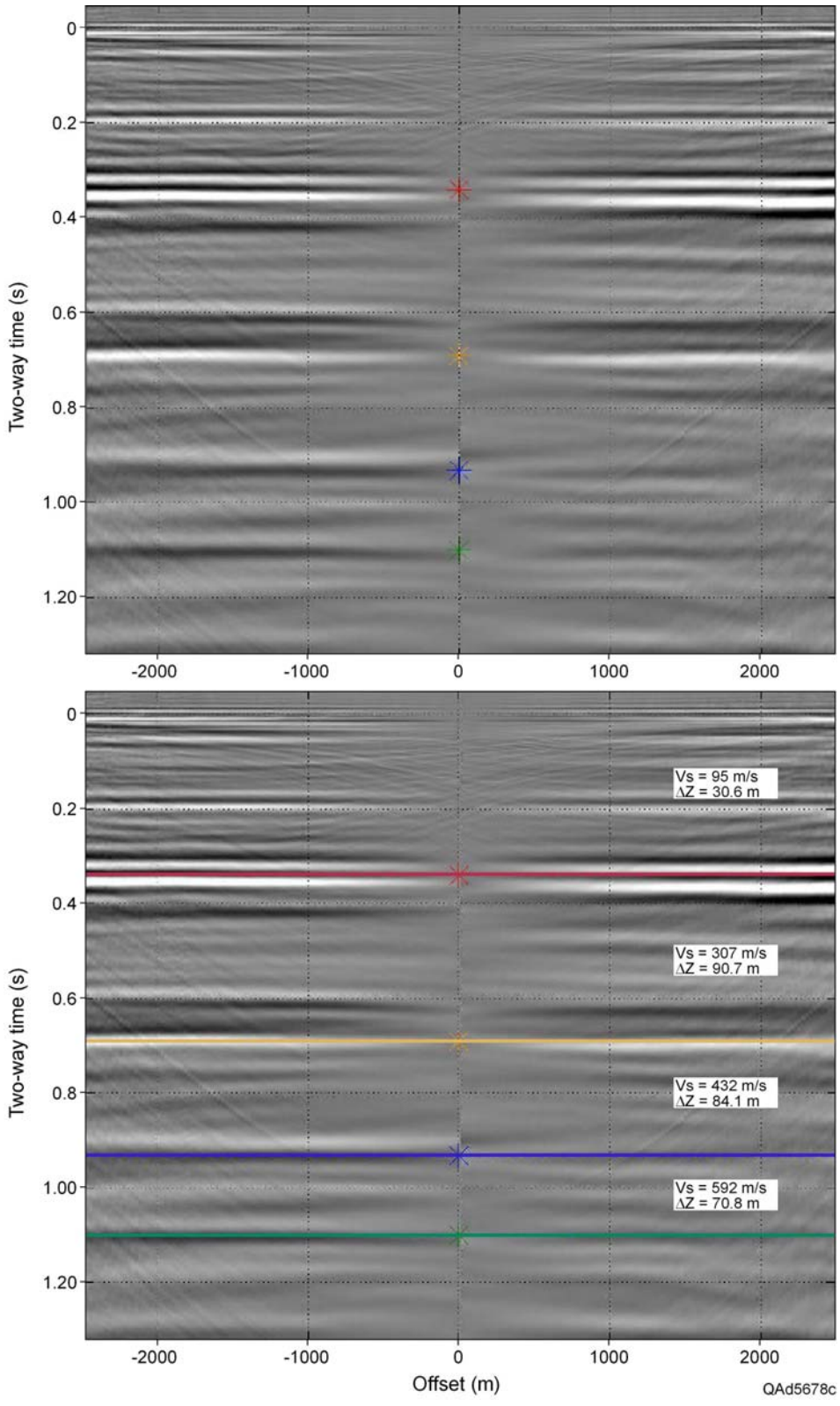
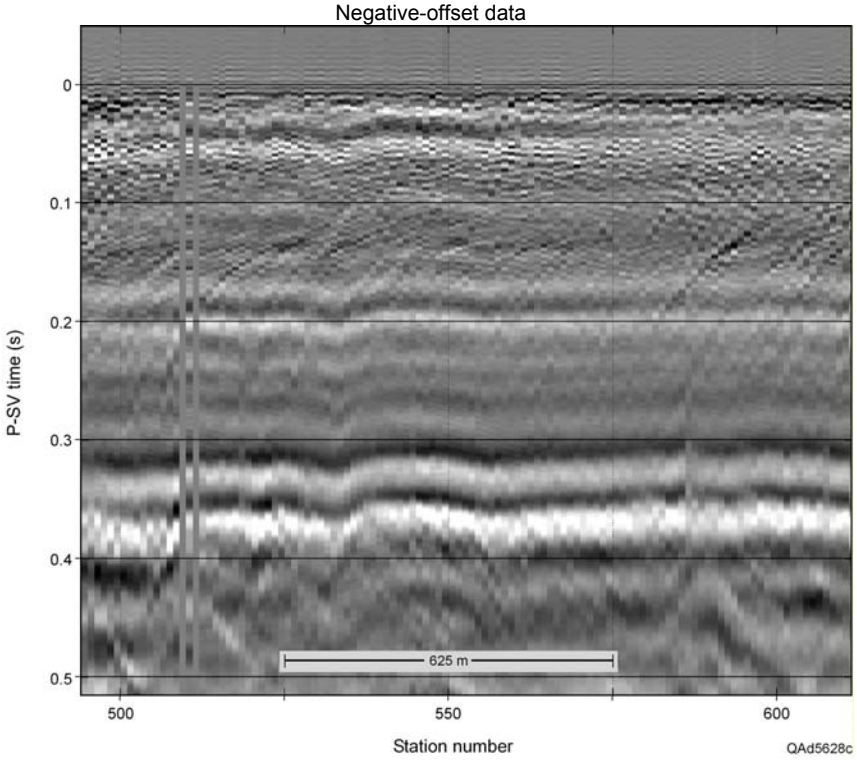


Figure 9, cont. P-SV reflectivity determined at one receiver station. NMO corrections have been applied to the data in panels (c) and (d).

We find that P-SV images made from data that are corrected for velocity moveout are a better description of near-seafloor geology than are images made from uncorrected data. An example of such an image comparison along Line A is provided as Figure 10. **Brute images** (panels 10a and 10b) made from uncorrected data have a large amount of diffraction-event noise, particularly evident in the first 200 ms of image time. Much of this diffraction noise is eliminated in the NMO-corrected data (panels 10c and 10d) even though the data are not migrated. Note that the positive-offset and negative-offset brute data emphasize different portions of shallow diffraction events. This behavior is best seen in the data window between 0.1 and 0.2 s. For negative-offset data, diffractions in this time window are dominated by diffraction arcs that slope down to the left (Fig. 10a). For positive-offset data, the same diffractions are dominated by events that slope down to the right (Fig. 10b). Why these differences in diffraction responses occur between positive-offset and negative-offset data will continue to be studied.

P-SV images of near-seafloor geology along the full extent of Line A are shown in Figure 11. These examples show that negative-offset data image geology across an interval located between 0.9 and 1.1 s below the seafloor better than do positive-offset data. The reason for this imaging difference between negative-offset and positive-offset data also needs further study. Any distinctions between the positive-offset and negative-offset images in the remainder of the image space are minor. There are thus three options that can be used as the P-SV near-surface image along Line A: (1) positive-offset image, (2) negative-offset image, or (3) the sum of the positive-offset and negative-offset images (Fig. 12). We use the negative-offset P-SV image (Fig. 12a) in the remainder of this discussion because this imaging option provides the best illumination of the geology across the P-SV image-time interval 0.8 to 1.2 s.

(a)



(b)

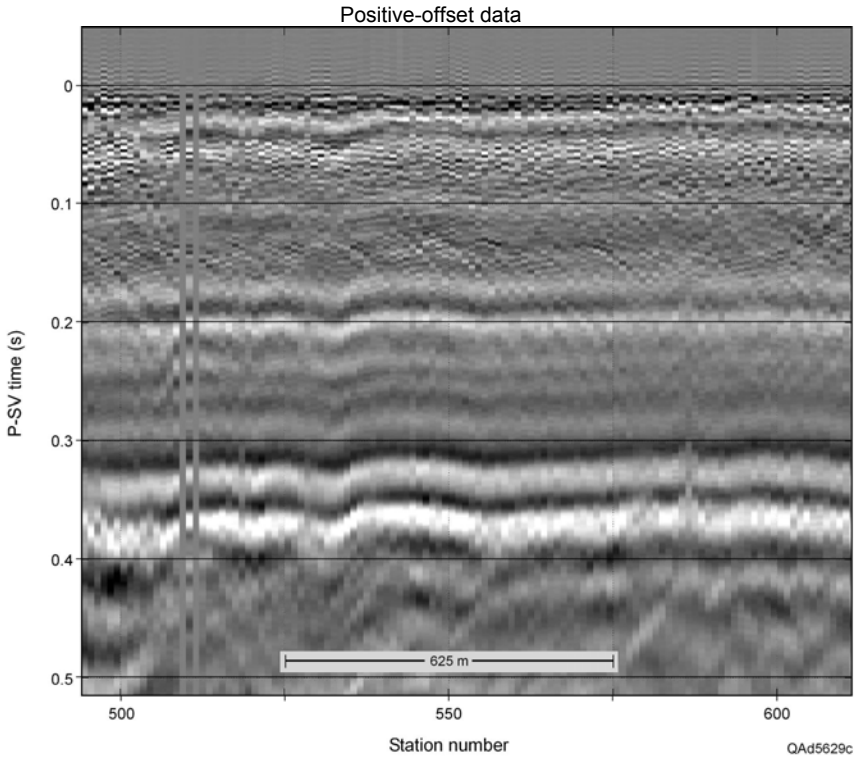
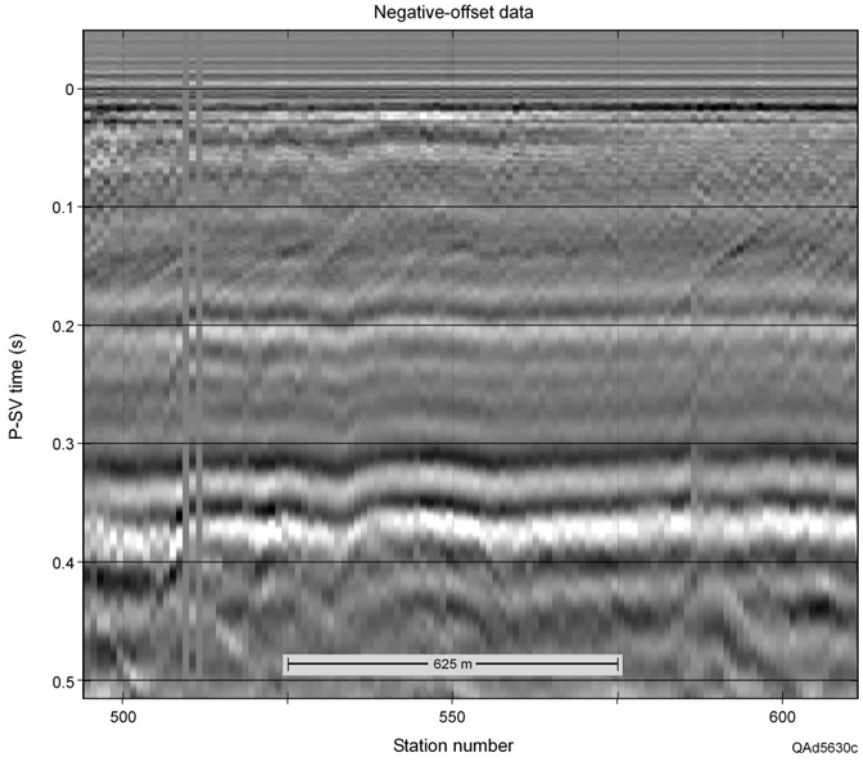


Figure 10. (a) Brute P-SV image using uncorrected negative-offset data. (b) Brute P-SV image using uncorrected positive-offset data.

(c)



(d)

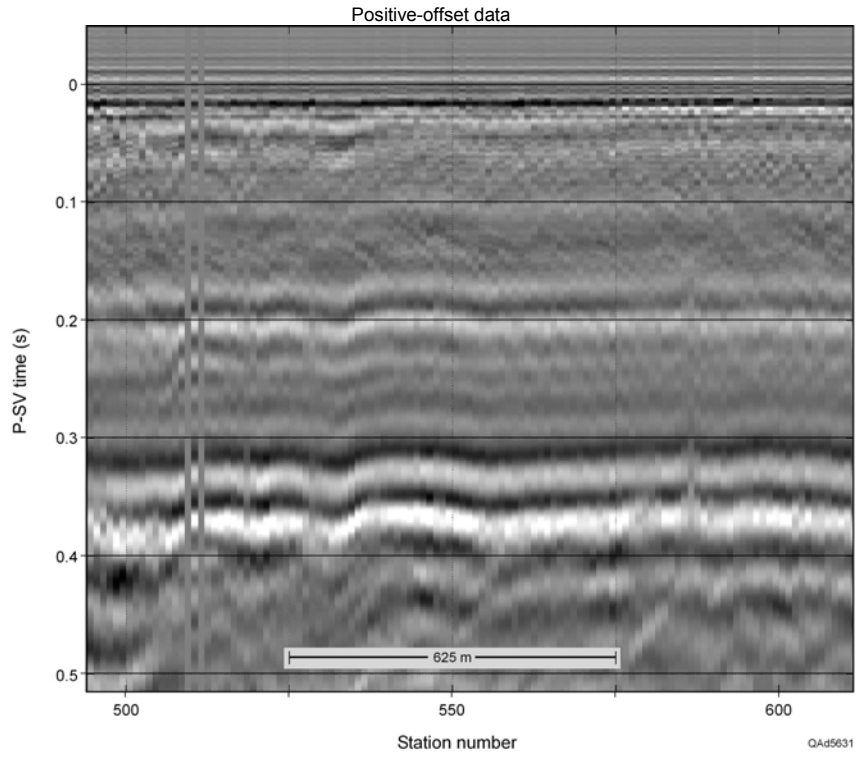


Figure 10, cont'd. (c) P-SV image using NMO-corrected negative-offset data. (d) P-SV image using NMO-corrected positive-offset data.

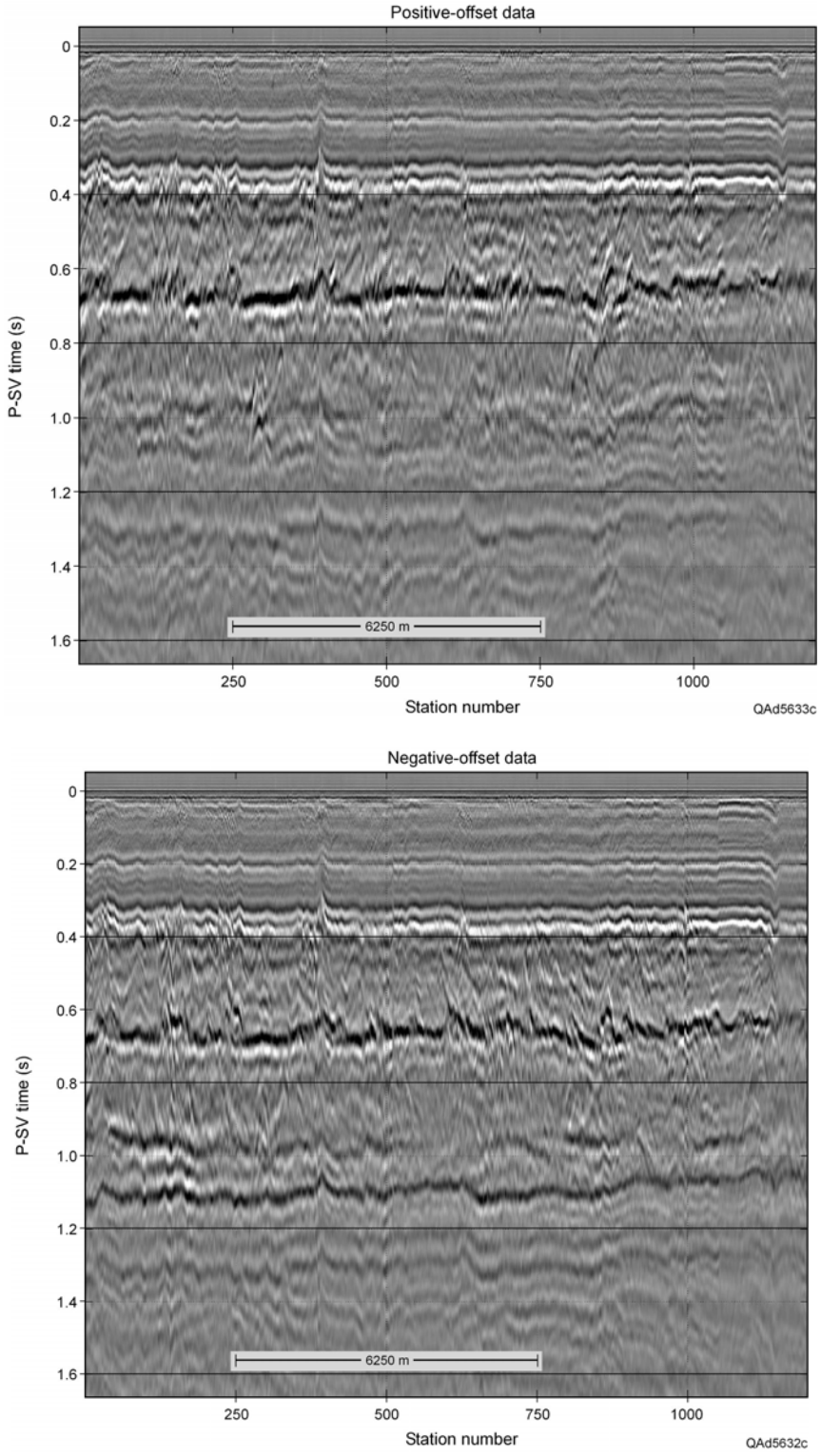


Figure 11. (Top) P-SV image made from positive-offset data along the full extent of Line A. (Bottom) P-SV image made from negative-offset data. The negative-offset data image strata between 0.9 and 1.1 s that are not well seen with the positive-offset data.

EGL's P-SV image is compared with the contractor's P-SV image in Figure 13. Because EGL's data-processing strategy creates a flat seafloor, the contractor image (Fig.7) has been flattened to the seafloor for easier image comparison. This flattening was done by applying a static shift to each CDP trace that equaled water depth divided by water velocity (1468 m/s). A considerable amount of near-surface data has been muted in the contractor's data processing, with the result that Layer 1 and the top portion of Layer 2 have been eliminated. This muting causes the base of Layer 2 in the contractor image to occur more than 500 ms earlier than where it is positioned in the EGL image. The EGL image provides an improved definition of geology that extends from the seafloor to the base of the **Paleoslide** layer (Layer 2), a layer of importance in the local area of this 4C OBC profile. Below Layer 2, the distinctions between the two images are not significant. The different structural dips exhibited by the images (such as the **Glide plane** even, another local feature of importance) are probably caused by the different techniques that were used to create a flat seafloor in the two imaging strategies.

To use both P-P and P-SV attributes in an interpretation of near-seafloor geology, it is necessary to depth register the P-P and P-SV images so that depth-equivalent data windows can be defined in each image space. The P-P and P-SV images generated by EGL are shown in a depth-registered form in Figure 14 with depth-equivalent horizons marked.

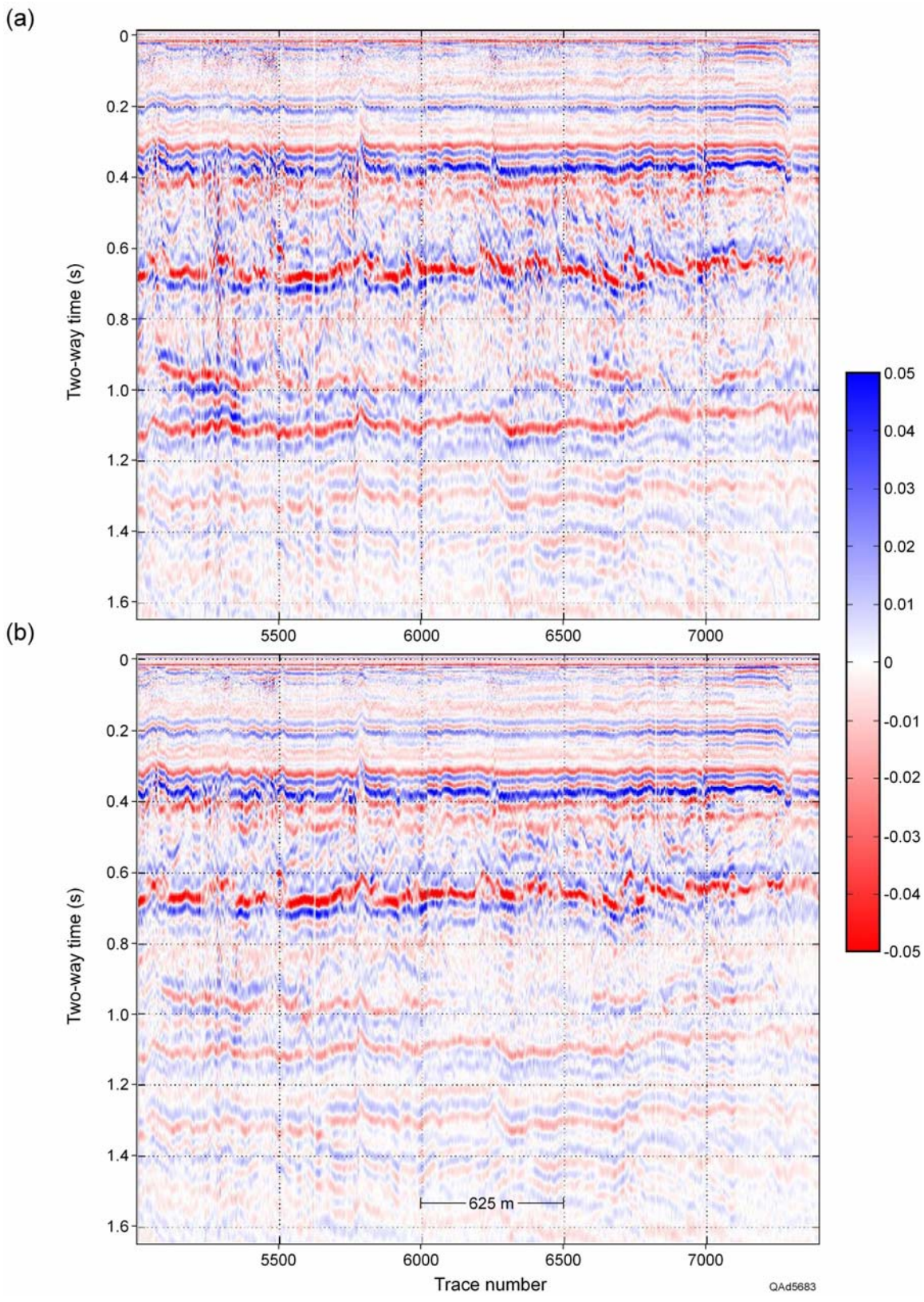


Figure 12. (a) Negative-offset P-SV image. (b) Sum of positive-offset and negative-offset P-SV images.

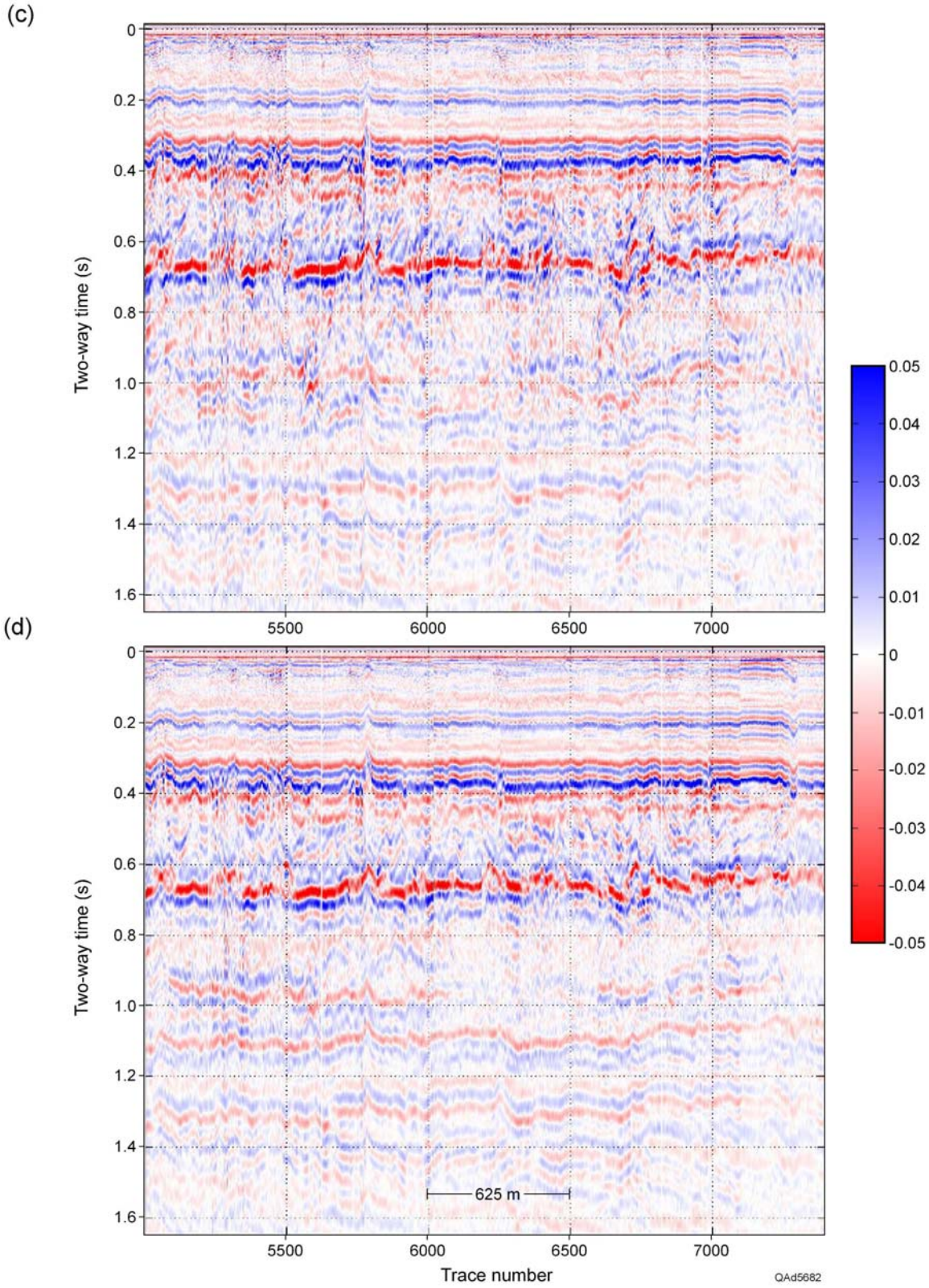


Figure 12, cont. (c) Positive-offset P-SV image. (d) Sum of positive-offset and negative-offset P-SV images.

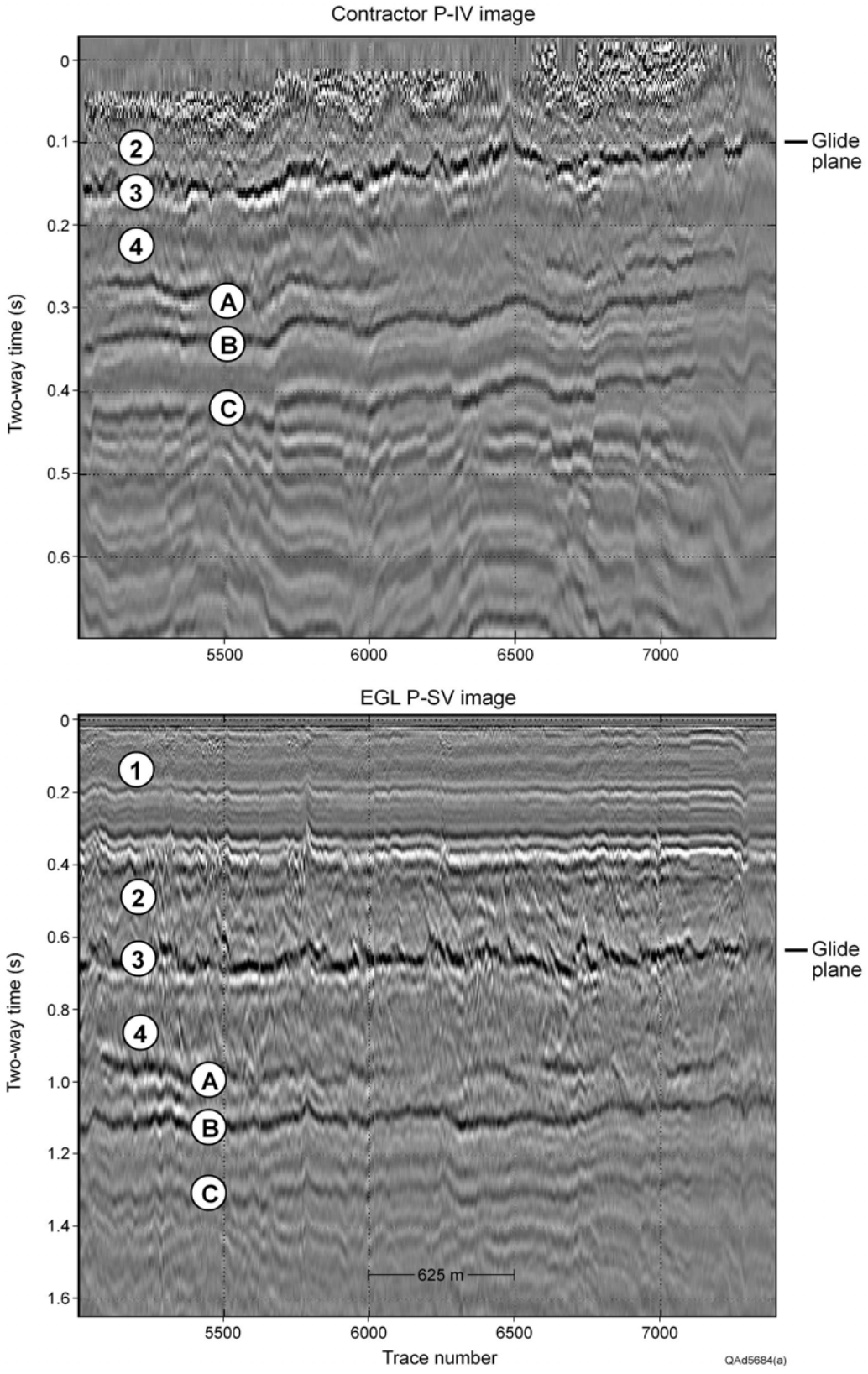


Figure 13. Comparison of contractor P-SV image with EGL's negative-offset P-SV image.

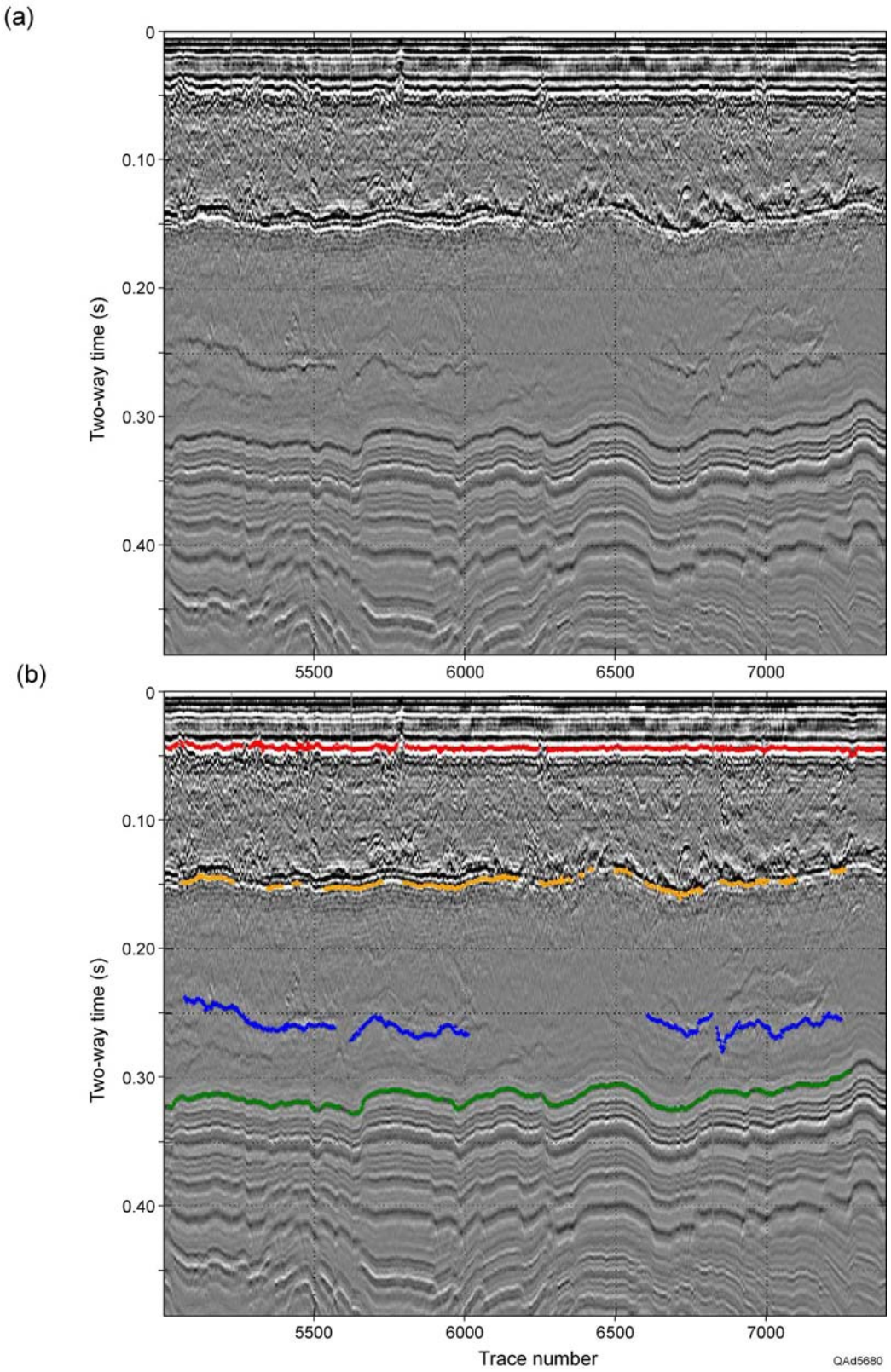


Figure 14. Depth registration of EGL P-P and P-SV images. (a) Unmarked P-P image. (b) Interpreted P-P image.

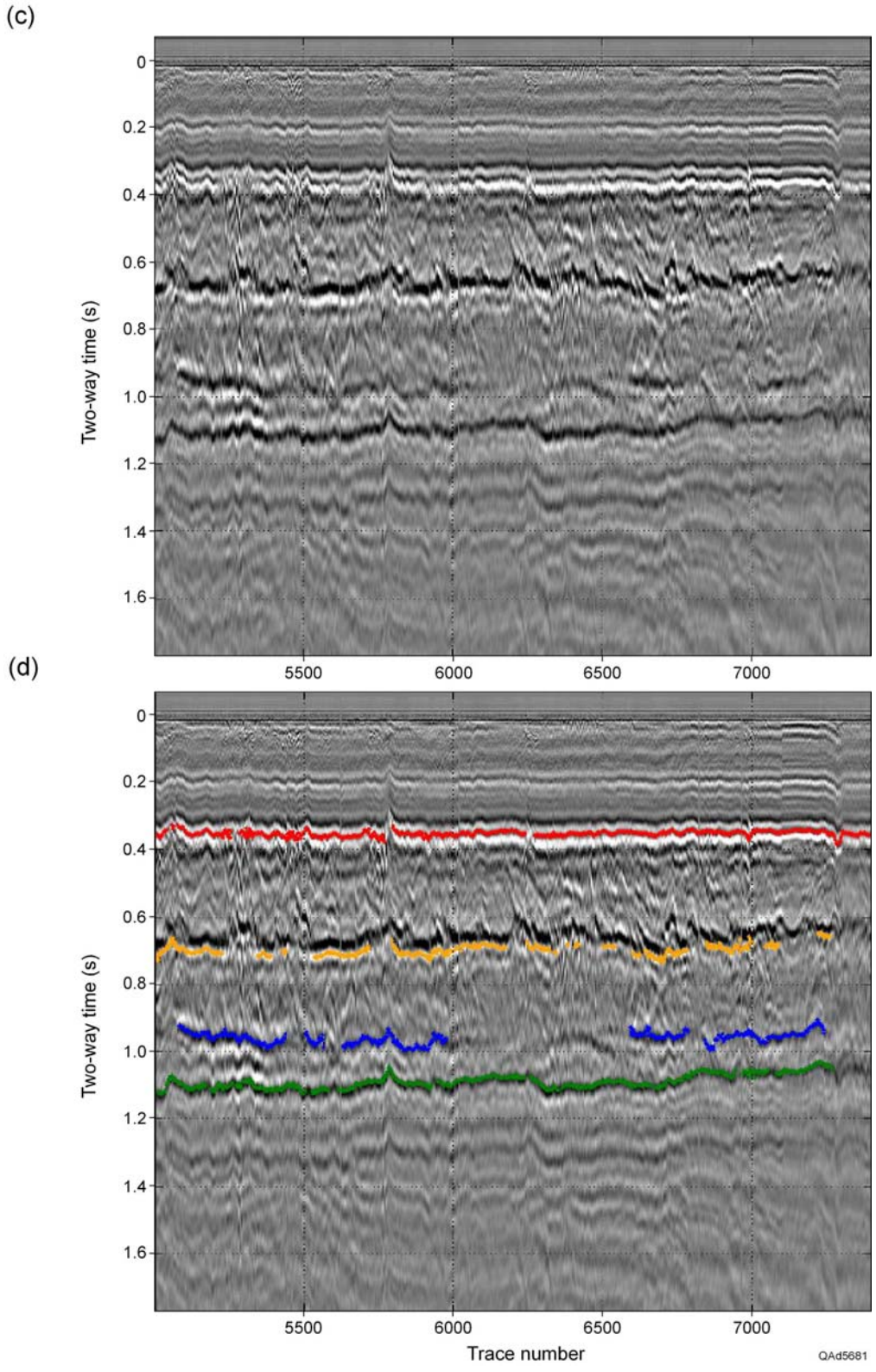


Figure 14, cont. Depth registration of EGL P-P and P-SV images. (c) Unmarked P-SV image. (d) P-SV horizons interpreted to be depth equivalent to the P-P horizons in b.

Conclusions

Important seismic-imaging software that was needed to create high-resolution P-P and P-SV images of near-seafloor geology at the hydrate monitoring station has been developed and tested using 4C OBS data similar to that expected to be acquired across Block MC 118. Test results indicate that the P-P resolution of strata within the first 5 m below the seafloor is improved when we use our new sensor-calibrated data for image construction. Our imaging strategy across all of the hydrate stability zone is proving to be superior to any contractor imaging that we have seen to date.

Reference

Backus, M. M., Murray, P. E., Hardage, B. A., and Graebner, R. J., 2006, High-resolution multicomponent seismic imaging of deepwater gas-hydrate systems: The Leading Edge, v. 25, p. 578-596.

Abbreviations and Acronyms

4-C: four-component
EGL: Exploration Geophysics Laboratory
MC: Mississippi Canyon
OBC: ocean-bottom cable
P-wave: compressional wave
P-SV: converted-shear mode (P-wave to SV-shear wave conversion)

Coupling of Continuous Geochemical and Sea-floor Acoustic Measurements

Subcontract to
DOE Award Number: DE-FC26-02NT41628

Final Report
April 1, 2006 – September 30, 2006

November 15, 2006

Jeffrey Chanton and Laura Lapham

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Abstract:
In May 2005, the Pore-Fluid Array (PFA) was installed on the northern flank of Mississippi Canyon 118. The PFA housed four OsmoSamplers within a sampler box that collected pore-fluids slowly over time in order to monitor the in situ methane concentrations and other dissolved constituents. In September 2006, the sampler box was retrieved with the submersible Johnson-SeaLink and the pore-fluids were analyzed for chloride and methane concentrations and stable carbon isotopic ratios. Analysis showed that the northern flank of MC 118 is characterized by brine and methane-rich fluids that have a distinct $\delta^{13}C\text{-}CH_4$ value, averaging -32.35±3.4‰, suggesting a mixture of biogenic and thermogenic methane. Since brine inhibits hydrate formation, the discovery of brine radically changes the hydrate stability zone in the northern region of MC 118. The sampler box was also replaced with a new box, ready to collect another time-series of pore-fluid samples. On this same cruise, two other instrument types were deployed in the shallow sediments (<50 cm deep). Pore-water equilibration instruments (peepers) and an OsmoLander were also emplaced directly adjacent to outcropping hydrate to be retrieved at a later date. In March 2007, MC 118 was revisited with the station service device (SSD) and one peeper was retrieved from Mandyville (see mound image, page 5). The pore-fluids from this peeper are still being processed.

Background: Hydrate stability is a function of *in situ* pressure, temperature, and methane concentration conditions. If these conditions change over time, the stability of hydrates could be adversely affected. Therefore, to assess hydrate stability, each of these conditions must be monitored over time. While pressure and temperature measurements are often made, *in situ* dissolved methane concentrations are not. Furthermore, since hydrates exclude salts upon formation, hydrate formation events may be followed by monitoring temporal changes in dissolved chloride and sulfate concentrations. Therefore, the goal of this research is monitor hydrate stability by quantifying the *in situ* methane and dissolved salt concentrations within hydrate-bearing sediments over time.

In situ methane concentrations are difficult to quantify because dissolved methane readily comes out of solution. Without the use of an *in situ* measurement device (ie underwater mass spectrometer), the samples must be collected from the seafloor, contained at *in situ* pressures, brought to the surface, and measured for methane concentrations. Yet, containing samples at in situ pressures is not a trivial task. Therefore, the quantification of in situ methane concentrations will be attained by testing three different instruments. These instruments are currently being tested on the seafloor and are described below.

1. **Pore-Fluid Array:** The Pore-Fluid Array (PFA) is made up of an interchangeable instrument package that houses four individual OsmoSamplers (Jannasch et al., 2004), a connector that allows the instrument package to be changed out while minimizing sample disruption, and a 10-meter long probe tip along which 8-filtered ports are evenly

spaced (Figure 1). At each port, pore-fluids are slowly pumped up the probe tip, across the connector, and into long length of small-diameter tubing coil using OsmoSampler technology to collect ~4 months data with week resolution. OsmoSamplers collect pore-fluids slowly over time using an osmotic differential created between a brine and DI-water reservoir within the pumps (Figure 2). Two of the four samplers were plumbed into a high-pressure valve that, when closed on the seafloor, kept the sample from degassing upon ascent through the water column. In May 2005, the PFA was deployed on the northern flank of Mississippi Canyon lease block 118 (MC 118), Gulf of Mexico.

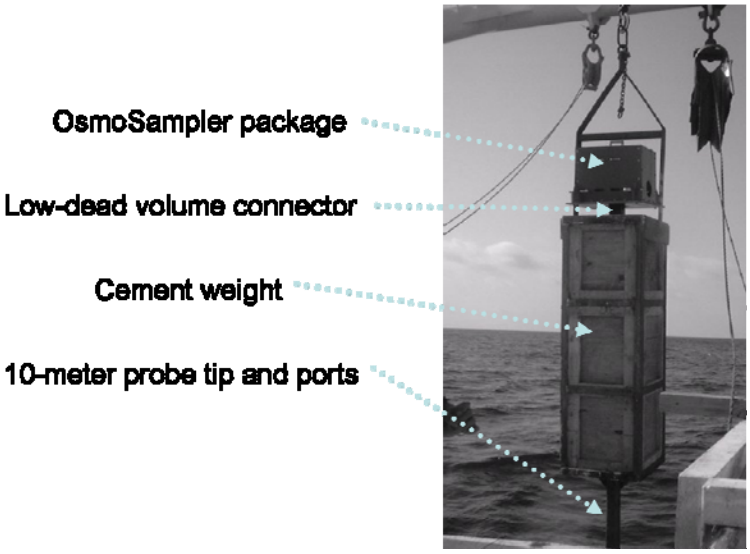


Figure 1: Picture of PFA off back of ship ready for deployment. The four parts that make up the PFA are labeled.

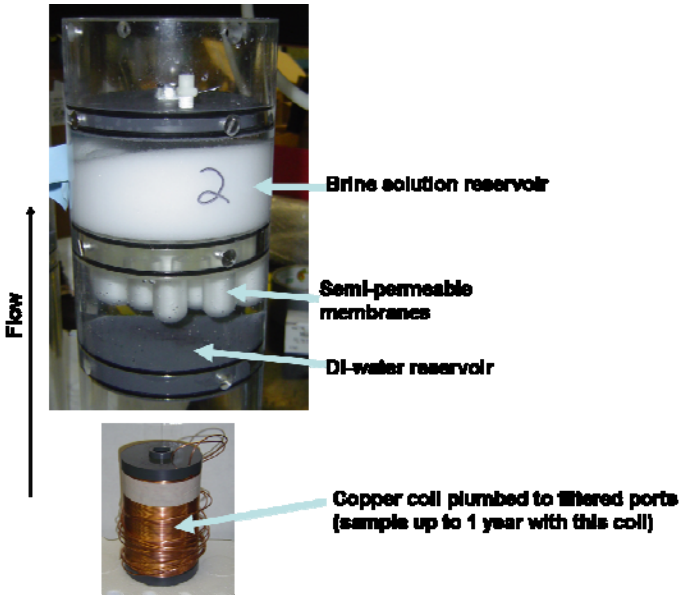


Figure 2: Picture of OsmoSampler and copper tubing spool (Jannasch et al., 1994; Jannasch et al., 2004).

2. **OsmoLander:** Using the OsmoSampler technology, the shallow sediments (upper ~50 cm) were also sampled with a modified PFA called the OsmoLander. The OsmoLander contains four OsmoSampler pumps (similar to the PFA), yet collects pore-fluids directly adjacent to a hydrate surface (Figure 3). Pore-fluids are collected through small tubing housed within a PVC T-handle that is 1, 2, 3, and 4 cm away from the hydrate surface (shown in Figure 2). This instrument contains short length coils to get a snap shot of the in situ methane concentration. It also allows for the determination of hydrate dissolution rates to be directly measured.

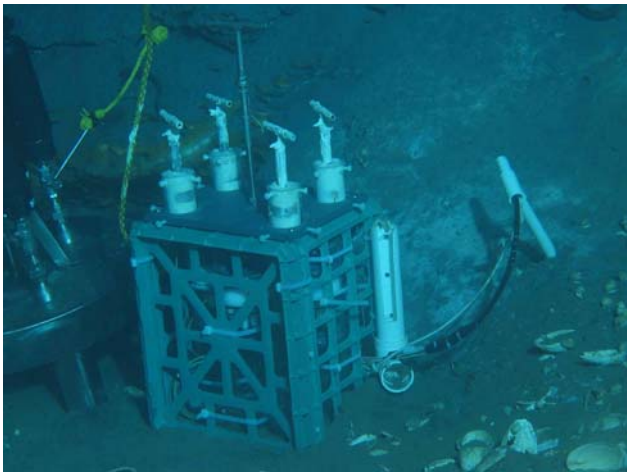


Figure 3: OsmoLander emplaced at MC 118. Four small T-handle valves are visible that will be closed when it is retrieved from the seafloor. To the right of the sampler, the PVC T-handle is visible where samples will be collected.

3. **Peepers:** Pore-water equilibration instruments (peepers) are used to passively collect fluids in shallow water systems to measure for dissolved constituents (Hesslein, 1976; Mayer, 1976). Peepers contain several sample reservoirs in close succession to result in a high resolution depth profile. The collection is attained by each reservoir being covered by semi-permeable membrane that, when placed in the sediments, equilibrates with dissolved constituents, including gases. However, since typical peepers are used in shallow water systems, they are not affected by changes in pressure when collected and do not contain the samples at in situ pressures. Since methane comes readily out of solution, the use of peepers in deep water systems is subjected to the pressure issues and may result in the loss of dissolved gases. Therefore, we are testing two modifications to the original peeper design (Figure 4). The first connects plastic bags to each sample reservoir, allowing evolved gases to expand into the bags (Figure 4a). And the second design uses cut-off glass syringes whose barrel is allowed to move during gas expansion (Figure 4b).

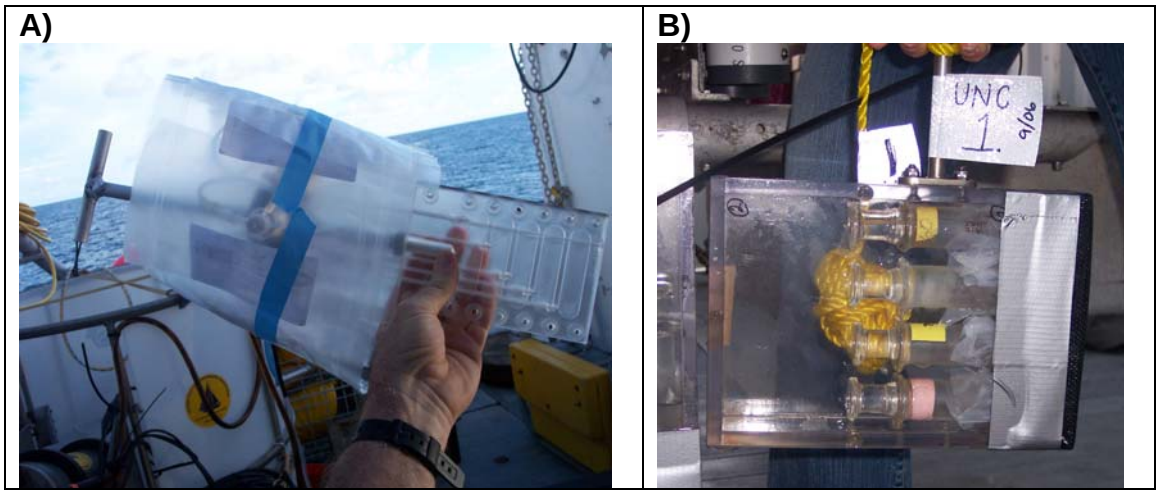


Figure 4: Photographs of modified peepers. A) Bagged peeper with sample reservoirs. B) Syringe peeper prior to deployment.

Results of research activities:

PFA results:

After 1.5 years, the PFA's instrument package was successfully recovered and the individual OsmoSamplers were found to be collecting from the overlying water, 1.2 m, 3.2 m, and 8.5 meters below the seafloor (mbsf; Figure 5).

From the sampler coils, pore-fluids were extracted and measured for chloride, sulfate, and methane concentrations and methane isotope ratios. The overall results showed normal seawater conditions in the overlying waters, averaging 549 mM chloride (Figure 6a) and 30 mM sulfate (Figure 7). At 8.5 mbsf, chloride concentrations averaged 4600 mM (Figure 6b); strongly suggesting the intrusion of brine fluids. Brine was further indicated by the absence of sulfate, 0.7 mM sulfate (Figure 7). As expected with brine fluids, they were also characterized by high methane concentrations, averaging 4.2 mM with a maximum of 14 mM (Figure 8). The $\delta^{13}C\text{-}CH_4$ values of this methane averaged -32.35±3.4‰, suggesting a mixed biogenic and thermogenic source (Figure 9).

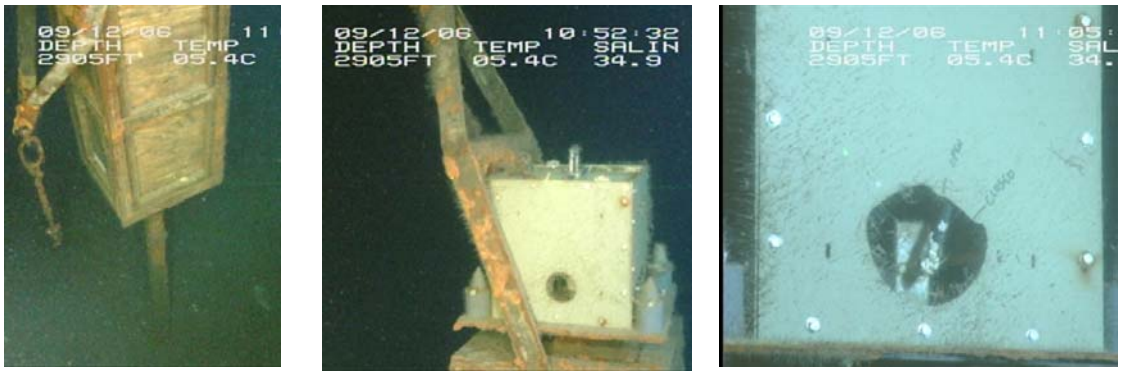
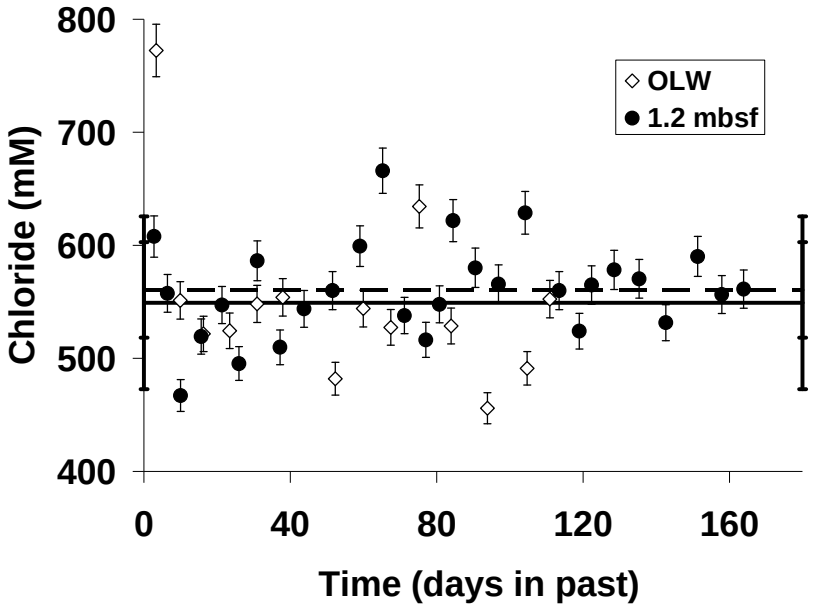


Figure 5: Seafloor photos of the PFA retrieval. A) The first sighting of the PFA showed it was standing upright and vertical about 2 meters out of the sediment. B) The OsmoSampler package shown with minimal biofouling and all parts intact. C) Although a little corroded, the high pressure valve was still intact.

A)



B)

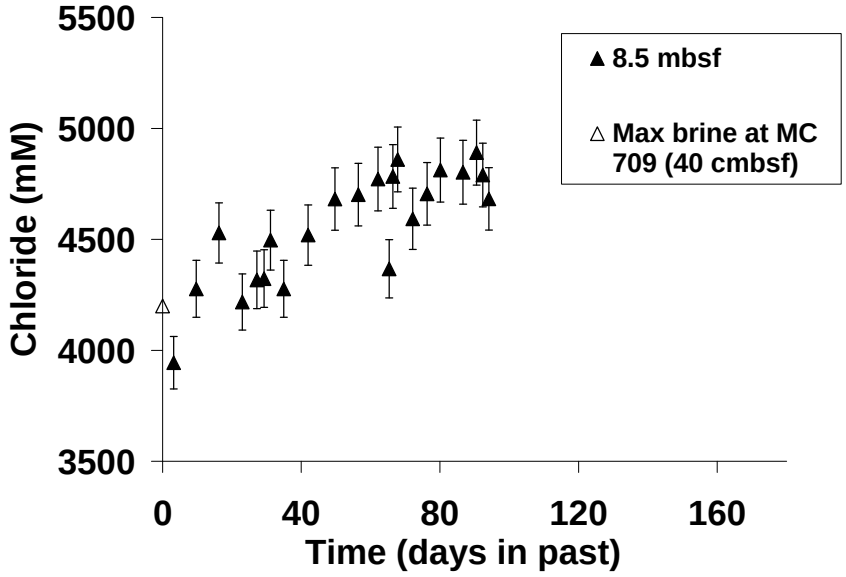


Figure 6: A) Chloride concentrations for overlying water (OLW) and 1.2 mbsf. The dashed and solid lines correspond to the overall average concentrations and standard deviations for 1.2mbsf and OLW samples. B) Chloride concentrations for 8.6 mbsf are plotted in black filled triangles. The open triangle is the chloride concentration measured at a nearby brine field, MC 709. Note the y-axis scale change between A and B. On each point, error bars represent 3% analytical error.

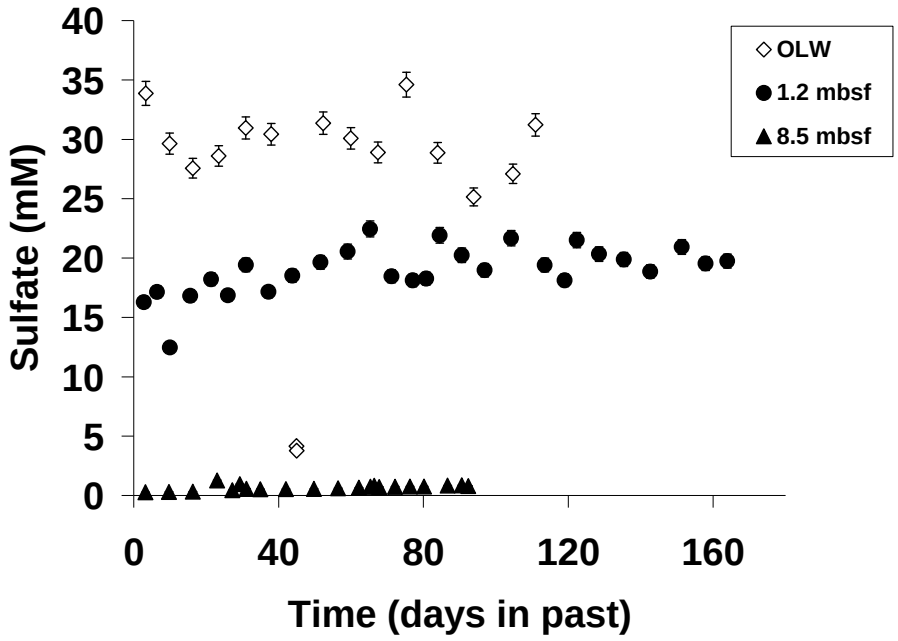


Figure 7: Sulfate concentrations for all three coils measured. On each point, error bars represent 3% analytical error.

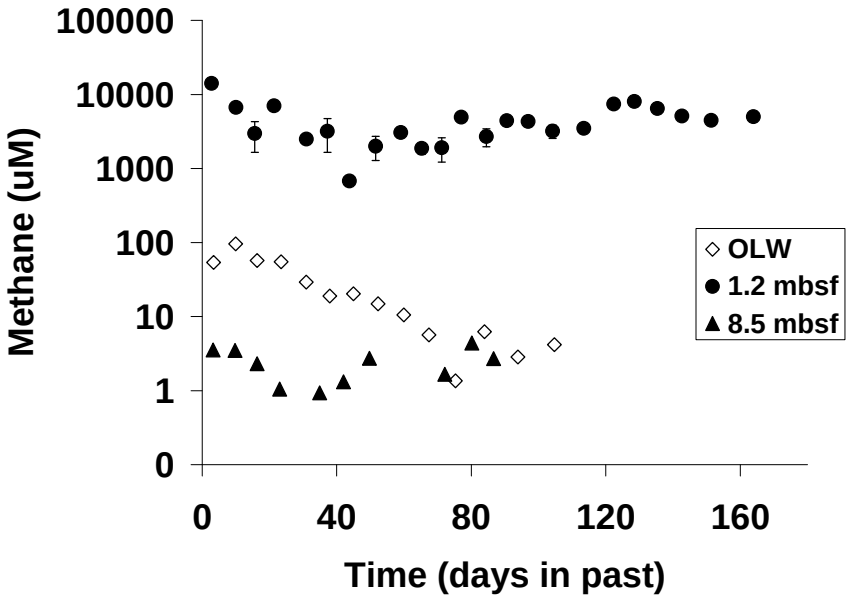


Figure 8: Methane concentrations for all three coils measured. Note log scale y-axis.

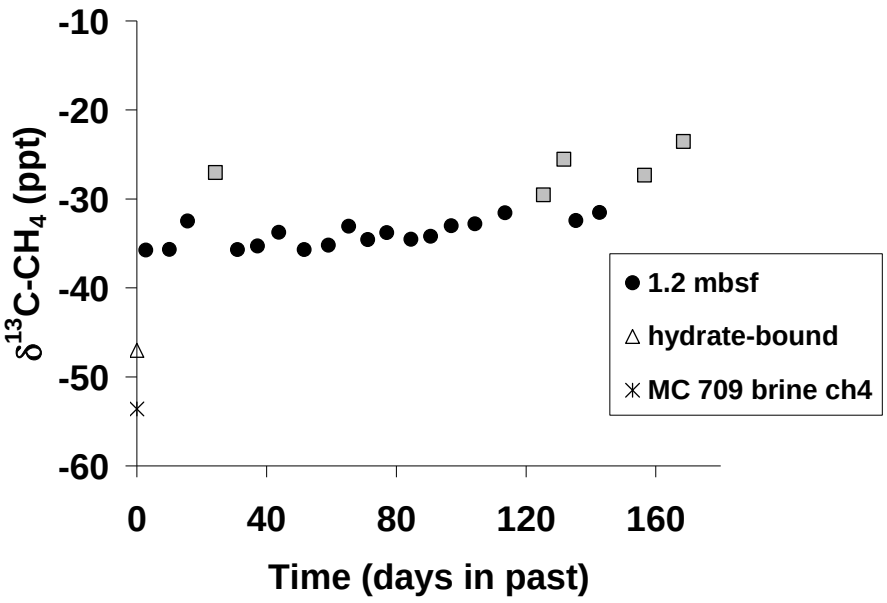


Figure 9: Methane isotope composition for 1.2 mbsf shown in black circles and gray squares. Symbols have standard deviation bars on them. Gray squares show values lying outside the average value. Also shown, open triangle is the hydrate-bound methane value as reported in Sassen et al. (2006) and the x-symbol is the methane stable isotope composition measured in brine fluid from a nearby lease block, MC 709 (see dissertation Chapter 6).

Emplacement of sea-floor instruments: In September 2006, six modified peepers were emplaced at MC 118 at three different sites (Table 1 and Figure 10).

Table 1: Summary of seafloor instruments emplaced at MC 118.

Site	# of Bagged Peepers	# of Syringe Peepers
Mandyville	1	0
Rudyville	2	2
Noakesville	1	0

Retrieval of sea-floor instruments: During the March 2007 cruise, we were able to retrieve one of the bagged peepers at Mandyville using the Station Service Device (instrument shown in Figure 10). There was no visible degassing of the samples upon ascent in the water column. The peeper seemed in good shape except the T-handle arm corroded at the junction to the sample reservoirs. However, this did not disrupt the samples.

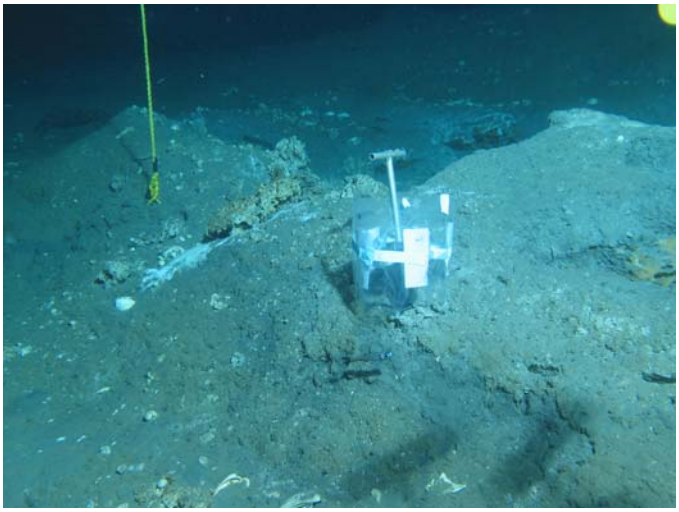


Figure 10: Sea-floor photograph of a bagged peeper at Mandyville. The yellow vertical line off to the left of the picture is marker #1.

Upon retrieval from the SSD manipulator arm, the peeper was sub-sampled and ~5 mL of pore-fluid was collected from 5 reservoirs. Fluids were placed into evacuated glass serum vials and frozen upside down to seal. Samples are currently being processed at Florida State University.

Publications:

Lapham L. L. (2007) In situ measurements of methane cycling in cold seep sediments containing gas hydrates and brines. Ph.D., University of North Carolina.

Presentations:

Lapham, L. L., J. P. Chanton, C. S. Martens, P. D. Higley, H. W. Jannasch, J. R. Woolsey, and K. Sleeper. 2007. Biogeochemical sensors: design and applications of the Pore Fluid Array for the Mississippi Canyon 118 Gas Hydrate Seafloor Observatory. Oral presentation by Ken Sleeper, Mid-South Area Engineering and Sciences Conference, University of Mississippi. Oxford, MS May 17-18.

Lapham, L. L., J. P. Chanton, C. S. Martens, P. D. Higley, H. W. Jannasch and J. R. Woolsey. 2007. Monitoring long term hydrate stability: in situ methane and the Pore Fluid Array (PFA). Oral presentation, Gulf of Mexico Hydrates Research Consortium Annual Meeting. Oxford, MS.

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Hesslein R. H. (1976) An in situ sampler for close interval pore water studies. *Limnology and Oceanography* **21**, 912-914.

Jannasch H. W., Johnson K. S., and Sakamoto C. M. (1994) Submersible, osmotically pumped analyzers for continuous determination of nitrate in situ. *Analytical Chemistry* **66**, 3352-3361.

Jannasch H. W., Wheat C. G., Plant J. N., Kastner M., and Stakes D. S. (2004) Continuous chemical monitoring with osmotically pumped water samplers: OsmoSampler design and applications. *Limnology and Oceanography: Methods* **2**, 102-113.

Mayer L. (1976) Chemical water sampling in lakes and sediments with dialysis bags. *Limnology and Oceanography* **21** (6), 909-912.

Sassen R., Roberts H. H., Jung W., Lutken C. B., DeFreitas D. A., Sweet S. T., and Guinasso Jr. N. L. (2006) The Mississippi Canyon 118 Gas Hydrate Site: A complex natural system. *OTC Paper #18132; Offshore Technology Conference*.

Microbial Activity Related to Gas Hydrate Formation and Seafloor Instabilities

Subcontract to
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FINAL REPORT

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Microbial Activity Related to Gas Hydrate Formation and Seafloor Instabilities

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ABSTRACT

This final report covers the contract work beginning 1 January 2005 and concluding 1 January 2007.

Location and extent of seafloor hydrate occurrences are influenced by mineral content, microbial activity, fluid properties and physical properties of the sediments and by the hydrocarbon gas flux through the sediments. The goal of the research was to provide data to help establish mechanisms of seafloor hydrate formations and to provide guidelines to eventually locate hydrate deposits suitable for gas production. The work supported the planning and installation of the Gas Hydrate Observatory.

Numerous sediments from Mississippi Canyon blocks 118 and 798 were analyzed in the laboratory for influence on forming gas hydrates. Hydrate formation rates and crystal initiation times in a series of cores were measured in the laboratory as a function of depth below seafloor and as a function of lateral displacement at the seafloor surface. Results suggest sulfate zone depth, bioactivity, pore-water salinity, mineral content, bioproducts coating sediment particles, and sediment particle sizes impact hydrate nucleation and formation in near-surface sediments.

A core to 30 mbsf from the Dufresne cruise at MC-798 provided a unique evaluation of deep hydrate formations in Gulf of Mexico sediments that could be compared to numerous cores of less than 6 mbsf depths from the Mississippi Canyon.

The laboratory results show sediments below the sulfate zone to more easily form hydrates. Near-surface sediments showed random effects on gas hydrate formation believed caused by different sets of bioproducts coating mineral surfaces in the sulfate zone. The depth of the sulfate zone is highly dependent upon methane flux through the sediments.

Basic smectite clay platelets were again verified to act as hydrate nucleation sites.

Five significant publications as well as the completion of PhD dissertation research and degree for one individual derived from this effort.

I. INTRODUCTION

A. Gas Hydrate Occurrence and Microbial Influences in Hydrate Zones

Most analyses of gas hydrates in the GOM have been done on the top 6 meters of sediments (Milkov and Sassen, 2000), although the bottom of the gas hydrate zone in the Gulf of Mexico might extend 200- 1000 m below sea floor (Milkov and Sassen, 2002). The Dufresne core MD02-2570 takes on added importance because it extends to depths of about 30 meters and allows the study of hydrate formation in sediments deeper than usual.

Microbial activity in the Gulf of Mexico around gas hydrate occurrences is prolific (Roberts, 2004; Sassen et al., 2001). For lack of research, it has been too easy to assume that extensive microbial occurrences near massive hydrate mounds are coincidental. The association is probably much more complex than just biogenic gases being supplied as guest gases for hydrates. Microbes insert abundant lipids into the hydrate –bearing sediments that may promote hydrates; these hydrates prefer the proximity of complex microbial consortia and chemosynthetic communities (Sassen et al., 1999).

In the Cascadia Margin, bacterial populations and activity were found to increase by about an order of magnitude throughout gas hydrate zones wherever hydrates occurred, except in places of high H_2S concentration (Cragg et al., 1996).

B. Laboratory Study of Bioagents and Gas Hydrate Relationships

When bacteria produce surfactants, the surface-active agent falls into one of five classifications: (1) hydroxylated and crosslinked fatty acids, (2) polysaccharide-lipid complexes, (3) glycolipids, (4) lipoprotein-lipopeptides, or (5) phospholipids (Kosaric, 1992; Fujii, 1998).

To test the hypothesis that biosurfactants could catalyze hydrate formation, a sample of at least one biosurfactant from each classification was obtained from commercial sources. The results were emphatic. These biosurfactants catalyzed hydrate formation in packed porous media (Rogers et al., 2003). The following effects of biosurfactants in the porous media were observed: (1) Hydrate formation rates were usually increased. (2) Hydrate induction times were usually decreased. (3) Specific mineral surface-biosurfactant interactions developed. (4) Very low threshold concentrations of biosurfactants were required to catalyze hydrates.

Porous media of sand and sodium montmorillonite packed in a laboratory test cell and saturated with seawater containing 1000 ppm of biosurfactant showed a two to four-fold increase in hydrate formation rate over a control of the same media saturated with seawater without surfactant. Of the biosurfactants tested, surfactin is classified a lipopeptide, and snomax and emulsan are polysaccharide-lipid complexes.

It is helpful to remember approximate depths of the hydrate zone as

compared to the depth of near-surface cores being analyzed. Typically, the hydrate zone depth would be about 200 mbsf in the Mississippi Canyon, whereas the Dufresne cores extended to 30 mbsf and available push cores reach to about 6 mbsf. In fact, most of the limited hydrate-formation data reported in the literature for GOM.

II. THEORY

A. Hypothesized Mechanism Affecting Near-Surface Hydrate Formation

Sulfate from the overhead seawater permeates the near-surface sediments and comes to equilibrium in this sulfate zone. Anaerobic oxidation of methane occurs in the sulfate zone. Archaea clusters work in consort with sulfate-reducing bacteria. The bacteria reduce sulfate to H_2S, and archaea concurrently oxidize methane to form CO_2. The CO_2 precipitates as carbonates at the point of anaerobic methane oxidation. As the upward methane flux increases through the sediments, the sulfate zone ascends to nearer the sediment-sea interface. For example, the bottom of the sulfate zone has been reported to be only a few centimeters deep near gas hydrate outcrops and methane gas vents. Carbonate nodules solidify and become an indicator of the current bottom of the sulfate zone or a previous sulfate boundary.

Bioproducts from the microbes in the sulfate zone differ from those below the sulfate zone, and the catalytic effects of those bioproducts on hydrate formation could be expected to differ. (The catalytic effect of bioproducts probably depends on whether there are distinct hydrophobic and hydrophilic components in the same molecular structure. The hydrophobic moieties collect the methane and the nearby hydrophilic moieties collect and structure water, thus setting up the nuclei for hydrate initiation. Anionic bioagents and anionic synthetic agents have proven to be hydrate catalysts.) The sediment particles in the sulfate zone may be covered with polymeric bioproducts that do not have distinguishing hydrophilic and hydrophobic components, contrasting to those below the sulfate zone. A nonionic polymeric coating of near-surface mineral particles could slow or prevent local hydrate formation.

If this hypothesis is used to help interpret the hydrate formation and induction curves generated in the laboratory from MC-118 sediments, then from generated curves one might determine the location of the sulfate zone and have a good indicator of the magnitude of the methane flux at that location.

III. EXPERIMENTAL PROCEDURE

A. Procedure for Analyzing Dufresne Cores

Sediment samples were taken from the approximately 30 m long core extracted from 28°04.26'N and 89°41.39'W in the Gulf of Mexico during the Marion Dufresne cruise. Generally, laboratory samples were chosen at 3-meter core intervals. The mud samples were immediately sealed in Zip-lock plastic bags and stored in air-conditioned rooms until tested.

To prepare samples for testing, constant 20 g weights of sediment were taken from each interval and dispersed in a constant 60 g weight of cleaned sand to provide adequate permeability and porosity of the packed media so that maximum surface area of sediments in each experimental run would be exposed to pressurizing hydrocarbon gas in the test cell. For tests, original pore waters saturated the porous media; no other water was added to the samples. For testing, the 60/20 sand/sediment mixtures were placed in a 60 ml Teflon container with twelve 1/8 in. holes drilled in the container walls for gas access. The sample container was placed in a 400 ml stainless steel test cell from Parr Instrument Company. An RTD resistance temperature detector was positioned just below the sand/sediment surface. A pressure transducer measured internal pressure of the reaction vessel. The cell was purged of air and then pressurized with natural gas (90% methane, 6% ethane, 4% propane) to 330 psig. After the system had equilibrated at 70°F in a constant temperature bath for two hours, pressure was adjusted to 320 psig and the system allowed to equilibrate for another hour. Then, the test cell was immersed in a constant-temperature bath at 0.5°C and data collected every 2 minutes with Omega Daqbook 120 equipped with DBK9 Data Acquisition System and DasyLab Software. Pressure versus temperature was plotted.

Induction time of the hydrates was defined as elapsed time between the calculated equilibrium pressure-temperature and the observed hydrate formation during system cool-down. The induction time was standardized by dividing by the induction time for the sediment test sample of 1.0 m depth.

Hydrate formation rate, as the number of moles of gas going into solid solution per unit time, was determined with the Peng-Robinson equation of state from data collected in 2-minute intervals. To standardize, maximum formation rate was divided by the maximum formation rate for the 1 m sediment control. Duplicate runs were made on each sample.

B. Analyzing Near-Surface Cores

Important features of the laboratory procedure for analyzing near-surface cores are listed below.

1. Twenty grams of mud samples are evenly dispersed through 60 grams of coarse Ottawa sand that has been cleaned. The reasons for doing this are the following: (a) to give maximum access of natural gas to the sediment samples, thus exposing maximum surface areas of the sediment particles to the reacting gas, (b) to provide larger porosities in which hydrates are allowed to form and expand, (c) to be able to utilize the small mud sample sizes.
2. The samples are tested for hydrate formation in Teflon containers. Teflon provides a hydrophobic surface that does not affect hydrate formation.
3. For testing, the samples are placed in annular spaces of concentric Teflon cylinders. Both cylinders have many gas-access holes spaced over their entire areas. This allows maximum contact of gas with sediments and prevents mass transfer from limiting hydrate kinetics.
4. Only original seawater removed with the cores is present in the tests.
5. Teflon containers with samples are placed in stainless steel Parr reactors, sealed, pressurized with natural gas and submerged in constant temperature baths maintained at 0.5^{o}C.
6. Pressures and temperatures are recorded continuously during the tests.

IV. RESULTS AND DISCUSSION

A. Hydrate Formation Rate Variation with Depth

The Marion Dufresne MD02-2570 cores extracted from 0- 30 mbsf (meters below seafloor) provide an opportunity to study hydrate formation in sediments below the 6 m commonly tested in the Gulf of Mexico. The approach was to evaluate sediments from the surface to the 30 m bottom in 3 m intervals.

The laboratory hydrate tests repeated the following conditions: (1) Only original in-situ pore water saturated sediment test samples. (2) Each sediment sample was dispersed in cleaned Ottawa sand to give adequate porosity and permeability for testing. (3) Sediment dispersion throughout the sand gave maximum contact of minerals with natural gas. (4) Natural gas of 90% methane, 6% ethane, and 4% propane pressurized the hydrate test cell.

Resulting gas-hydrate formation rates are given in Table I and plotted in Figure 1. Each tabulated value is an average of duplicate, multiple, independent runs.

TABLE I. Gas-hydrate formation rates of sediments from Dufresne MD02-2570

Depth, meters	Formation Rate, mmol/hr	Standardized Form. Rate
0.00	0.00 Did not form	0.00
1.00	5.26	1.00
3.00	20.37	3.87
6.00	22.02	4.19
9.00	26.32	5.00
12.00	27.06	5.14
15.00	39.02	7.42
18.00	37.15	7.06
21.00	35.13	6.68
24.00	27.79	5.28
27.00	24.87	4.73
27+ (Plotted as 30 m)	23.96	4.56

An apparent trend in the gas-hydrate formation rates as a function of distance below sea floor (mbsf) can be detected in Fig. 1. Hydrates would not form in the nearest-surface sediments--even after sustaining hydrate-forming conditions for 96.5 hours. (This zero-depth test was terminated at 96.5 hours.) As depths increased, however, hydrate formation rates in the sediment samples increased until a maximum occurred for the mud at 15- 20 mbsf.

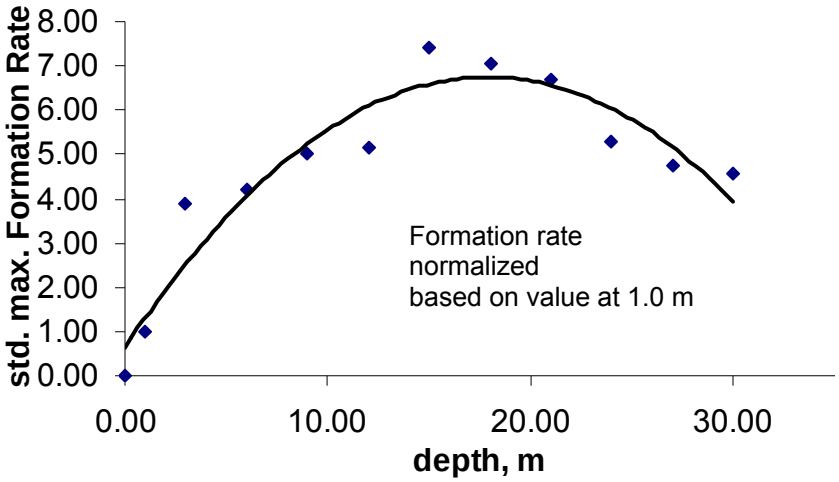

Fig. 1. Evaluation of core sediments for rate of hydrate formation

The correlation of hydrate formation rate with depth in Figure 1 may be represented by the regression Equation (1).

$$FR = -0.0191\,D^2 + 0.6823\,D + 0.6512 \qquad (1)$$

In the equation FR is the standardized maximum formation rate, D is the depth of sediments as meters. The R^2 for the correlation is 0.9034.

B. Hydrate Induction Time Variation with Depth

Sediment samples from Dufresne MD02-2570 were generally tested every 3.00 meters. Exceptions were a surface sample and a sample 1.00 meters below the surface. In the context of hydrocarbon gas migrating through seafloor sediments, induction time might be considered an indication of the gas residence time necessary to initiate hydrates. Therefore, induction time may be taken as one indication of the propensity for hydrate occurrence.

In Table II are the gas hydrate induction times for each sample depth; each data point represents an average of multiple runs. A standardized, dimensionless time is calculated by taking the induction time of the 1.00 sample as the reference. In the case of the surface sample, note that gas hydrates had not formed after 95.6 hours under hydrate conditions.

TABLE II. Gas-hydrate induction times of sediments from Well MD02-2570

Depth, meters	Induction Time, hr	Standardized Induction Time
0.00	Did not form.	∞
1.00	4.33	1.00
3.00	5.82	1.34
6.00	2.00	0.46
9.00	1.00	0.23
12.00	0.53	0.12
15.00	0.42	0.10
18.00	0.37	0.08
21.00	0.60	0.14
24.00	0.63	0.15
27.00	0.58	0.13
27+ (Plotted as 30 m)	0.43	0.10

The induction time-depth trend is more readily envisioned with the help of Figure 2.

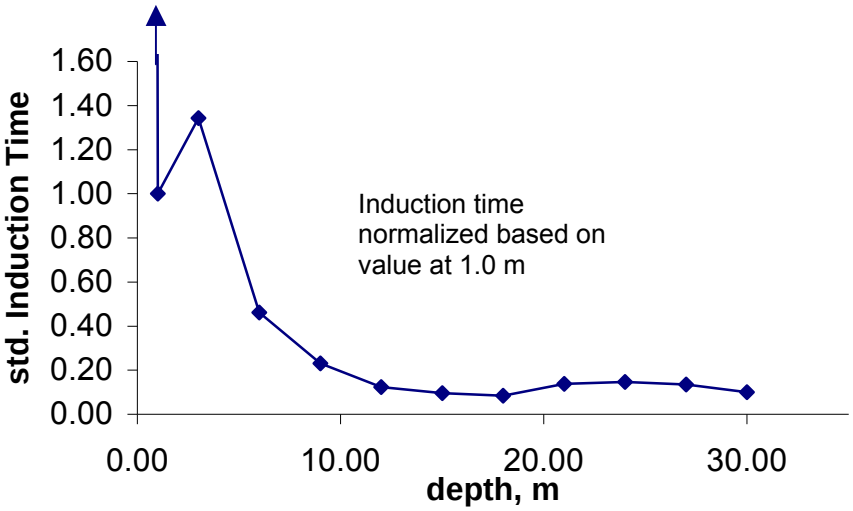

Fig. 2. Hydrate induction times for the Dufresne core.

A rapid decrease in induction time, i.e., an improvement in the ease with which hydrates initially form, is evident down to an approximate 12 m depth. There, the induction time reaches a minimum and remains at that rapid initiation for the remainder of the 30 m.

In the top few meters of near-surface sediments, the trend is disrupted.

It is helpful to superpose the induction time and formation rate curves in Figure 3, where the two phenomena are compared.

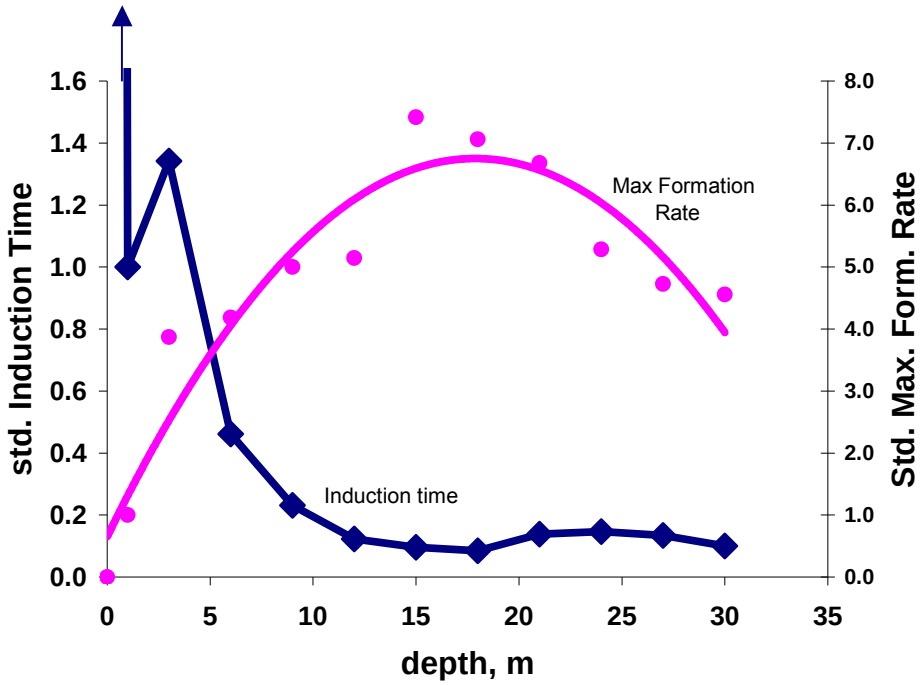

Fig. 3. Relative formation rates and induction times of gas hydrates

Induction time, the rapidity of hydrate initiation, primarily depends upon density and quality of nucleation sites. General studies in our laboratory of hydrate formation in sediments suggest the importance of smectite clay particles and the presence of bioproducts that may adsorb on those small clay particles as promoting short hydrate induction times, although apparently there are other influences on induction time that remain an enigma. The bioproducts bring hydrocarbon gas and structured water together at the nucleation site, as compared to their random meeting, thus reducing induction time.

After hydrate initiation, the rate of hydrate particle agglomeration must obviously depend on mass (hydrocarbon gas as well as water) transfer rate, heat transfer rate, surface area on which hydrates form, porosity for hydrate growth, temperature, pressure, bioproducts, and mineral surfaces—an imposing array of variables. Consideration is given to mass transfer rates, heat transfer rates, temperatures, and pressures constant in these experiments.

From the Dufresne MD02-2570 data, it is concluded from Figure 3 that hydrates occur in the sediments with varying difficulties and rates as a function of depth below the seafloor.

C. Silt, Clay, Sand Compositional Change with Depth

Sand, silt, and clay contents were analyzed for each of the samples of the 30 m core extracted during the Dufresne cruise.

In order to compare results directly with the hydrate formation rate and induction time trends, the sand/silt/clay contents were normalized and plotted versus depth in Figure 4.

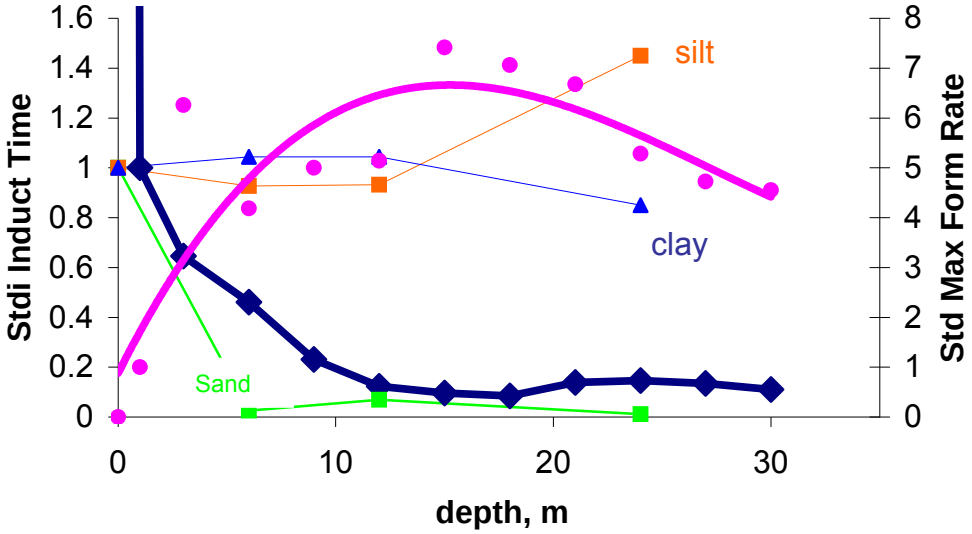

Fig. 4. Sand/silt/clay contents

It is interesting that breaks in the trends of sand/silt/clay roughly occur near where the breaks develop in induction time and formation rate trends. Although no definitive conclusion can be drawn from this limited number of data points, the relative trends suggest the need for future verification in other cores and suggest tangential experiments that could be undertaken.

D. Clay Content of Dufresne Sediments with Depth

Clay minerals in each sediment sample of the Dufresne core were analyzed with depth and the percent compositions are presented in Table III. These data represent compositions of particles ≤ 2 μm diameter.

TABLE III. Clay content of MD 02 2570

Depth (m)	% smectite	% illite	%chlorite	% kaolinite
3	32	43	8	18
6	40	37	6	18
9	26	45	6	23
12	43	32	5	20
15	39	37	7	17
18	30	45	6	20
21	10	69	10	11
24	29	50	9	12
27	30	43	8	19
27.1	12	67	10	11

In Table III it is seen that kaolinite and chlorite represent a lower fraction of clay content, and the percentages of these two minerals remain fairly constant with depth. It therefore seems more important to concentrate on the smectite and illite contents, so these clay contents are plotted versus depth in Figure 5.

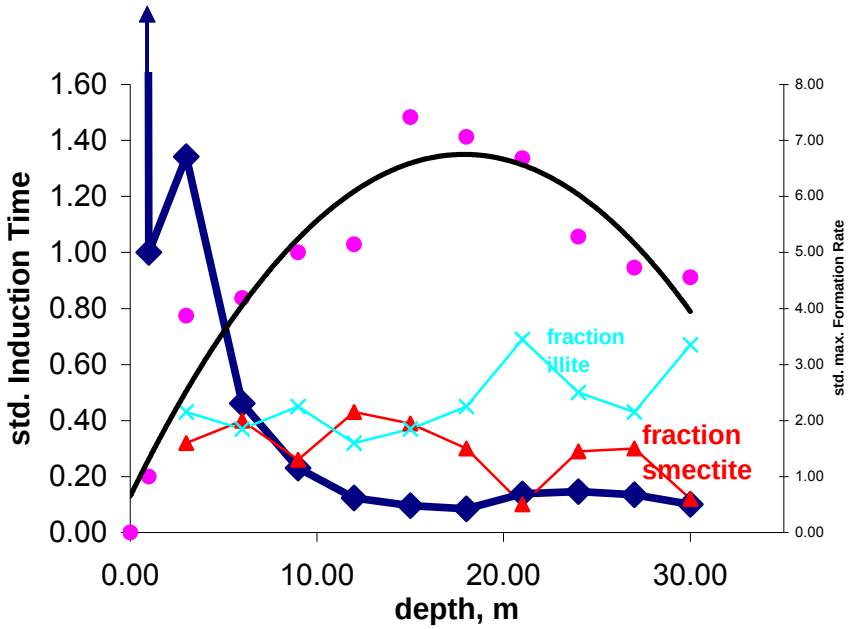

Fig. 5. Predominant clay content of sediments; <2 micron diameter particles

E. Sediment Particle Sizes with Depth

The Dufresne MD02-2570 cores are especially useful because they extend to about 30 mbsf, much deeper than any other cores available to this project.

Particle size distributions were obtained for the MD02-2570 sediments for three depths: 1.5, 9.0, and 27.0 mbsf. The analyses were conducted with a

Malvern MasterSizer Laser diffractor instrument. The instrument determines particle volume distribution from laser diffraction patterns of a cloud of the particles, and the data are presented on the basis of an equivalent spherical diameter. The instrument evaluates size ranges from 0.02 μm to 2000 μm. From the measurements, specific surface areas, surface weighted mean diameters and volume-weighted-mean diameters are presented in Table IV.

TABLE IV. Particle sizes of MD02-2570 sediments

Sample depth, m	Specific surface area, m^2/g	Surface weighted mean dia, μm	Volume weighted mean dia, μm
1.5	3.04	1.974	7.680
9.0	2.92	2.056	9.003
27.0	2.43	2.472	7.206

It is evident in Table IV that mean particle diameter generally increases with depth. Comparison of volume-weighted mean diameters with surface-weighted mean diameters, show a difference in size distributions with depth that suggest a large number of small particles in the sediments.

Smaller particles should decrease induction time by providing numerous nucleation sites. The smaller particles would also more likely be coated with bioproducts that could increase or decrease induction time depending on the bioproduct composition. Furthermore, bioproducts vary with depth. For example, near the seafloor sulfate-reducing bacteria act in consort with methane oxidizing archaea as the dominant microbial action. Below the sulfate zone, a different microbial activity and consortia exists.

The larger particles may influence hydrate formation rate by providing a larger porosity of the porous media in which the hydrates can expand. The large particle size distribution observed in these analyses seemed to substantiate the trend of hydrate formation rates with depth in the MD02-2570 sediments, where rates peaked near 10- 20 m depth, as detailed in earlier reports.

F. Near-Surface Sediments of MC-118

(1) Core 11, MC-118. Formation rates and induction times determined in laboratory measurements of Gulf of Mexico (GOM) sediments (Dufresne MD02-2570 cores) show distinct trends to 30-m depths. The results are now compared to shallower cores from different locations in the Mississippi Canyon.

Generally, when induction times decrease, hydrates begin forming more quickly. This can be important when gases percolate through sediments and have a limited residence time. After the hydrates are initiated, higher formation rates favor hydrate accumulations in the sediments.

Presented in Fig. 6 are formation rates/induction times of laboratory hydrates developing in the indigenous water-saturated sediments of MC118,

Core 11. The patterns of formation rate and induction time in Fig. 6 are somewhat atypical patterns in that induction times increase at about 200 cm depth.

In interpreting the data, the atypical behavior could mean that the bottom of the sulfate zone has not been reached at 297.5 cm—the deepest sample from Core 11. If so, this would mean a relatively low methane flux through the sediments. It could also suggest turbulent mixing of top sediments. In the laboratory, anionic bioagents increase the formation rates of hydrates and decrease the induction times of hydrates. Since different microbial communities exist above and below the sulfate zone, each community would be associated with a unique bioproduct. These bioproducts may have significantly different effects on gas-hydrate formation.

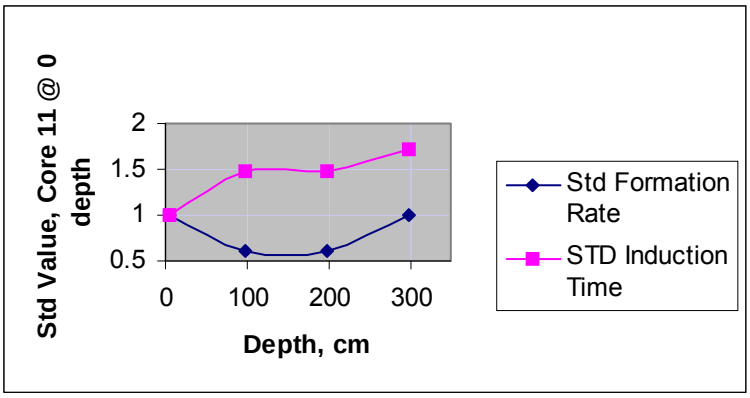

Fig. 6. Hydrate formation in Core 11 from MC-118

(2) Core 04, MC118. In Fig. 7, analysis of sediment from MC798, Core 04, gives a more typical pattern of induction time decrease with depth similar to that observed in the deep Dufresne core.

Possibly, the bottom of the sulfate zone could be within a few centimeters of the surface; this would explain patterns of the formation rates and induction times. If so, a relatively high methane flux might pass through the sediments at this core location.

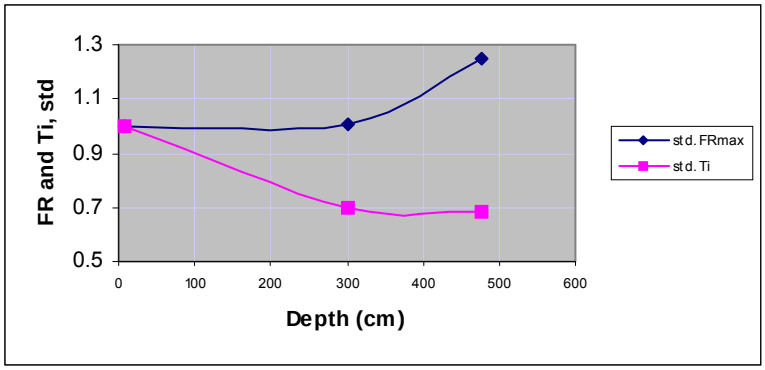

Fig. 7. Hydrate formation in Core 04 from MC-798.

The laboratory-generated hydrate curves were interpreted with help from the stratigraphic analyses of Dr. C. Brunner as well as the comments on the mud logs that were noted during core retrieval.

G. Patterns of Hydrate Formation with Sediment Depth

Norm Pattern. Hydrate formation rates and hydrate induction times differ widely as a function of depth in sediments from near-surface GOM cores. However, patterns demonstrated in Figures 8, 9, and 10 repeat fairly consistently in these three cores composed primarily of homogeneous mud from block MC-798. (The lithostratigraphy was established by Dr. Charlotte Brunner, University of Southern Mississippi, during analysis of sediments from the same core.)

In the three cores, hydrate formation rates increased with depth until a maximum was reached as compared to surface values. The induction times show decreases with depth until a minimum is reached. The patterns are similar to the formation rate and induction time patterns of the deep Dufresne core.

High Salinity. Compare Fig. 4 for the Dufresne core with the 'norm pattern' of Figure 8 through Figure 10, where the homogeneous core samples of Figure 8 through 10 are termed the norm. Below 200 cm bsf, it is evident that formation rates decline and induction times increase with depth below the surface of Core 05 in Fig. 11 from MC 798 of Figure 4 (28^{o} 4.0000 N, 89^{o} 42.0003 W).

These formation rates and induction times denote that hydrates are increasingly more difficult to form as depth increases below 200 cm bsf. Dr. Brunner's analyses of samples from the same core found "high pore water salinity 200 cm to bottom of core…" The hydrate tests of these sediments, therefore, seem to verify the known retarding action of saline waters on hydrate formation.

Sulfate Zone. It is hypothesized that one of the most important factors in hydrate formation in near-surface sediments is the depth of the sulfate zone. The shallower the sulfate zone depth, the greater the methane flux through the zone. The microbial communities working in the sulfate zone differ from those below the zone. Bioproducts differ in the zone. Recall that biopolymers/biosurfactants have been shown in our laboratory to have a significant effect on hydrate formation. Because of the anaerobic oxidation of methane in the sulfate zone and the reduction of sulfate, carbonate nodules as well as hydrogen sulfide occur there.

In Figure 13 (MC 118, Core 29; 28^{o} 51.3293' N and 88^{o} 29.4996' W) are the plots of formation rates and induction times for sediments from Core 29 that reached a depth of 120 cm. In the Mud Log at the time of coring was noted that shells occurred at 21 cm depth. Figure 13 indicates a maximum in both

formation rate and induction time at this 21 cm depth. The Mud Log also noted a sulfur smell at 80 cm and 115 cm. Minimums occur in formation rates and induction times at these points.

In Figure 11 (MC 798, Core 05; 28^{o} 4.0000 N and 89^{o} 42.0003 W) are the plots of formation rates and induction times for sediments from Core 05 that reached a depth of 600 cm. Carbonate nodules were observed at 240 and 260 cm. At these depths, Fig. 11 indicates minima and maxima in formation rates and induction times.

Again, in Figure 14 with Core 06, MC 798 (28^{o} 85.3904 N and 89^{o} 39.4997 W) a maximum is reached on hydrate formation rate and a minimum on induction time at the point where fine-grained carbonates occur from a 140 cm to 240 cm depth interval according to Dr. Brunner's lithostratigraphy.

More data are needed for a conclusive interpretation, but these multiple cores indicate some substantial alterations in hydrate-formation propensity at depths where carbonate nodules or sulfur smell (probably H_2S) occur.

In Figure 12 (MC 118, Core 13, 28^{o} 52.55' N; 88^{o} 28.7' W) is the plot of formation rates and induction times as measured in the laboratory for sediments from Core 13 that reached a depth of 300 cm bsf. In the Mud Log at the time of coring it was noted that between 56 and 130 cm disseminated shells occurred. The laboratory tests of hydrate formation in these sediments indicated a minimum was reached in both rate and induction time over the depth increment where the disseminated shells occurred. These carbonate nodules may typify the bottom of the sulfate zone, or where the bottom of the sulfate zone was at one time.

H. Microbial Activity

In Figure 15 for MC 118, Core 12 (28^{o} 52.45' N and 88^{o} 29.2' W), the Mud Log states the depth interval from 20 to 70 cm was bioturbated. The plots of hydrate formation rates and induction times from laboratory data show in this region an increase of formation rate and a decrease in induction time, consistent with the expectation that these particular bioproducts cause the same sort of hydrate promotion as the ones tested in the laboratory.

Similarly, in Cores 08A and 08B of Figure 9 and Figure 10 the laboratory hydrate formation rates and induction times from the sediments show an increase of formation rate and a decrease in induction time over the interval of 200 to 300 cm depth where Dr. Brunner's lithostratigraphy shows microbial action occurring.

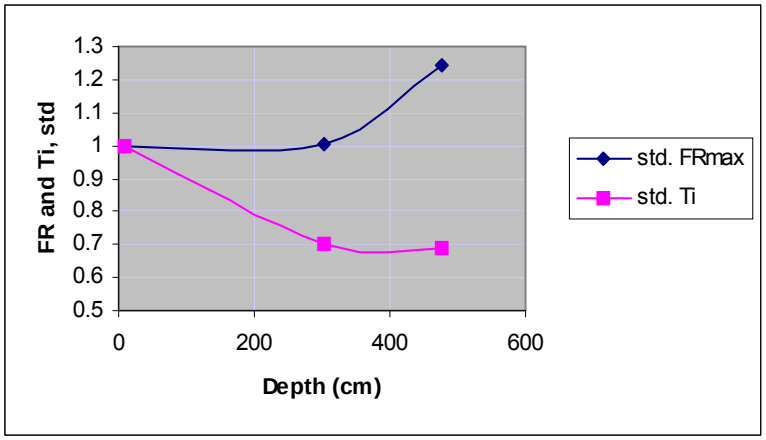

Fig. 8. Hydrate formation in Core 04, MC-798 (28° 8.1176 N, 89° 39.6689 W)

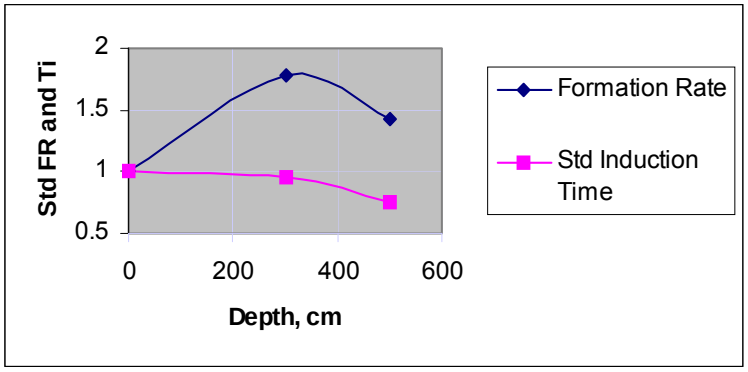

Fig. 9. Hydrate formation in Core 08A from MC-798 (28° 2.8914 N, 89° 44.4297 W)

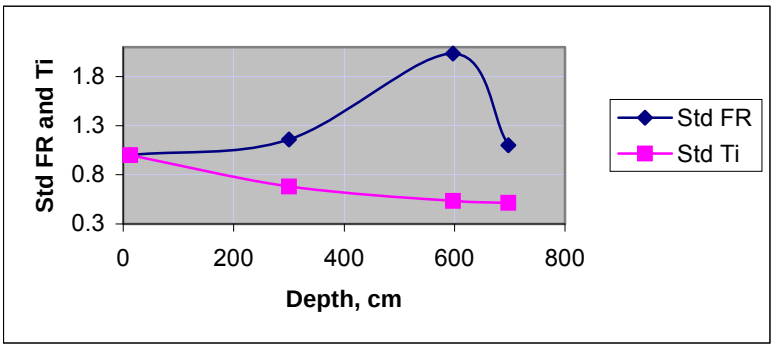

Fig. 10. Hydrate formation in Core 08B from MC-798 (28° 2.8183 N, 89° 44.4321 W)

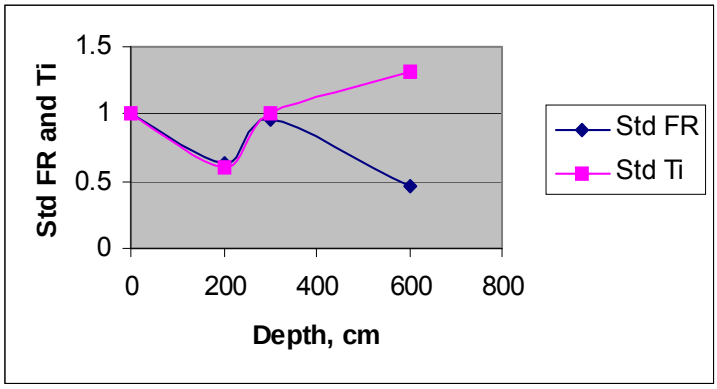

Fig. 11. Hydrate formation in Core 05 from MC 798 (28° 4.0000 N, 89° 42.0003 W)

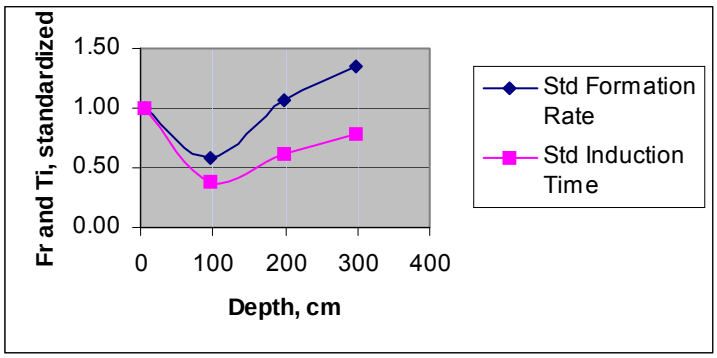

Fig. 12. Hydrate formation in Core 13 from MC 118 (28° 52.55' N, 88° 28.7' W)

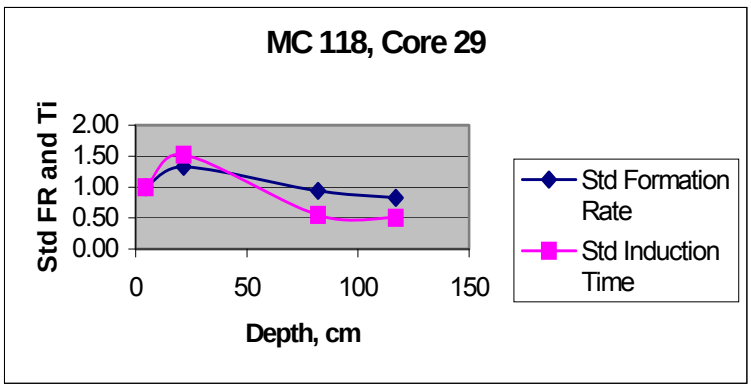

Fig. 13. Hydrate formation in Core 29 from MC 118 (28° 51.3293' N and 88° 29.4996' W)

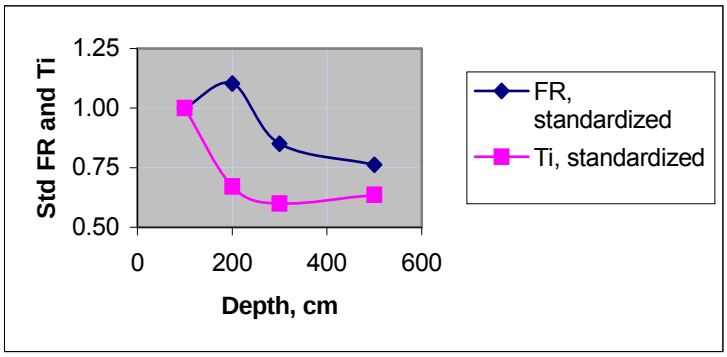

Fig. 14. Hydrate formation in Core 06, MC 798 (28° 85.3904 N and 89° 39.4997 W)

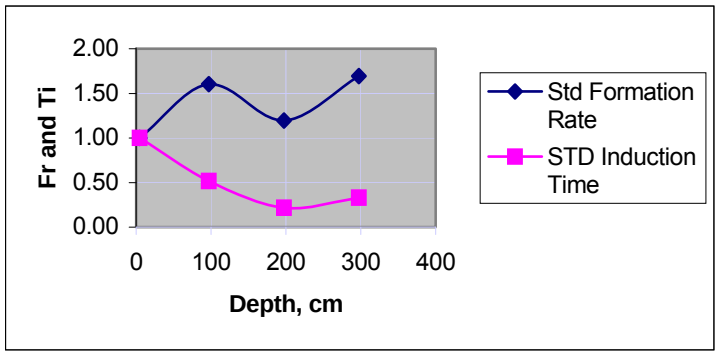

Fig. 15. Hydrate formation in Core 12, MC 118 (28° 52.45 N and 89° 29.2 W)

I. Laboratory Analysis of Cores from MC-118 Observatory Site

Samples from cores BC1, BC2, BC3, BC4, and BC9 were analyzed in the laboratory for hydrate formation rate and hydrate induction time. (A map of the Observatory Site is given in Fig. 16.) Sediments containing indigenous waters were mixed in the laboratory with Ottawa sand in the weight ratio of 75/25 sand/sediment to improve gas permeability, increase porosity of the packing, and increase mineral-gas contact. Pressures, temperatures, cooling rates, and gas compositions were kept constant during each analysis. These near-surface samples were taken from the MC-118 Observatory Site on June 9 and June 10, 2006, utilizing box cores.

Multiple experimental runs were made with each sample analyzed. Therefore, the average values of hydrate formation rate (Fr_{max}, mmol/h) and hydrate induction time (T_i, hours) in Table V for most cases are averages of 3 to 5 repetitive runs.

TABLE V. Composite results

Sample	Fr_{max}, (mmol/h)	T_i (hours)
BC-1	52.5	0.43
BC-2	53.4	0.49
BC-3	71.9	1.49
BC-4	64.0	1.35
BC-9	50.8	1.81

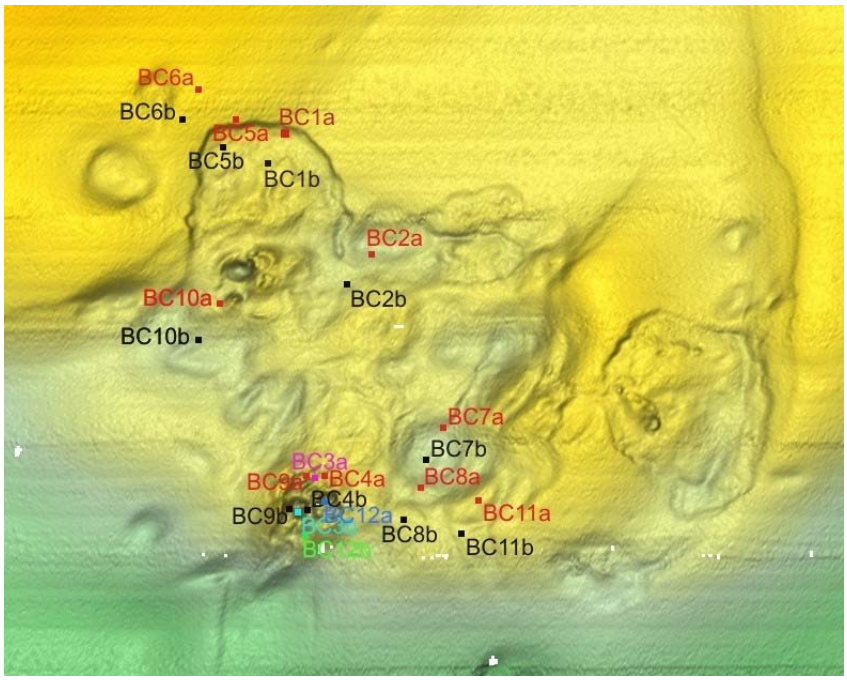

Fig. 16. Map of Observatory Site and location of samples analyzed.

As given in Fig. 17 and Fig. 18, formation rates and induction times are similar for the sets of cores BC1/BC2 and BC3/BC4. This observation is reasonable since the cores are in proximity to each other, as can be seen on the map of Fig. 16. In Fig. 18, Sample BC9 induction times are shown to be more unique. It may be noteworthy that only Sample BC9 is fairly saturated with crude oil. This covering of mineral surfaces with the oil could reduce nucleation sites.

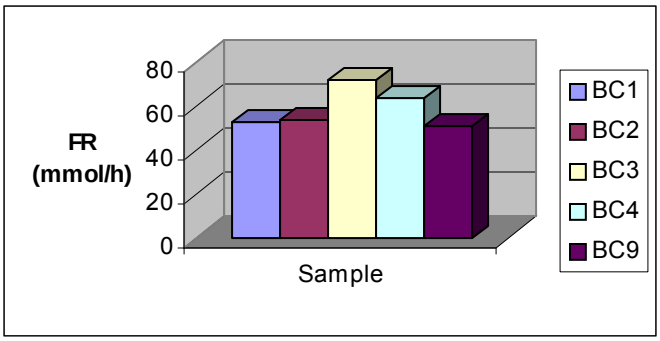

Fig. 17. Hydrate formation rates of sediments.

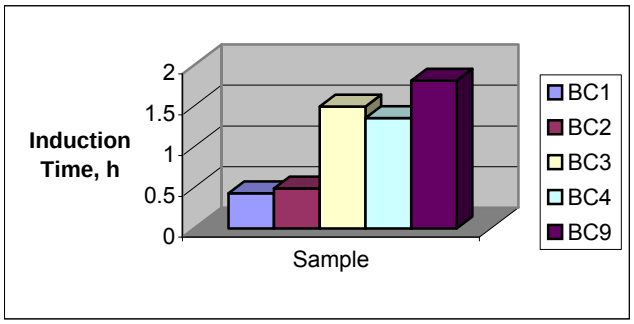

Fig. 18. Hydrate induction times of sediments.

J. Publications of the Work

The following articles, based on the work of this grant, were published in refereed journals. Acknowledgements were made of DOE grant support through the Gulf Coast Gas Hydrate Consortium at the Mississippi Mineral Resources Institute of the University of Mississippi.

Dissertation research was done under the grant and one PhD was awarded as a consequence.

1. Rogers, R.E., Zhang, G., Dearman, J., Woods, C., "Investigations into surfactant/gas-hydrate relationship," *J. Petrol. Sci. & Tech.* **56** (2007) 82-88.
2. Zhang, G., Rogers, R.E., French, W. T., and Lao, W., "Investigation of microbial influence on seafloor gas-hydrate formations," *Marine Chemistry*. **103** (2007) 359- 369.
3. Kelleher, B.P., Simpson, A.J., Rogers, R.E., Dearman, J., and Kingery, W.L., "Effects of natural organic matter from sediments on the growth of marine gas hydrates," *Marine Chemistry.* **103** (2007) 237- 249.
4. Rogers, R.E., Sassen, R., Dearman, J.S., and Zhang, G., "Factors prompting seafloor experiments to investigate microbial/hydrate

relationships," presented at 16th International Offshore and Polar Engineering Conference & Exhibition, San Francisco, May 28- June 2, 2006.
5. Dearman, J.L., Gas Hydrate Formation in Gulf of Mexico Sediments. Ph.D. dissertation, Mississippi State University, Swalm School of Chemical Engineering, April 9, 2007.

CONCLUSIONS

A. Dufresne MD02-2570 Core of 30-m Depth

a. A correlation exists between hydrate formation rate and depth of the sediments below seafloor. Hydrate formation rate in the evaluated sediments is most rapid at about 15 - 18m depth.
b. A correlation exists between hydrate induction time and depth of the sediments below seafloor. Hydrate induction time, for samples evaluated reaches a minimum at about 12 m and remains at that brief induction time to the bottom of the core at 30 m.
c. Silt, sand, and clay percentages in the sediments show trends with depth that suggest a contributing factor to the hydrate formation ease.
d. Smectite, illite, chlorite, and kaolinite percentages in the sediments were determined. Smectite and illite may influence the hydrate formation trends found in the tests.

B. Near-Surface Cores from Mississippi Canyon

a. Gas-hydrate formations vary as one moves laterally,at near-surface depths of the seafloor in Mississippi Canyon. These near-surface variations usually differ from the distinct patterns of hydrate formation rates and induction times observed in the 30-m deep Dufresne core sediments. However, even the Dufresne sediments gave near-surface variations in hydrate formation. It is hypothesized that extent and depth of the sulfate zone is a primary cause of the variations, because in the sulfate zone a different microbial community exists along with different bioproducts. The depth of the sulfate zone varies with methane flux from below.
b. High salinity areas in the sediments were shown to retard hydrate formation.
c. Carbonate nodules in the sediments were significant. At these points, maximum formation rates and minimum induction times were observed.

C. Hydrate Nucleation Centers

a. The work indicates that smectite clays promote hydrate formation by basic platelets sloughing off the clay mass and these small platelets acting as nuclei for hydrate formation. Anionic bioproducts may collect in the interlayers of the platelets or on the platelet surfaces and also become involved in the mechanism of hydrate promotion.
b. It is thought that the variety of bioproducts existing with depth in the sediments may mask particle size effects—that is, some bioproducts may promote hydrates and others may coat particles and retard hydrate formation.
c. Sediments with crude oil exhibited longer hydrate induction times, probably because of covering nucleation sites.

D. Publications

The DOE support of this work has allowed publication of 4 articles in national and international journals during the period of performance.

The funding has also supported the dissertation research and awarding of the Ph.D. for one graduate student.

EXPERIMENT TO GENERATE SHEAR WAVES IN THE SEA FLOOR AND RECORD THEM WITH A HORIZONTAL LINE ARRAY

FINAL REPORT

Paul Higley: Principal Investigator
Specialty Devices, Inc.
Wylie, Texas

EXPERIMENT TO GENERATE SHEAR WAVES IN THE SEA FLOOR AND RECORD THEM WITH A HORIZONTAL LINE ARRAY

The integration and application of the Input/Output Corporation's (I/O) three axis accelerometer sensor to the Horizontal Line Array is desirable as the resolution, accuracy and low frequency response of this accelerometer sensor is superior to that of marine 3-axis geophone sensors. The application of this sensor to the Sea Floor Observatory has required adapting the communications system used in its normal seismic application to the communications requirements of the Sea Floor Observatory. I/O developed this sensor as part of a highly integrated seismic system which can collect data from tens of thousands of these sensors every 10 to 20 seconds. This requires very fast data transmission for which I/O has developed a data interface that is both proprietary and elegant. The adaptation of portions of this data transmission scheme and repackaging of this data collection scheme was a significant challenge to the integration of the sensors into the SFO data retrieval system.

In an effort to simplify the data communications and control electronics I/O developed an SCI circuit card with a proprietary custom IC which combines the functions of a large amount of the custom circuitry in the recording truck. The efforts in the Spring of 2007 centered on utilizing this new approach to the problem. Both I/O and SDI wrote software to finally resolve this communications problem. The SCI card communicated directly with the present ALI cards following a software upgrade to the ALI cards. I/O completed the software upgrade in April. During May of 2007 SDI integrated the updated ALI circuitry and the new SCI card with communications software for system test and data collection. The power requirement of this system is now 12 vdc and 48 vdc. The 12 vdc will be generated from the PCB and with the modification of the PCB design in 2007 to 48 vdc from 24 vdc the 48 vdc can now be supplied to the data collection array without further conversion.

The new SCI circuitry and new software cured the last of the major problems preventing the performance of a test of this technology in a format that will lend itself to installation on the sea floor. The new combination of cards and software was packaged and tested at sea with the MMRI Sled combination S and P wave source in June 2007.

The in-water test was performed with successful recovery of accelerometer shear data generated from the MMRI developed seismic gun shear sled. This test was conducted in Biloxi, Mississippi using the University of Mississippi's R/V Kit Jones as the shooting boat and a second boat was utilized as the recording boat. The test included using multiple accelerometer sensors coupled with hydrophone sensors to simulate the sensor packages to be used on a down-hole array or the earlier planned horizontal line arrays. The shear phones were installed on the sea floor with three methods of handling the coupling of the sensor to the soft mud sea floor. One sensor array was lowered to the bottom and slightly pressed

into the mud bottom, one array was encased in a compartmentalized sand bag as developed by ARCO Exploration Company and one sensor array was installed and pressed approximately 2 ½ feet into the seafloor as is planned to be done by a sled-borne plow system. Multiple data lines were shot using various shot point offsets and shot spacing. The shear data exhibited excellent signal to noise ratios with the shear data from the I/O sensors appearing to have better signal to noise ratio than that from the hydrophones. Mechanical packaging was designed for housing the accelerometers and the data collection interface electronics for these accelerometers but has not been implemented as there may be the opportunity to reduce the electronics physical size in the near future.

Considerable support was received from Input/Output Corporation in Houston, Texas in the development of the software to function with the Input/Output electronics with both the SDI developed software package to address the SCI/ALI electronics interface and a software package from I/O becoming available on the same day. Both software packages performed well with the I/O package providing better graphics displays during data collection and the SDI package lending itself better to the planned DATS data collection platform. Further discussions with Input/Output management has lead to the possibility of further refinement of the electronics to better suit the application of the Sea Floor Observatory. These refinements will remove unnecessary functions on each circuit board and reduce the overall dimensions of the circuit boards. The reduced size will greatly affect the size of the pressure housing needed for installation at the depths of the Sea Floor Observatory.

APPENDIX C:
Gulf of Mexico Hydrates Research Consortium publications: 2000 - 2008

Publications and Presentations (*indicates peer reviewed)

2000

*McGee, T.M., 2000: A single-channel seismic reflection method for quantifying lateral variations in BSR reflectivity. Marine Geology, 164/1-2, 29-35.

*McGee, T.M., 2000: Pushing the limits of high resolution in marine seismic profiling. Journal of Environmental and Engineering Geophysics, 5, 43-53.

*McGee, T.M., 2000: High-resolution seismic profiling on water. Majorana Center of Scientific Culture School of Applied Geophysics, 10th Course: Development of Geophysical Methods with Application to Shallow Targets, Annali di Geofisica, 43, 1045-1073.

McGee, T., and Lowrie, A., 2000: Impact of hydrates on planetary evolution. Proceedings of the 31stInternational Geological Congress, Rio de Janeiro, Brazil.

*McGee, T.M., and Woolsey, J.R., 2000: A remote station to monitor gas hydrate outcrops in the Gulf of Mexico. Annals of the New York Academy of Science, 912, 527-532.

Roberts, H., J. Coleman, J. Hunt, Jr., and W. Shedd, 2000: Improving interpretation of sea floor geology, biology from remote sensing. Offshore, Volume 25, n. 9, p. 126-128.

*Zhong, Y., and R. Rogers, 2000: Surfactant Effects on Gas Hydrate Formation. Chemical Engineering Science, Volume 55, n. 19, p. 4175-4187.

2001

Hvozdara, L., 2001: Long-term Observation in the Marine Environment using Mid-Infrared Spectroscopic Techniques and Quantum Cascade Lasers. Montpellier, France, Fourth International Conference on Mid-Infrared Optoelectronics Materials and Devices, April 2-4.

Hvozdara, L., 2001: Quantum Cascade Lasers in Mid-Infrared Spectroscopy. Turku, Finland, 1st International Conference on Advanced Vibrational Spectroscopy, August 19-24.

Janotta, M., and B. Mizaikoff, 2001: Organically Modified Sol-Gels – Novel Recognition Layers for Infrared Optical Sensors. Blarney, Ireland, Fifth Euroconference on Environmental Analytical Chemistry: The Impact of Biosensors and Bioanalytical Techniques on Environmental Monitoring, September 8-12.

Lapham, L., D. Albert, J. Chanton, and C. Martens, 2001. Light hydrocarbon distributions and sulfate reduction rates in sediment porewaters near exposed gas hydrates. American Society of Limnology and Oceanography Annual Meeting.

McGee, T.M., Lutken, C.B., Goebel, V.S. and Woolsey, J.R., 2001: Seismic images of structures associated with gas hydrates near the sea floor: initial results. Proceedings of the 63rd Conference of the European Association of Geoscientists and Engineers, Amsterdam, The Netherlands.

McGee, T.M, and Woolsey, J.R., 2001: Pushing the limits of seismic resolution in deep water. Proceedings of the Eleventh International Offshore and Polar Engineering Conference, Stavanger, Norway.

Mizaikoff, B., 2001: Mid-Infrared Fiberoptic Chemical Sensors – From the Lab into the Field. Blarney, Ireland, 5th EurocMonference on Environmental Analytical Chemistry, The Impact of Biosensors and Bioanalytical Techniques on Environmental Monitoring, September 8-12.

*Roberts, H., 2001: Fluid and gas expulsion on the northern Gulf of Mexico continental slope: Mud-prone to mineral-prone responses. in C. Paull and W. Dillon, eds., Natural Gas Hydrates: Occurrence, distribution, and detection, American Geophysical Union, Geophysical Monograph, Volume 124, p. 145-161.

Roberts, H., R. Sassen, and A. Milkov, 2001: Seafloor expression of fluid and gas expulsion from deep petroleum systems, continental slope of the northern Gulf of Mexico. Houston, TX, GCSSEPM Research Foundation 21st Annual Research Conference, Petroleum Systems of Deep-Water Basins, December 2-5.

Rogers, R.E., and Lee, M.S., 2001: Biosurfactant from Microbial Activity in Ocean Sediments Enhances Gas Hydrate Formation. Presented at The Geological Society Earth System Processes- Global Meeting, Sponsored jointly by the Geological Society of London and Geological Society of America, Edinburgh, Scotland, June 24- 28, 2001.

Rogers, R.E., Lee, M.S., and Kothapalli, C.R., 2001: Biomolecules' Effects on Gas Hydrate Formation at Sand/Clay Interfaces. Presented at 2001 AIChE Annual Meeting, Reno, NV, Nov. 4- 9, 2001.

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*Sassen, R., S. Losh, L. Cathles III, H. Roberts, J. Whelan, A. Milkov, S. Sweet, and D. DeFreitas, 2001: Massive vein-filling gas hydrate: relation to ongoing gas migration from the deep subsurface in the Gulf of Mexico. Marine Petroleum Geology, Volume 18, p. 551-560.

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Wang X.-C., R. F. Chen, J. Whelan and L. Eglinton, 2001: Contribution of "old" carbon from natural marine hydrocarbon seeps to sedimentary and dissolved organic carbon pools in the Gulf of Mexico. Geophysical Research Letters, 28, 3313-3316.

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Abrams, M., and J. Whelan, 2002: Near-Surface Hydrocarbon Migration: Mechanisms and Seepage Rates. Vancouver, BC, Canada, The American Association of Petroleum Geologists Hedberg Research Conference, April 7-10.

Cathles, L., C. Dofu, and H. Roberts, 2002: Estimation of the hydrate gas content of the Bush Hill vent site, Green Canyon Block 185, Gulf of Mexico. The American Association of Petroleum Geologists Annual Meeting, March 10-13, Houston, TX.

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Geresi, E., 2002: Seismic Images of Geological Structures associated with Gas Hydrates near the Sea floor in the Mississippi Canyon Blocks. Houston, TX, The American Association of Petroleum Geologists Annual Meeting, March.

*Geresi, E., Lutken, C., McGee, T., and Lowrie, A., 2002: Complex geology and gas hydrate dynamics characterize Mississippi Canyon Block 798 on the upper continental slope of the northern Gulf of Mexico. GCAGS Transactions, 52, 309-321.

Hvozdara, L., N. Pennington, M. Kraft, M. Karlowatz, and B. Mizaikoff, 2002: Quantum Cascade Lasers for Mid-Infrared Spectroscopy, Vibrational Spectroscopy. Volume 30, p. 53-58.

Janotta, M., and B. Mizaikoff, 2002: Novel Recognition Layers for Mid-Infrared Evanescent Wave Sensors based on Organically Modified Sol-gels. Southeastern Regional Meeting of the American Chemical Society, Charleston, SC, November 13-16.

Karlowatz, M., 2002: Recent Developments in the Field of Mid-Infrared Fiberoptic Sensors for the Marine Environment. The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy (PITTCON), New Orleans, LA, March 17-22.

Karlowatz, M., F. Vogt, and B. Mizaikoff, 2002: An Automated Sample Preparation System for Volatile Compounds Applied for Infrared Evanescent Wave Sensor Calibration. Southeastern Regional Meeting of the American Chemical Society, Charleston, SC, November 13-16.

*Lowrie, A., Carol Lutken, Erika Geresi, Richard H. Bennett, Richard Faas, Tom McGee, 2002: Natural Gas Hydrates: Permanent Earth Constituents Impacting Sediment Strength and Continental Margin Evolution. Canadian Recorder: Natural Gas Hydrates, v. 27, n. 8, p. 13-27.

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Lowrie, A., McGee, T.M., and Lerche, I., 2002: Natural gas hydrates: Geologic constituents from the birth of the planet to the present. Paper #14032, Proceedings of the Offshore Technology Conference, Houston, Texas.

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*Janotta, M., A. Katzir, and B. Mizaikoff, 2003: Sol-gel Coated Mid-Infrared Fiberoptic Sensors. Applied Spectroscopy, Volume 57, p. 823-828.

Janotta, M., and B. Mizaikoff, 2003: Sol-gel Based Mid-Infrared Evanescent Wave Sensors for Detection of Nitro-Compounds in Aqueous Solution. Orlando, FL, The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy (PITTCON), March 9-14.

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*Lutken, Carol, Allen Lowrie, Erika Geresi, Richard Bennett, Richard Faas, Bradley Battista, and Tom McGee, 2003: Interpretation of high resolution seismic data from a geologically complex continental margin, northern Gulf of Mexico, GCAGS/GCSSEPM Transactions Volume 53, pp 504-516.

Lutken, Carol, Allen Lowrie, Erika Geresi, Charlotte Brunner, and Thomas McGee, 2003: Unexplained Geologic Features within the Hydrate Stability Zone, Upper Slope Mississippi Canyon, Northern Gulf of Mexico. Geoscience Horizons: Seattle 2003, Abstracts with Programs, Geological Society of America, p. 619.

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*Mizaikoff, B., 2003: Mid-Infrared Fiberoptic Sensors. Analytical Chemistry, Volume 75, p. 258-267.

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