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Fire in the Ice

Vol. 8, Iss. 4 Methane Hydrate Newsletter

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Laboratory Investigation of Hydrate Production through CO_2-CH_4 Exchange

By ConocoPhillips – University of Bergen Hydrates Team

Early in 2002 researchers at the University of Bergen and ConocoPhillips Reservoir Engineering lab ran an experiment to determine whether carbon dioxide could be successfully sequestered within hydrate by replacing the methane. While there was some earlier experimental evidence supporting this exchange mechanism in bulk hydrates, the question of how well it would work for hydrates found in nature was uncertain. The University of Bergen's experience with thermodynamic calculations on hydrate phase transitions indicated a good likelihood that this process would proceed "relatively rapidly," under conditions found in nature. ConocoPhillips had significant experience in designing and running flow in porous media experiments within a MRI-compatible sample holder that could generate important 3-D information within the sample on the progress of an experiment.

The design concept is very simple – by utilizing the rigid pore space found in a Bentheim sandstone core as a host, hydrate is formed. The initial design of the sandstone core has the halves separated by a thin, fitted spacer of high-density polyoxymethylene (POM) to enhance the available surfaces for hydrate formation and carbon dioxide exchange (Figure 1). The spacer also provides a useful reservoir for collecting methane that is released from the hydrate.

Figure 1: Halves of Bentheim sandstone core fitted with a 4 mm thick spacer of POM that was used for many of the hydrate formation and production tests.

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Fire in the Ice is published by the National Energy Technology Laboratory to promote the exchange of information among those involved in gas hydrates research and development.

This newsletter is available online at http://www.netl.doe.gov/MethaneHydrates

Interested in contributing an article to *Fire in the Ice*?

This newsletter now reaches more than 1000 scientists and other individuals interested in hydrates in sixteen countries. If you would like to submit an article about the progress of your methane hydrates research project, please contact Jennifer Presley at 281-881-8986.

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The sample holder is cooled using a circulation system that is filled with Fluorinert™. The system also provides a confining pressure on the sleeve holding the core without contributing to the MRI signal. Various gases and water are supplied to the core holder through a set of high-precision pumps located at a distance away from the MRI so as to minimize any effect on the signal (Figure 2). The greatest design challenge was determining how to get the cooling and fluid flow systems that were linked to the core holder to work when inside the superconducting magnet of the MRI system.

Despite the inevitable problems that accompany first experiments and a shortage of available time, the results from the hydrate formation as viewed by 3-D MRI images were satisfying. As cooling began, the initial state showed the water-saturated core with methane in the spacer and in the end pieces (Figure 3A). The constant-pore pressure system allowed for the addition of methane as it was consumed during hydrate formation.

Taking advantage of the different relaxation properties of free water, methane gas and ice/hydrate, the MRI images are sensitive to the presence of free water and methane gas in the pores or spacer. But the MRI did not detect the presence of hydrate as it formed in the core. The spatial resolution of the MRI images (~ 0.7 mm voxel length in the long axis of the core) did not allow for monitoring of what happened within individual pores, instead it indicated the process that occurred within clusters of pores.

The high salinity brine used in the first experiment limited the amount of hydrate formed so there was some remaining water signal in the core halves after hydrate formation stopped (Figure 3B). After a period of time the excess methane in the spacer was flushed from the system with carbon dioxide at the same conditions of 4° C and 8.3MPa (Figure 3C). The only remaining signal came from the free water retained in the core halves.

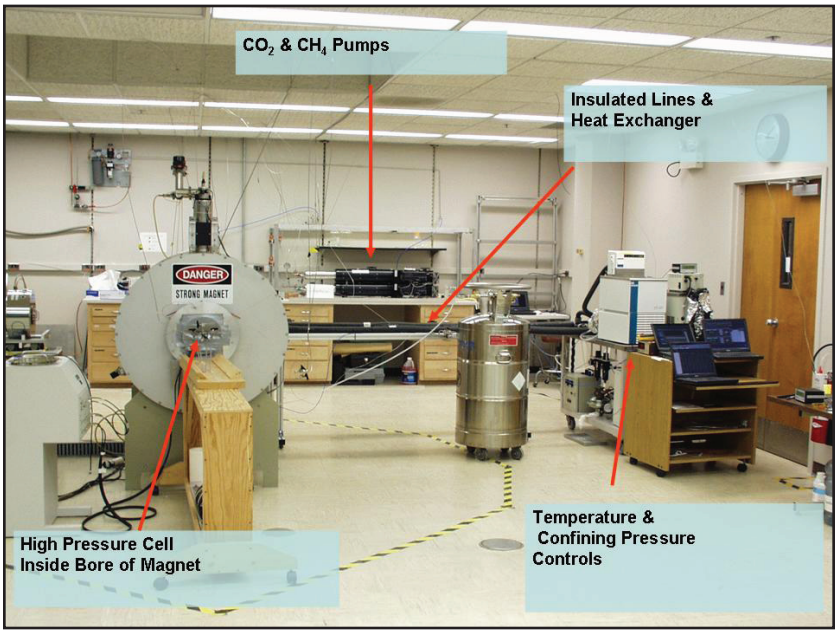
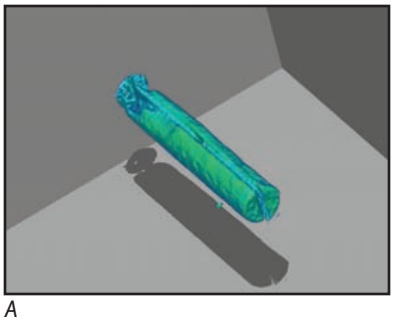


Figure 2: MRI laboratory at the ConocoPhillips Bartlesville Technology Center where many of the hydrate experiments were conducted. The MRI's superconducting magnet required the various pumps and temperature-control baths to be located at a distance from the sample holder placed in the magnet's bore.



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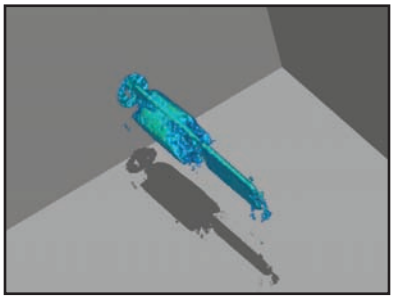

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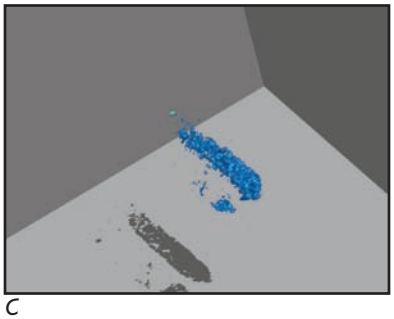

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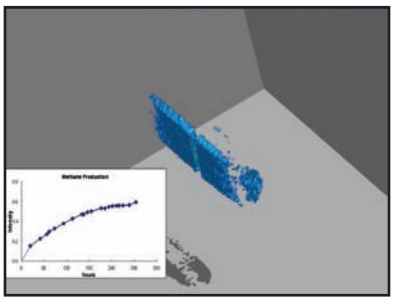

D

Figure 3: MRI images of Bentheim core halves saturated with water and methane during hydrate formation and methane production following injection of carbon dioxide. As sample is cooled to 4° C (A) the loss of signal at the far end of the core indicates initial hydrate formation. After a period of time hydrate has formed in much of the core (B) leaving only un-reacted water in some of the pores and methane in the spacer and end pieces. Displacement of the methane in the spacer with carbon dioxide (C) leaves only the un-reacted water signal in the pores. With time the buildup of signal in the spacer (D) indicates the accumulation of methane from the hydrate-saturated core.

The truly remarkable aspect of the experiment followed. The MRI signal intensity in the spacer started to increase after a waiting period of 24 hours and continued for 600 hours until a steady-state value was reached (Figure 3D). During that time there was consumption of carbon dioxide in the sample cell as measured by its pump. Most importantly, there was no evidence of MRI signal in the region occupied by the hydrate-saturated core halves during the time that methane was accumulating in the spacer.

The interpretation was that methane diffused from the pore space into the spacer region where it was detected by the MRI. The source of methane was its release from the hydrate as the carbon dioxide replaced it in the structure. The volume of detected methane far exceeded the amount that could be found as free gas in the pores after hydrate formed. The rate of methane diffusion into the spacer along with the absence of any evidence of free water or gas in the core halves during the exchange process was most surprising.

This experiment has been repeated numerous times with similar results each time. Despite changes in initial water saturation, brine composition, and core orientation, hydrate forms in these samples quickly and efficiently as determined by the combination of methane gas consumption curves, and decreases in MRI signal intensity. ConocoPhillips and the University of Bergen were awarded a patent on the carbon dioxide – methane exchange process in hydrates without the release of free water.

A second series of experiments focused on making measurements of permeability at variable hydrate saturations during formation and dissociation. Permeability reduction followed hydrate formation in many of these samples, culminating in measureable values even when all of the free water in the pores was converted into hydrate (Figure 4).

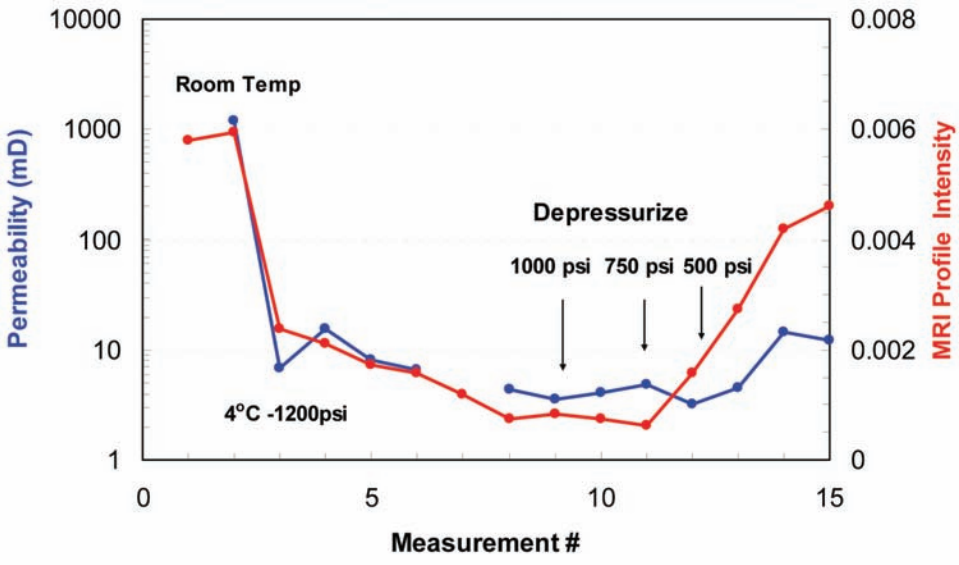

Figure 4: Permeability changes in Bentheim core (blue) match the decrease in MRI intensity that is measured during hydrate formation. Hydrate dissociation that occurs following a drop in pressure is seen in the MRI images as intensity increases. The permeability in this particular experiment does not recover as hydrate dissociates to original free water and methane gas.

Carbon dioxide was injected at one end of the intact core plug and methane was produced at the other end in these experiments. Other experiments measured the changes in permeability as the hydrate dissociated following depressurization steps. The recovery of permeability to initial levels was not observed in many of these tests, rather the loss of permeability may be due to redistribution of fluids in the pore space.

Experiments continue at ConocoPhillips and the University of Bergen to determine critical data that can be used in simulations of a reservoir-scale field test that is anticipated to be conducted on the North Slope of Alaska in collaboration with the USDOE and NETL. This future experimental work will include a wider range of sediment types, including fine-grained unconsolidated sands and silts. These new experiments will continue to use MRI technology to monitor the status of the hydrate on the scale of multiple pores and thereby provide a useful insight into hydrate formation and exchange.

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Bernie Baldwin – *Green Country Petrophysics*

SELECTED READINGS

Stevens, J., Baldwin, B., Graue, A., Ersland, G. Husebø, J., Howard, J. Measurements of hydrate formation in sandstone. *Petrophysics*, 2008. 49(1): 67-73.

Stevens, J., Howard, J., Baldwin, B., Ersland, G., Husebø, J., and Graue, A., Experimental hydrate formation and production scenarios based on CO_2 sequestration, in: Proceedings of the 6th International Conference on Gas Hydrates (ICGH 2008), Vancouver, British Columbia, Canada, July 6-10, 2008.

Graue, A., Kvamme, B., Baldwin, B., Stevens, J., Howard, J., Aspenes, E., Ersland, G., Husebø, J., Zornes, D. Environmentally friendly CO_2 storage in hydrate reservoirs benefits from associated spontaneous methane production, in: *Offshore Technology Conference Proceedings*, Paper 18087. 2006.

Effects of Reservoir Heterogeneity on Productivity of Gas Hydrate Reservoirs

By Brian J. Anderson (West Virginia University and NETL) and participants in the International Methane Hydrate Code Comparison Project

Recently, an international group conducted a series of numerical simulations of idealized gas hydrate occurrences in nature to compare the performance of various simulation approaches in predicting gas hydrate production. In order to assist in this comparison, the geologic characterizations used in the comparison studies were intentionally simple with assumptions of uniform reservoir properties throughout the modeled reservoirs. These exercises were extremely successful in enabling substantial improvements in all the participating codes; however, in many cases, these results predicted long "lag" times (an initial period of water production with minimal or no gas production) and modest peak gas production rates. This article presents an overview of new simulations that employ geologic characterizations that capture the natural heterogeneity of the modeled reservoirs. The key finding is that such variations have surprising positive benefits on production, including the elimination of the lag time and substantial increases in peak production rate.

Long-Term Simulations

Upon completion of a history-matching effort based on Modular Dynamics Testing (MDT) from the Mt. Elbert-01 Stratigraphic Test Well at the Milne Point Unit on the Alaskan North Slope (see FITI, Spring 2008), the code comparison group applied the information gained to producing first-order estimates of the potential long-term (50-yr) productivity of the gas-hydrate bearing sands in the Prudhoe Bay region (see Anderson, Suggested Reading). Three separate cases were conducted. Problem 7a examines a deposit similar to the Mt. Elbert site (Figure 1). Problem 7b is based on a slightly warmer and thicker accumulation such as those that exist at the Prudhoe Bay Unit (PBU) L-Pad site. Problem 7c is a down-dip and warmer version of the L-Pad case. In all three cases, a standard set of parameters were used based on those found in Problem 6 (the history matches to the MDT data). The parameters chosen were consensus values based on the experiences of the various groups in attempting to match the MDT data for the C2 formation at Mt. Elbert. Also, for all three cases, a vertical well using depressurization to 2.7 MPa was used for gas hydrate production.

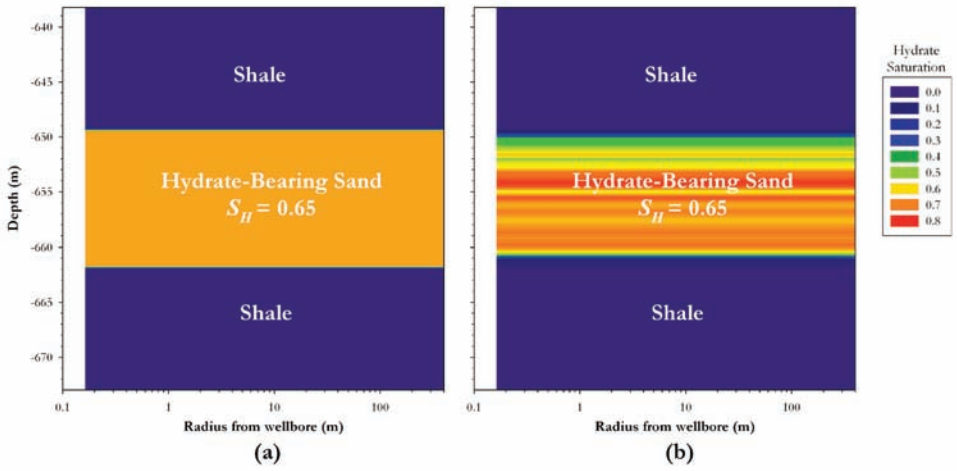

Figure 1: Schematic of the Mt Elbert C-Unit Reservoir using (a) a homogeneous reservoir and (b) a heterogeneous reservoir based on log data from the Mount Elbert well.

Permeability (mD)	Shale Zone: 0.0 Hydrate Zone: 1000 md radial 100 md vertical
Porosity (%)	Shale Zone: 10 Hydrate Zone: 35
Pore Compressibility (Pa^{-1})	10^{-9}
Rock Density (kg/m^3)	2650
Rock Specific Heat (J/kg/K)	1000

Table 1: Problem 7a rock properties.

Problem 7a: Mt. Elbert-like formation

Problem 7a utilized the known data for the Mt Elbert C-Unit such as porosity, temperature, depth, and hydrate saturation, in addition to the relative permeability parameters found in the history-matching performed in Problem 6. The model domain was a 2-D (Figure 1, Table 1), radial system, 450 m in the radial direction and 152.5 m in the vertical direction. In the vertical direction, 70 m (10 grid blocks) of an impermeable "shale" layer was placed on the top and bottom of a 12.5 m (50 grid blocks) gas hydrate-bearing sand layer. In the radial direction, 80 logarithmically-distributed grid blocks with an innermost block radius of 0.131 m were used.

As one might expect, given the low initial temperature of the reservoir modeled in Problem 7a, the modeled gas production rates over the 50-yr life of the reservoir were uniformly low. This system has very limited *in situ* heat to provide for the endothermic hydrate dissociation reaction. The bottom-hole pressure used in the simulations was 2.7 MPa, slightly above the quadruple point in order to keep from forming ice in the reservoir.

One notable result that was found using all of the participating simulators was the existence of a lag time before meaningful gas rates were realized. An average lag time of 13.5 years was found among the simulators participating in the Code Comparison Project (Anderson, et al. 2008).

Heterogeneity of the reservoir

One major assumption in the description of the Mt. Elbert C-Unit as modeled in the Code Comparison Project Problem 7a is that the reservoir has uniform properties throughout the hydrate-bearing sediment. This assumption is made for simplicity and to facilitate consistent models used by each of the groups. However, due to the relatively cold temperatures found in the Mt. Elbert C-Unit, the intrinsic heterogeneity of the reservoir can play an important role in the predicted rates of gas production. Shown in Figure 2 is the NMR-derived hydrate saturation through the C-Unit. As evidenced by the graph, the saturation, as well as the sediment porosity and the immobile water phase, can vary significantly. By implementing a 50-layer model (shown in Figure 2 as the grey points) to represent the hydrate saturation (SH), porosity (Φ), and irreducible water saturation (Sw,ir) we have modeled the heterogeneous reservoir using both HydrateResSim and CMG STARS.

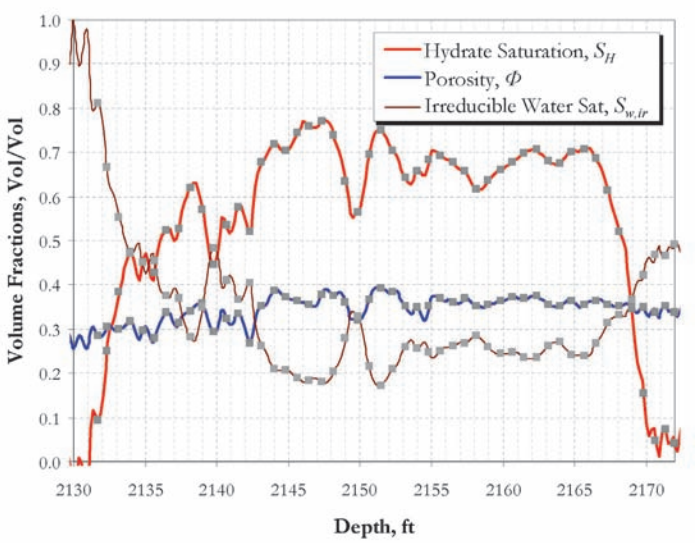

Figure 2: NMR log-derived hydrate saturation (SH) and irreducible water saturation (Sw,ir) plus the density log porosity (Φ) for the Mt. Elbert C-accumulation. Solid lines represent the log data and the points represent the 50-layer model used in reservoir simulations.

A comparison of the predicted gas rates for the heterogeneous and homogeneous models can be seen in Figure 3 and Figure 4 for the simulation of the Mt. Elbert C-Unit using CMG STARS and HydrateResSim. As can be seen in Figure 3, the predicted gas rates from the two simulation codes do show remarkable consistency, particularly in the first 10 years of the simulation. Most importantly, during these first 10 years, one can see that the heterogeneous reservoir exhibits much higher gas production rates compared to the homogeneous reservoir. In Figure 4, we show the results of the CMG STARS simulations out to 50 years. Once the homogeneous reservoir has developed a significant surface area to allow for sufficient depressurization, the rates of the homogeneous and heterogeneous reservoirs become similar.

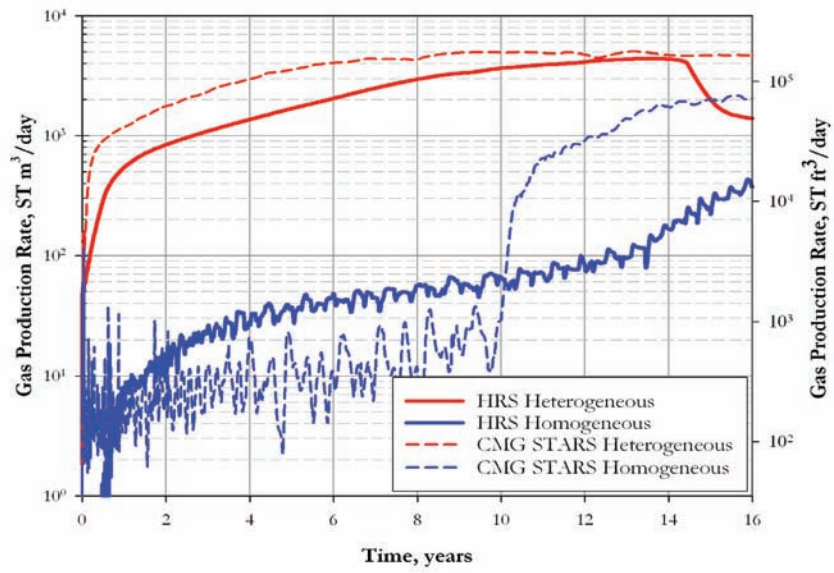

Figure 3: Gas production rate data for the heterogeneous (red) and homogeneous (blue) representations of the Mt. Elbert C-Unit using both HydrateResSim (solid lines) and CMG STARS (dashed lines).

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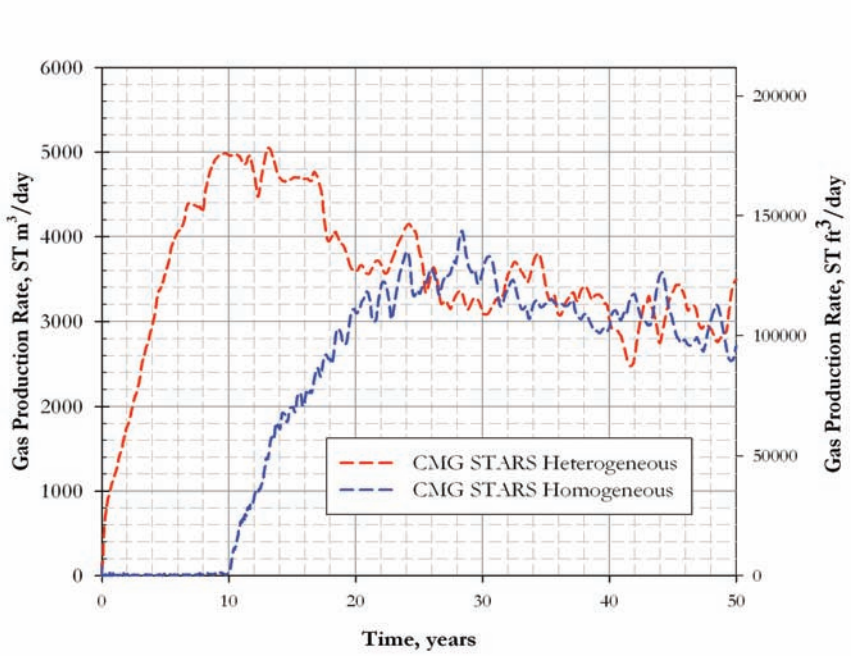

Figure 4: Gas production rate data for the heterogeneous (red) and homogeneous (blue) representations of the Mt. Elbert C-Unit using CMG STARS.

However, when considering the economic viability of gas production from hydrate reservoirs (as with any recoverable resource) the net present value is much more strongly dependent on the earliest years. Therefore, the early productivity of the heterogeneous reservoir compared to the homogeneous reservoir should prove to be a significant finding of this investigation of the effects of reservoir heterogeneity on gas productivity.

The Code Comparison Study Team provides updates on model outputs and detailed scenario definitions to the methane hydrate R&D community through the NETL methane hydrate web site (http://www.netl.doe.gov/scngo/NaturalGas/hydrates/index.html). The suggested readings below are also available on the website. To obtain more information about this study, please contact Brian Anderson (brian.anderson@mail.wvu.edu) or Kelly Rose (kelly.rose@netl.doe.gov).

SUGGESTED READINGS

Anderson, B., J. Wilder, M. Kurihara, M. White, G. Moridis, S. Wilson, M. Pooladi-Darvish, Y. Masuda, T. Collett, R. Hunter, H. Narita, K. Rose and R. Boswell. 2008. *Analysis of Modular Dynamic Formation Test Results from the "Mount Elbert" Stratigraphic Test Well, Milne Point, Alaska.* Proceedings of the 6th International Conference on Gas Hydrates, Vancouver, British Columbia, Canada.

Wilder, J., G. Moridis, S. Wilson, M. Kurihara, M. White, Y. Masuda, B. Anderson, T. Collett, R. Hunter, H. Narita, M. Pooladi-Darvish, K. Rose and R. Boswell. 2008. *An International Effort to Compare Gas Hydrate Reservoir Simulators*. Proceedings of the 6th International Conference on Gas Hydrates, Vancouver, British Columbia, Canada.

Investigating gas hydrate as a factor in accretionary margin frontal ridge slope failures and cold seep biogeochemistry

By The 2008-007-PGC onboard science team

During August 2008, a research expedition (2008-007-PGC) was carried out offshore Vancouver Island on the northern Cascadia Margin (Figure 1) to study the role of gas hydrate in slope stability and cold seep biogeochemistry. The cruise was organized by the Geological Survey of Canada (GSC) as part of the Earth Science Sector, Natural Gas Hydrate Program, Natural Resources Canada (NRCan). This international collaboration included McGill University, University of Victoria, the U.S. Geological Survey, Florida State University, and the U.S. Department of Energy.

Wide-spread slope failures – Could gas hydrate destabilization have played a role?

Many of the frontal ridges on the northern Cascadia accretionary prism show signs of massive failure as detected from multibeam bathymetry data (Figure 2). The intent to investigate these collapse structures was initiated during the Integrated Ocean Drilling Program (IODP) Expedition 311, when a set of four deep boreholes was established at Site U1326 within one of the frontal ridges of the accretionary wedge (Riedel, et al., 2006). The original proposed IODP drill site for the frontal ridge was located too close to the main slump (now referred to as 'Lopez Slide') and had to be moved for safety reasons only a few weeks prior to IODP Expedition 311. The frontal ridge was subsequently investigated using ocean-bottom seismometers (OBSs) and a series of closely-spaced, single-channel seismic profiles to define the structural setting of the frontal ridge (Lopez, 2008). The seismic analyses suggest the frontal ridge slumps may have originated along the pre-slump Bottom Simulating Reflector (BSR) horizon as a result of pore pressure increases resulting from the glacial eustatic cycle or shaking caused by periodic mega-thrust earthquakes along the Cascadia subduction zone (Lopez, 2008). These slope-destabilizing pore pressure increases may have been enhanced by hydrate dissociation.

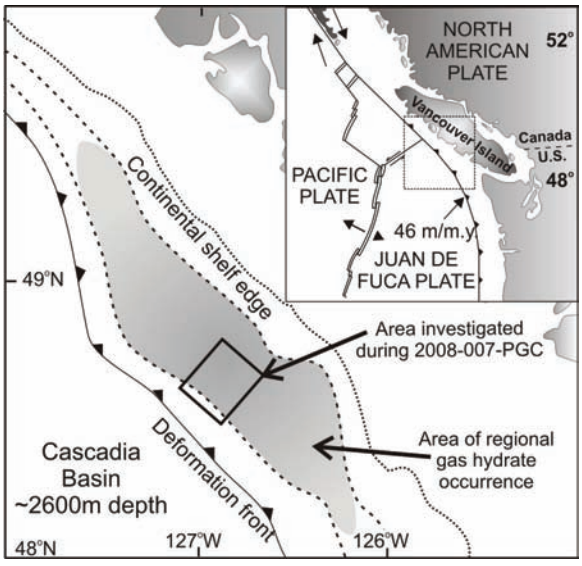

Figure 1: Area of investigation on the northern Cascadia Margin.

During the recent cruise 2008-007-PGC, 10 cores were collected at several slump-areas along the margin (Figure 2) to study the cause and timing of the frontal ridge slumps. Four cores at 'Lopez Slide' were collected from within the headwall, apron, and sole of the slumped material. Directly south of this slide, another slump feature named 'Slipstream Slide' was also studied. The 'Slipstream Slide' is a series of en echelon, box-like rotated slump blocks originating between a pair of transverse faults that cross-cut the frontal ridge. The five cores from this slide include two locations within the headwall scarp and three locations penetrating the slumped material from the apron to the toe of the slump. One additional core from a slump-feature further south ('Chunk Slide') was recovered near a prominent out-runner block of slump-material.

Preliminary sedimentological descriptions and analyses, combined with pore-water sulfate gradients and physical property data, suggest the slump occurrences are not related to the last mega-thrust earthquake that occurred at the N. Cascadia subduction zone in January 1700 (e.g. Satake, *et al*., 1996), and may not be related to the regional gas hydrate system. However, the slumps could have been triggered by earlier such earthquakes. Further analyses and age determinations are underway to assess the possible linkages between these slumps and mega-thrust earthquakes as well as other possible trigger mechanisms such as eustatic sea level changes. To assist these efforts, several samples were collected for dedicated geo-mechanical testing of sediments from the slump-headwall.

Methane bubble plumes suggest more vigorous fluid advection than thought

An additional goal of the expedition was to improve our understanding of carbon cycling in cold vents and active methane venting, manifested as large bubble-plumes detected by multi-frequency echo-sounding (Figure 3). In total, four new large-scale gas plumes were discovered during the cruise 2008-007-PGC (the locations of all known plumes are shown in yellow in Figure 2). Prior to IODP Expedition 311 in 2005, only one large methane plume, Bullseye Vent, had been identified in the general region of gas hydrate

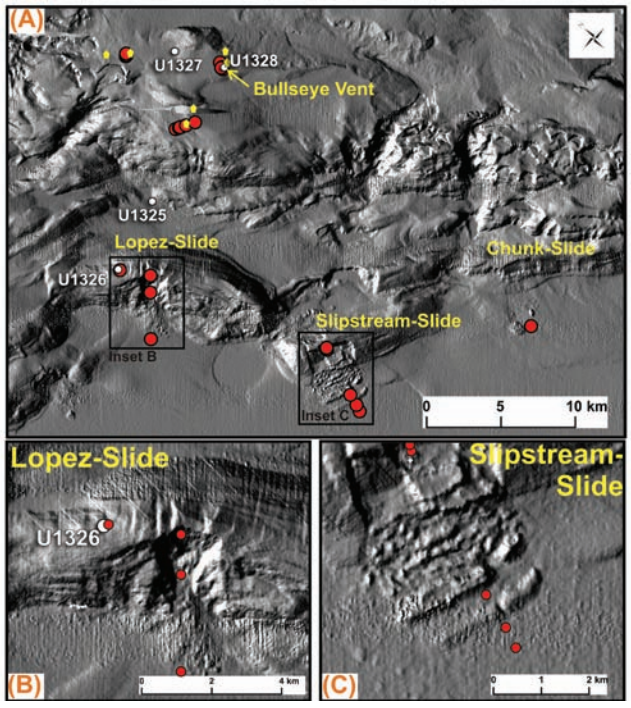

Figure 2: (A) Image showing multibeam bathymetry data across a part of the northern Cascadia Margin highlighting the many frontal ridge collapse features along the accretionary prism. (B) close-up view of Lopez-Slide, (C) close-up view of Slipstream-Slide. Core locations for the most recent expedition are shown as red dots; location of the IODP Expedition drill sites are shown in light pink; gas plumes are shown in yellow.

stability offshore Vancouver Island. The bubble plumes often reach to a water depth of ~500 m, which coincides with the top of gas hydrate stability within the water column. This observation suggests that rising methane gas bubbles may be coated by a thin film of gas hydrate, which dissociates, leaving the gas bubble to dissolve above the methane hydrate stability zone.

The multidisciplinary coring program employed during the cruise 2008-007-PGC included high-resolution sampling for microbiological, geochemical, geophysical, and sedimentological studies. A series of cores were taken from Barkley Canyon, Bullseye Vent and two newly discovered vent sites near Bullseye Vent, (one about 5 km west, the other about 6 km north of Bullseye Vent). From these cores, an extensive suite of pore fluid and sediment samples was collected to obtain new insight into methane oxidation and hydrocarbon degradation in hydrate-bearing cold seep sediments (see "Application of Rhizon Samplers to Obtain High-Resolution Pore Fluid Records During Geochemical Investigations of Gas Hydrate Systems," this issue.). The capacity of the anaerobic sedimentary 'biofilter' to block methane emissions to the water column is generally assumed to be limited by the rate at which sulfate penetrates the seafloor and by competition for sulfate via alternate diagenetic pathways. However, oxidized ferromagnetic minerals and manganese might also contribute to the oxidative potential of the anaerobic microbial consortium. The biogeochemical program was explicitly designed to determine if oxidized minerals influence the rates, processes, and microbial agents that consume methane and hydrocarbons along the northern Cascadia Margin.

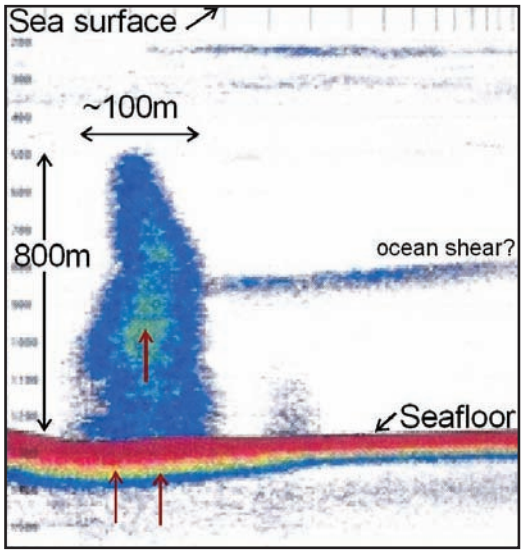

Figure 3: Image of a gas plume detected with a 18 kHz, hull-mounted echosounder, previously observed near Bullseye vent during a cruise in 2006 (Vidalie, 2007), indicating that methane gas is actively released at this vent, bypassing the formation of methane hydrate. IODP Expedition 311 drilling at Site U1328 in the centre of Bullseye Vent, as well as many piston cores taken in and around Bullseye vent, provided detailed understanding of the local plumbing system, which is characterized by thick cap of massive gas hydrate within the top 40 meters below the seafloor. Bullseye Vent is the focus of the upcoming NEPTUNE long-term monitoring studies.

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A. Schlesinger – *University of Victoria*
G. Standen – *Geoforce*
A. Stephenson – *University of Victoria*
S. Taylor – *NRCan-GSC*
W. Waite – *U.S. Geological Survey*
X. Wang – *McGill University*

The amount of methane that escapes the marine gas hydrate reservoir may impact ocean chemistry and the global carbon budget. Previous models of gas hydrate formation suggest pervasive fluid flow from deep within the accretionary prism supports gas hydrate formation near the base of gas hydrate stability (Hyndman and Davis, 1992). The new observations of many large methane plumes suggest a significant quantity of methane escapes this methane trap. New budget calculations are required to account for this pathway, which also has implications on gas hydrate resource estimates.

These investigations will be linked to other gas hydrate studies supported by the NEPTUNE project, which is scheduled to deploy long-term sea-floor monitoring stations on the northern Cascadia Margin in 2009 (Willoughby, *et al*., 2008).

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Figure 4: Onboard science team (from left to right): R. Haacke, M. Hogg, X. Wang, A. Schlesinger, L. Esteban, T.S. Hamilton, R. Enkin, J. Pohlman, P. Neelands, M. Riedel, S. Taylor, A. Stephenson, L. Lapham, W. Waite, K. Rose, G. Middleton. Missing from photo: G. Standen, G. Spence, and R.D. Hyndman .

Do Paleo Hydrates Play a Major Role in Deepwater Biogenic Gas Reservoirs in Krishna-Godavari Basin?

By Nishikanta Kundu, Nabarun Pal, Neeraj Sinha, I. L. Budhiraja (Reliance Industries Ltd. India)

The presence of large quantities of biogenic gas in the deepwater Krishna-Godavari (K-G) Basin pose some interesting questions regarding the origin, migration, and accumulation of this gas. Here we put forward a possible relationship between a world class multi-trillion-cubic-foot gas accumulation and destabilization of paleo-hydrate in deepwater channel sands.

The K-G Basin has several large gas discoveries in the deep water Plio-Pleistocene multi-stacked, sinuous channel-levee complexes. The present study is focused mainly in the upper-slope region of the Godavari River mouth (Figure 1). The reservoir gas is primarily bacterial generated at low temperature through decomposition of organic matter by anaerobic microorganisms from thermally immature source rocks. In marine sediments methane is produced mainly during CO_2 reduction by hydrogen, while acetate fermentation is another process that is dominant in fresh water deposits. The factors that control the level of methane production after sediment burial are anoxic environment, sulfate deficient conditions, suitable temperature, salinity (< 4M Cl^-), and availability of organic matter. Thus the depth of significant production of bacterial gas depends on the local geothermal gradient and rate of sedimentation which may vary from basin to basin and over time within a single basin.

The area under discussion in the K-G Basin has an average geothermal gradient of 4.2º C/100 m and sedimentation rate of 1000 m/My. It is interesting to note that both the sedimentation rate and geothermal gradient here are higher than the optimal rates required for conventional biogenic

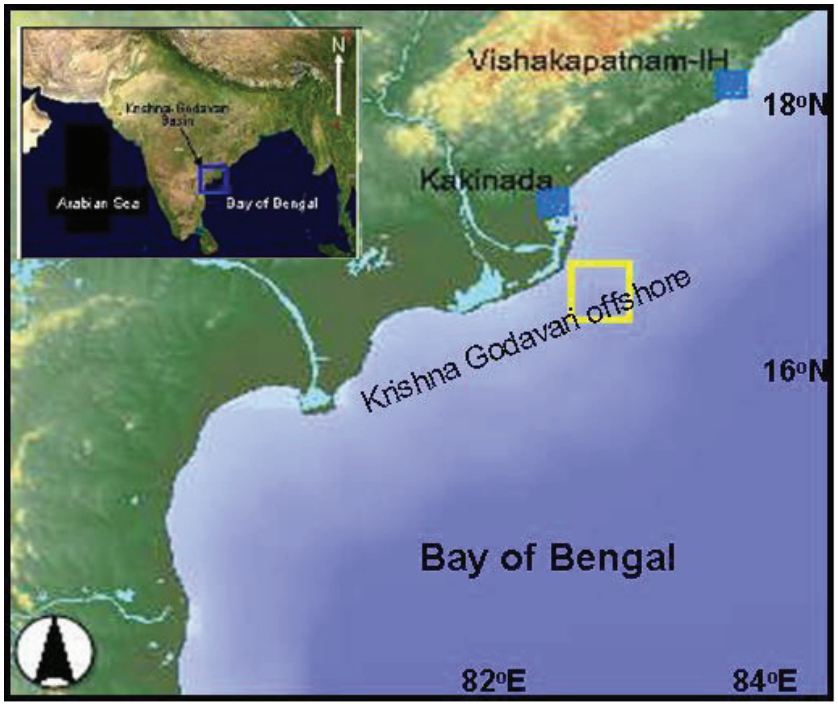

Figure 1: Location of Krishna-Godavari Basin in the eastern coast of India. Yellow box indicates the study area.

gas reservoirs such as the Po Valley or offshore Louisiana. One possible explanation of such an accumulation can be generation of gas by bacterial activity in deep water sediments and their retention/concentration by formation of gas hydrate under suitable conditions. Upon subsequent sedimentation, these gas hydrates may then become unstable upon reaching higher temperatures and thereby release huge amounts of gas. In this article the possibility of formation of hydrate at various stratigraphic layers and their subsequent destabilization to form large gas reservoirs is discussed.

One dimensional burial history modeling in drilled wells is carried out using PETROMOD 1D™ (v 9.0) to calculate the paleo P-T conditions for each stratigraphic layer (identified using high resolution nannofossil data). These models are calibrated with measured pressure, temperature and heat-flow data of the respective wells. Paleo water depth considered for the model at various age intervals is calculated using biostratigraphy from the wells in conjunction with the standard sea level curves.

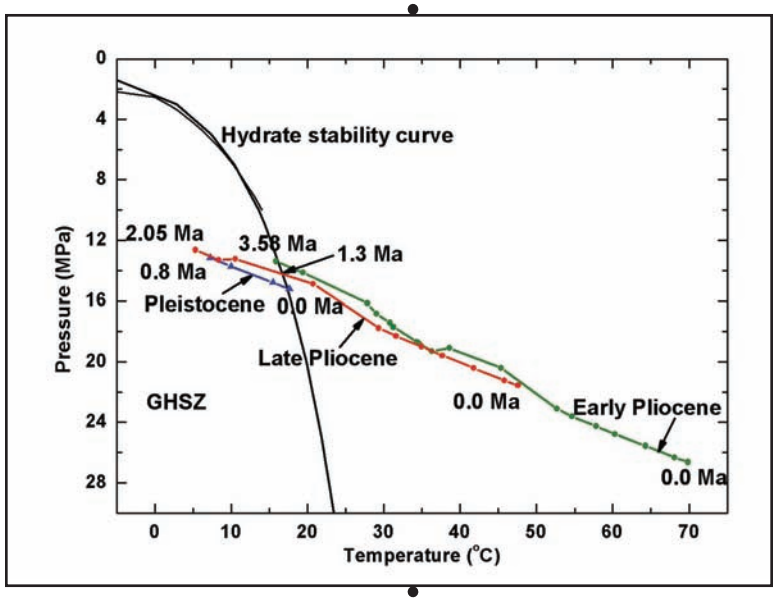

Figure 2: P-T history of three representative layers from a drilled well. The Pleistocene layer (blue line) is within the GHSZ all through out its history; the reservoir sand (Late Pliocene, red line) was within the GHSZ from 2.05 to 1.3 Ma and was free of hydrates from 1.3 Ma to present day; Early Pliocene layer (green line) started depositing from 3.58 Ma and has never entered within the GHSZ.

Pressure and temperature variations with time of each individual unit are extracted from the calibrated 1D burial history model for different wells and plotted together with the gas hydrate stability field. In Figure 2 the P-T history of three representative layers (Pleistocene, Late Pliocene and Early Pliocene) of a drilled well (water depth 1277 m) is shown. The Early Pliocene section in the well has never been within the hydrate stability field, while the Late Pliocene reservoir sand was within the gas hydrate stability zone (GHSZ) from 2.05 to 1.3 Ma and free of hydrate after that until present day. However, the Pleistocene layer is within the GHSZ all throughout its history. This model of the stability relation matches with the present day hydrate occurrence in the Pleistocene section evidenced from well logs. Similar exercises have been carried out for several other wells.

The P-T history as described above support formation of gas hydrate and their destabilization at different times; actual hydrate formation depends on the availability of enough methane and water within the pore spaces. Availability of methane depends on the degree of methanogenesis and/or supply from matured source rocks from deeper layers. In these wells, the measured total organic carbon (TOC) of the various lithologic units varies from 1.5 to 2 % which is conducive for bacterial activity to produce biogenic methane. When the P-T condition is favorable this gas, together with the available water, will produce gas hydrate. The thickness of the hydrate layer, however, depends on the amount of time it remained within the stability field, which is mainly controlled by the sedimentation rate of the overlying units.

The spatial-temporal variation of hydrate formation and its destabilization is also studied along a NW-SE cross section passing through a discovered deepwater gas field (Figure 3A-C). The model is constructed using Petromod

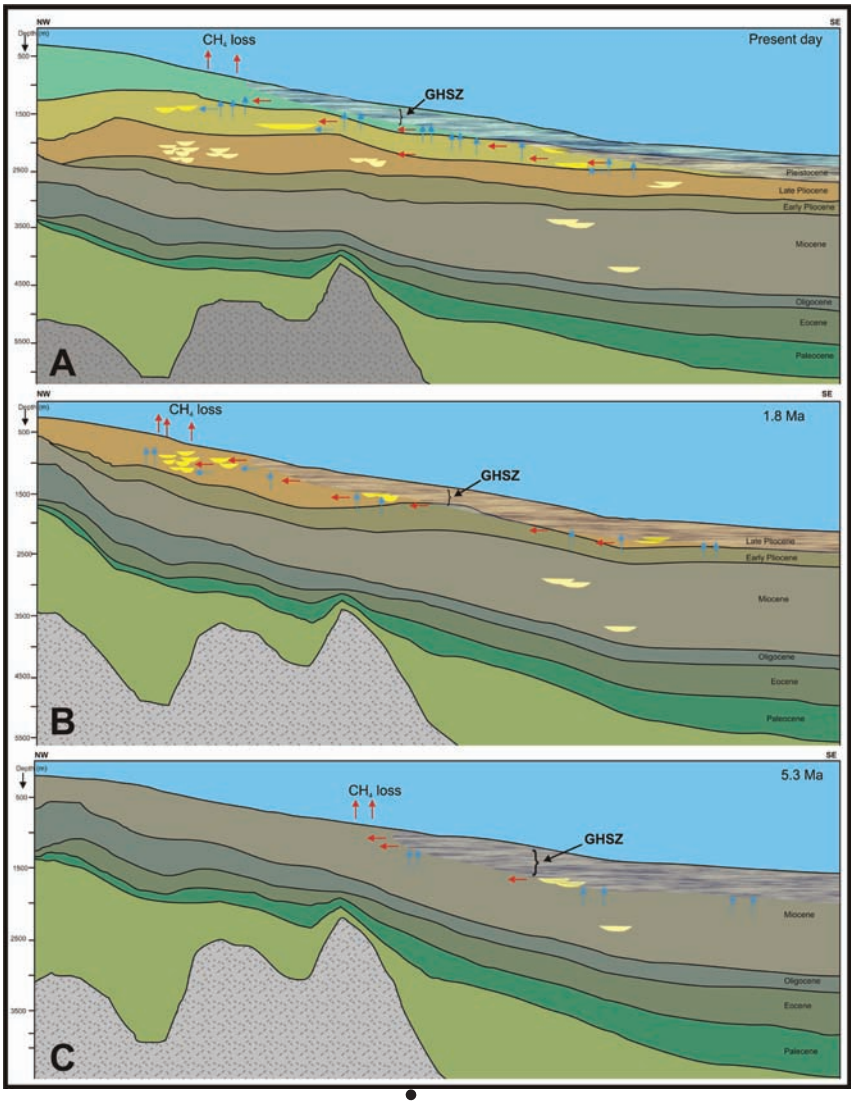

Figure 3: 2-D Paleo-hydrate model along the discovered gas field in K-G Basin at different geological times. (A) Geological section showing GHSZ (shaded area) and gas filled channel sands. (B) GHSZ at Pliocene, calculated by removing the Pleistocene and younger sediments. (C) Model GHSZ at Miocene calculated by removing Pliocene and younger sediments. Yellow color sands depict active charging from gas hydrate destabilization and methanogenesis at respective times. Chalk color channel sands were charged previously. Red arrows indicate gas released from hydrate destabilization. Blue arrows indicate methanogenesis.

software where paleo sections are generated by stripping out younger sediments. The gas bearing reservoir sands (channel levee complex) in the up-dip part belongs to Late Pliocene and Pleistocene age, while in the deeper areas, some reservoirs are also of Miocene age. It is observed that P-T conditions were favorable for hydrate formation from Miocene onwards.

However, not all reservoirs were entirely within the GHSZ. Because of burial, deeper layers extended out of the stability zone, triggering hydrate destabilization. The released gas might then have charged the nearby sands and may have migrated up dip or laterally, depending on the shale-sand ratio of the carrier beds. It must be noted that although some reservoirs were never within the GHSZ, they also could be charged by gas released from destabilized hydrates from down dip areas. In the discussed gas-field the presence of aerially extensive thin beds in the levee/ inter-channel areas is established through conventional cores and high resolution seismic attribute analysis. These thin beds favor lateral migration of released gas from hydrate destabilization. Hydrate melting is generally associated with release of low saline water and precipitation of carbonates. Presence of authigenic carbonate cement in reservoir sands and low saline pore water provide further evidence for the destabilization of gas hydrate.

Our study furnishes a possible explanation of the large gas accumulation in the K-G Basin by the destabilization of the paleo hydrate. The following sequence of geological events might have worked together to form this gas reservoir in the following sequential order: deposition of organic rich sediments in deep water → bacterial activity in a reducing environment (methanogenesis) → formation of gas hydrate → increase of temperature leading to melting of hydrate and release of gas → migration and subsequent entrapment in porous and permeable sand bodies.

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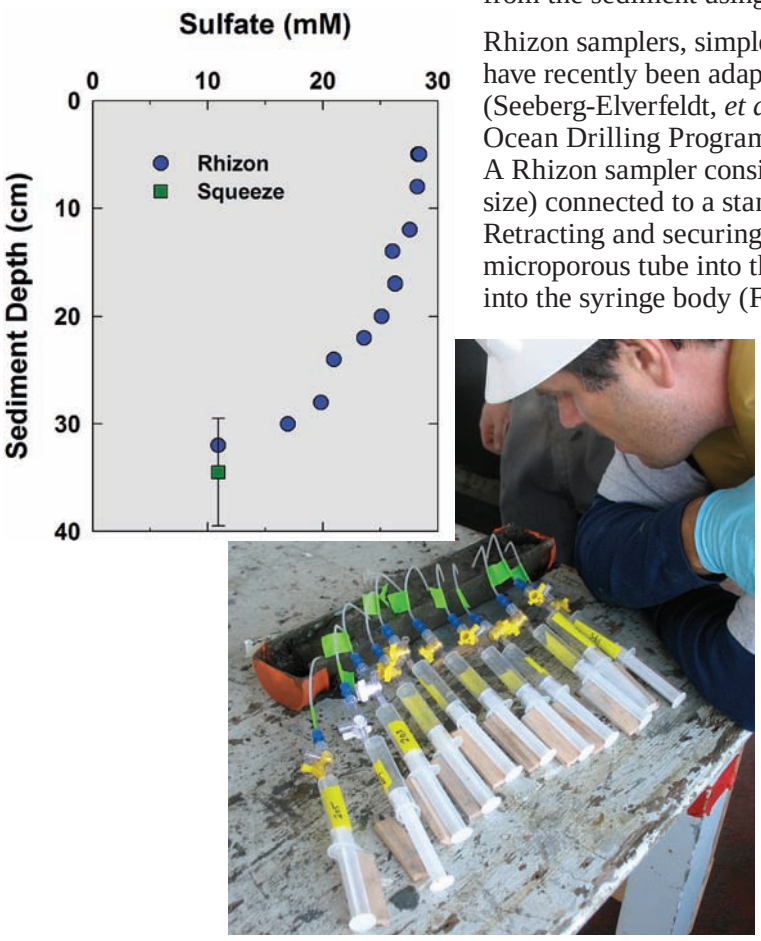
Application of Rhizon Samplers to Obtain High-Resolution Pore Fluid Records During Geochemical Investigations of Gas Hydrate Systems

By J.W. Pohlman (USGS), M. Riedel (McGill University), W. Waite (USGS), K. Rose (USDOE), and L. Lapham (Florida State University)

Obtaining accurate, high-resolution profiles of pore fluid constituents is critical for characterizing the subsurface geochemistry of hydrate-bearing sediments. Tightly-constrained downcore profiles provide clues about fluid sources, fluid flow, and the milieu of chemical and diagenetic reactions, all of which are used to interpret where and why gas and gas hydrate occur in the natural environment. Because a profile's quality is only as good as the samples from which the data are obtained, a great deal of effort has been exerted to develop extraction systems suited to various sedimentary regimes. Pore water from deeply buried sediment recovered by scientific drilling is typically squeezed with a hydraulic press (Manheim, 1966); whereas pore water in near-surface, less consolidated sediment is more efficiently pushed from the sediment using compressed gas (Reeburgh, 1967) or centrifugation.

Rhizon samplers, simple devices developed by the soil science community, have recently been adapted to sampling pore fluids in marine sediments (Seeberg-Elverfeldt, *et al*., 2005), including cores recovered on Integrated Ocean Drilling Program (IODP) Expedition 302 (Dickens, *et al*., 2007). A Rhizon sampler consists of a microporous tube (0.1 µm nominal pore size) connected to a standard syringe via PVC tubing and a luer-lock fitting. Retracting and securing the syringe plunger with a spacer after inserting the microporous tube into the sediment creates a vacuum that pulls pore fluids into the syringe body (Figure 1).



The time required to collect fluid using the Rhizon is similar (~ 1-2 hr) if not longer than that required by other methods, and the total volume of fluid recovered (<10 ml) by Rhizon sampling is less than that obtained by traditional squeezing methods (<35 ml). The Rhizon sampling technique, however, offers several advantages: 1) the geometry of the Rhizon samplers makes it possible to obtain samples at higher spatial resolution along a sediment core; 2) minimal exposure to air means pore waters are subjected to less chemical alteration during the collection process; 3) Rhizon sampling is non-destructive, meaning the sediment record is maintained; and 4) in contrast to sediment compaction during the squeezing process, pulling fluid from the sediment matrix by vacuum extraction is less likely to alter the chemical composition of some analytes. In spite of these striking advantages, Rhizon samplers are

Figure 1: High-resolution Rhizon sampling of a core section collected at Barkley Canyon. The close spacing of the Rhizon samplers was required to obtain the high-resolution sulfate profile for this core section (inset). For comparison, a 10-cm section (indicated by vertical bar) from the base of the core was processed by the traditional compressed gas squeezing method after the Rhizon samplers were removed (inset, green square with vertical bar denoting sample length). Similar results were obtained by each method. Without the high-resolution sampling; however, the obvious curvature in the sulfate profile would be obscured, and subsequent interpretation of its implications would be limited.

only beginning to gain widespread acceptance for pore water sampling in gas hydrate-bearing and other deep water marine sediment systems.

During Cruise 2008-007-PGC along the northern Cascadia Margin (see "Investigating Gas Hydrate as a Factor In Accretionary Margin Frontal Ridge Slope Failures and Cold Seep Biogeochemistry," this issue.), we utilized Rhizon samplers as a component of our pore water sampling program, which also included traditional squeezing of whole round core sections using compressed gas. Based on results from the analysis of sulfate and chloride concentrations, we demonstrated that Rhizon samplers provide a level of resolution not possible by sediment squeezing (Figure 1), and that analytical results from samples acquired by both methods are comparable (Figure 2). Furthermore, the non-destructive aspect of the Rhizon sampling allowed us to develop a sampling program that was integrated with the studies of our fellow sedimentologists, geophysicists, and microbiologists. At sites where small volumes of pore water were sufficient to address the research questions at hand (<8 ml), we used Rhizon samplers exclusively. In other instances, particularly at seep sites where large pore water volumes exceeding 25 ml were required to satisfy the sample requests, we utilized both Rhizon sampling and squeezing techniques. Additional comparative studies from other inorganic and organic pore water constituents will allow us to more rigorously evaluate the advantages and pitfalls of each technique.

Given the exceptional performance, simplicity, and portability of the Rhizon samplers, we consider them an essential component in the toolbox of any gas hydrate geochemist investigating pore water profiles in shallow subseafloor sediment.

A

B

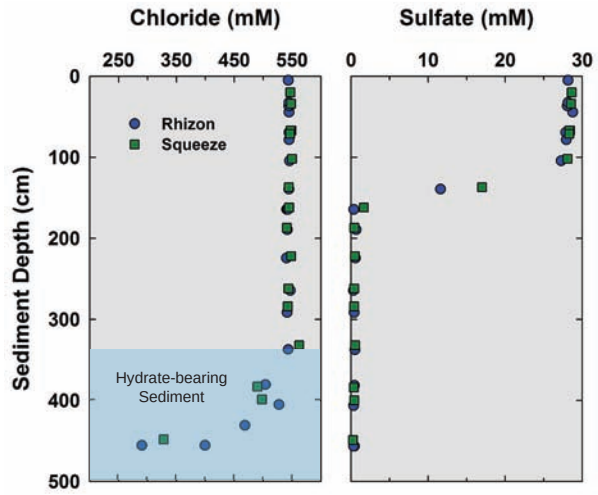


Figure 2: (A) Implementation of Rhizon samplers within the cruise 2008-007-PGC core processing factory. Team members (clockwise from left): Bill Waite (USGS), Kelly Rose (USDOE), John Pohlman (USGS), Greg Middleton (NRCAN), Michael Riedel (McGill), Laura Lapham (FSU) (B) Comparative chloride (left panel) and sulfate (right panel) profiles from fluids sampled by Rhizon samplers (Blue circles) and traditional compressed gas squeezing (green rectangles) at the Bullseye vent cold seep. Concentrations measured from each sample type are largely indistinguishable. Low chloride values below ~330 cm indicate dissociation of the massive gas hydrate present in the bottom of the core. The slightly lower Rhizon chloride values in the hydrate-bearing section likely reflect incomplete dissociation of gas hydrate during the Rhizon sample extraction timeframe.

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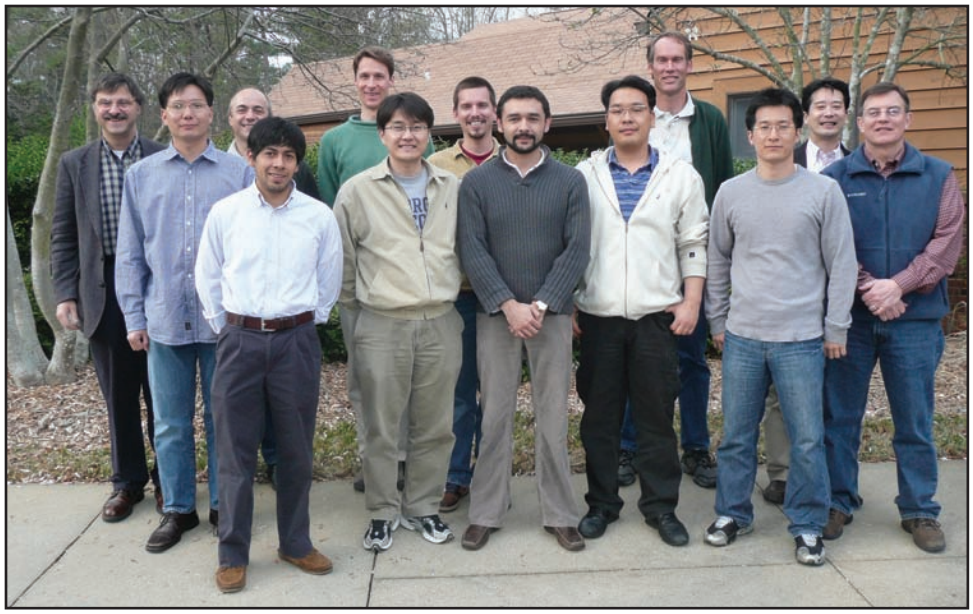
Workshop Summary: Physical Properties of Gas Hydrate-Bearing Sediment

By W.F. Waite (U.S. Geological Survey), J.C. Santamarina (Georgia Institute of Technology)

A wide range of particle and pore scale phenomena, often coupled, determines the macro-scale response of gas-hydrate bearing sediment to changes in mechanical, thermal, or chemical conditions. Predicting this macro-scale response is critical for applications such as optimizing the production of methane from gas-hydrate deposits, or determining the role of gas hydrates in global carbon cycling and climate change.

A proper understanding of gas-hydrate bearing sediment's rich and complex phenomenology requires the input of researchers from diverse disciplines, including geomechanics, geochemistry, and geophysics. To provide this increasingly multi-disciplinary field with a review of the most relevant physical properties of hydrate-bearing sediments, an intensive three-day workshop was held in Atlanta (March 16-19, 2008). The workshop, sponsored by the Department of Energy and the U.S. Geological Survey, was organized by Bill Waite (USGS) and Carlos Santamarina (GaTech). Eight researchers and five graduate students participated (see figure below), bringing together a wide range of expertise on the physical properties of hydrate-bearing sediments.

Attendees drafted a comprehensive summary of the current state of electrical, mechanical, thermal, and fluid flow properties of hydrate-bearing sediments. The document also reviews issues of solubility, hydrate formation, spatial variability in natural systems, and volume change upon dissociation. Each section includes tabulated data, predictive models, and an extensive bibliography. The manuscript will be submitted for peer-review later this year. Draft versions can be obtained from Bill Waite (wwaite@usgs.gov) or Carlos Santamarina (jcs@gatech.edu).



Attendees of the "Physical Properties of Hydrate-Bearing Sediment Workshop." Front row, left to right: Nicolas Espinoza (GaTech), Tae-Sup Yun (Lehigh Univ.), Douglas Cortes (GaTech), Jongwon Jung (GaTech), Jaewon Jang (GaTech). Back Row, left to right: Bill Winters (USGS), Hosung Shin (GaTech), Carlos Santamarina (GaTech), Bill Waite (USGS), Brandon Dugan (Rice Univ.), Tim Kneafsey (LBNL), Kenichi Soga (Cambridge Univ.), Jack Germaine (MIT).

Nine New Methane Hydrate Research Projects Announced by DOE/NETL

The DOE-NETL Methane Hydrate Program has expanded its portfolio of research and development projects with the addition of nine projects that focus on improving our understanding of gas hydrate's role in the natural environment and its potential as a new source of natural gas.

Gas Hydrates in the Natural Environment

Texas A&M University (Corpus Christi, Texas) and the Scripps Institute of Oceanography, in collaboration with U. California-Santa Barbara and U. Southern Mississippi, will study the volume of methane that escapes to the atmosphere from deepwater expulsion sites in the Gulf of Mexico. The project will study methane fate in the water column and will detect hydrocarbon seep locations using satellite data, that will be used to extrapolate regional estimates of methane escaping to the atmosphere.

University of Alaska, Fairbanks (Fairbanks, Alaska) will lead a study in collaboration with the USGS, of methane emissions associated with arctic thermokarst lakes (freshwater lakes formed from melting permafrost). Work will focus on investigation of the potential link between methane emissions and dissociation of methane hydrate.

University of California, Santa Barbara (Santa Barbara, Calif.) will conduct field and laboratory studies of aerobic methanotrophy in marine environments. Understanding the potential to oxidize methane and the fate of methane as it travels through the water column will help researchers understand the role methane hydrate may play in global climate change.

University of Chicago (Chicago, Ill.), in collaboration with the USGS, will develop a two-dimensional global model linking sediment, oceans, and the atmosphere that will be used to perform simulations at regional and global scales to assess methane dissociation related to changing environmental conditions and whether any released methane is likely to make its way into the atmosphere.

University of Delaware (Newark, Del.) will estimate rates of methane degradation through oxidation and examine methanotrophic microbes responsible for oxidizing methane in Arctic coastal waters and seafloor sediments. The effort will fill key knowledge gaps regarding the extent of hydrates and fate of methane in arctic coastal waters and seafloor.

Gas Hydrate Production Technologies

ConocoPhillips (Houston, Texas) will study the opportunities for conducting the first field trial of a promising and unique gas hydrate production method that injects CO2 into the reservoir to replace methane molecules in the gas hydrate, freeing methane for production using conventional techniques (see associated article, this issue).

North Slope Borough (Barrow, Alaska) will continue to study opportunities to drill, log, core, and test a hydrate accumulation in association with free gas the Barrow region of the Alaskan North Slope (see FITI, Spring-Summer, 2007). In the proposed field test, researchers will monitor gas hydrate behavior as the pressure is decreased through production of free gas trapped beneath the hydrates.

Announcements

Gas Hydrate Exploration Technologies

Oregon State University (Corvallis, Ore.) will study the impact of variations in regional heat flows on continental margins as a tool to predict where gas hydrates are likely to occur. As such, they will integrate a new, high-quality data set from offshore India into existing data already under analysis to create heat flow maps of the region.

Scripps Institution of Oceanography (La Jolla, Calif.) will conduct controlled source electromagnetic surveys at three sites in the Gulf of Mexico and undertake complementary lab studies with the USGS, Lawrence Livermore National Laboratory, and MIT. These efforts will increase understanding of how to detect and characterize gas hydrate via this remote sensing method

Call for Papers - Gas Hydrates Symposium

The 237th American Chemical Society National Meeting – Fuel Division will take place in Salt Lake City, Utah, on March 22 – 26, 2009. During the meeting, the Gas Hydrates Symposium well be held, highlighting the state-of-the-art research and developments currently being made in the international hydrate research community. Depending upon the number of papers submitted there will be three to four sessions to include the topics of Natural Gas Hydrates in Energy Production, Recovery, Assessment; Industrial Applications of Gas Hydrates and H_2 Storage in Clathrates (Held jointly with the Physical Chemistry division).

To present an oral paper, submit abstract (150-word limit) and preprint paper (2 pages) via the ACS website at http://oasys.acs.org/acs/237nm/fuel/papers/index.cgi. Scroll down and select "Oral: Gas Hydrates & Clathrates" and then click the "Submit Topic Selection" button. Preprints of papers will be published in the ACS Fuel Division Proceedings. Deadline for abstract submission is October 31, 2008.

For more information contact Carolyn A. Koh at ckoh@mines.edu or E. Dendy Sloan at esloan@mines.edu.

CALL FOR ABSTRACTS: 2009 AAPG/SEPM Annual Meeting in Denver, Colorado

The 2009 Annual meeting of the AAPG will be held June 7-10, 2009 in Denver Colorado. The meeting will include both poster and oral sessions on the topic of "Hydrates - Sedimentology and Resources". These sessions are intended to feature work that describes gas hydrate occurrence, behavior, and resource potential in either marine or arctic settings. Abstract submission for this session is now open and will close on November 4th. Instructions for submitting an abstract can be found at http://aapg2009ace.abstractcentral.com/login.

The National Research Council to Review Hydrate R&D Program

On September 11, 2008 The National Research Council held its first formal meeting regarding the "Assessment of the Department of Energy's Methane Hydrate Research and Development Program: Evaluating Methane Hydrates as a Future Energy Resource" in Washington, D. C. This formal review looks at the progress made under the methane hydrate research and development program and will make recommendations for future methane hydrate research and development needs as part of the Energy Policy Act of 2005, Section 968.

The study includes:

- a brief review of hydrate research conducted by DOE and its partners from 2000-2005,
- a detailed review of hydrate R&D conducted by DOE and partners from 2005-2008,
- a review of the process by which past and current R&D has been and is being conducted including domestic interagency coordination; collaboration with academies and industry; international cooperation and collaboration; and the advisory and peer-review mechanisms.

The NRC will also evaluate future R&D needs and make recommendations concerning: the potential for methane hydrate to contribute to the domestic natural gas supply, changes to the current program of R&D; and coordination of interagency, academic, and industrial research and partnerships, (domestically and internationally), and graduate education and training in hydrate research.

A formal report on the NRC's findings will be issued at the end of the project in approximately 21 months. More information on the review can be found at http://www8.nationalacademies.org/cp/projectview.aspx?key=48952.

Council of Canadian Academies
Conseil des académies canadiennes

Council of Canadian Academies Releases Report at ICGH

The Council of Canadian Academies was recently released the findings of a 13-member panel of experts that were tasked with finding the answer to a question posed by Natural Resources Canada: *What are the challenges for an acceptable operational extraction of gas hydrates in Canada?*

The panel, composed of experts in the fields of geophysics, geology, chemistry, engineering, biology, economics, political science, safety, and social impacts, concluded that Canada is well positioned to be a global leader in exploration, research and development, and eventual production of natural gas from gas hydrate. However, given the need for further research to better quantify the large-scale stand alone commercial production of gas hydrate resource and the economic, environmental and technical uncertainties involved, commercial production is not likely to take place within Canada for at least two decades.

The expert panel presented and released its summary document – the *Report in Focus, Energy from Gas Hydrates: Assessing the Opportunities & Challenges in Canada* – at the International Conference on Gas Hydrates held in Vancouver, B.C. in July, 2008. That document can also be found on the Council's website http://www.scienceadvice.ca/hydrates.html.

JAMES ROBERT WOOLSEY, JR.

1936 - 2008

Research Professor – University of Mississippi

Director of the Mississippi Mineral Resources Institute, the Center for Marine Resources and Environmental Technology, and the Seabed Technology Research Center of the NOAA National Institute for Undersea Science and Technological at the University of Mississippi.

In Memoriam

By Carol Lutken, Associate Director of Research Programs, Mississippi Mineral Resources Institute, the Center for Marine Resources and Environmental Technology

Family, friends, colleagues, mentors, and students gathered in Oxford, Mississippi in mid-July to celebrate and pay tribute to the amazing man that was Dr. Bob Woolsey. Although Bob's life had come to a tragic end just days earlier, those that came together for his memorial service were there to be a part of the send-off for a beloved family member and friend. Bob was a man that was a truly gifted teacher and scientist, as well as a visionary scholar. The greatest of his many talents was his ability to nurture the best in those with whom he worked, whether at home, in the office, at the shop, in the field or at sea.

A native of Savannah, Georgia, Bob's professional and personal interests knew no geographic boundaries. His formal education began in Georgia; his M.S. in Geology from Mississippi State University; and his Ph. D., with emphasis in Marine Processes, came from the University of Georgia. He served as a Reserve Officer and Aviator for the U.S. Navy, working primarily with anti-submarine and mine warfare. He furthered his knowledge in Ocean Science and Engineering at the Naval Post Graduate School, Monterey, CA.

Prior to joining the School of Engineering at the University of Mississippi in 1980, Bob worked as a contractor in industry and with the United Nations, specializing in marine mineral exploration, mining, and related environmental engineering. His work mainly involved marine placer deposits and environmental issues related to marine and fluvial alluvial dredging for industrial and precious minerals in North and South America, the Mediterranean, West Africa, Southeast Asia and the South Pacific. For his cooperative work in microbial filter design, Bob was awarded an honorary Ph. D. from the Moscow Mining Institute. It was during his time working on a United Nations project in Myanmar (then Burma), that he married Georgia native Maxine Upson while on leave in Singapore.

As Director of the Mississippi Mineral Resources Institute (MMRI), Bob worked mainly with energy and industrial minerals. Bob guided the Institute toward the responsible development of the state's mineral resources, providing lawmakers with the data necessary to make informed decisions regarding its future. More recently, he had been guiding efforts to produce biodiesel from cooking oil and other plant sources to power MMRI's equipment and vehicles.

Bob's responsibilities were expanded with the establishment of the Department of the Interior's Minerals Management Service's Center for Marine Resources and Environmental Technology (CMRET) and NOAA's Seabed Technology Research Center (STRC) programs. These centers were developed primarily to conduct projects of research and investigation of offshore energy/mineral resources and related environmental studies. The STRC and CMRET have served both industry and government agencies in providing scientific and technical council and assistance to various mineral resource and environmental programs throughout the U.S. Exclusive Economic Zone, with primary focus on the Gulf of Mexico.

In the late 1990s, Bob became interested in gas hydrates: how they had come to be where they are, why they are not found in other places, the dynamics of their formation and dissociation. Finding others with similar interests was something at which Bob excelled, and The Gulf of Mexico Hydrates Research Consortium was the result of his drive to get hydrates research moving in the Gulf. Efforts of the Consortium are focused on research and development of new ocean observing and survey systems, technologies, and methodologies for use in gas hydrate research. The Consortium's primary goal is the design and development of a multi-sensor seafloor observatory for monitoring near-seafloor hydrocarbon systems of the deep, northern Gulf of Mexico. The Consortium also provides technical and financial support to students researching gas hydrate.

Since the Consortium's inception in 1999, there have been hundreds of members and about 30 actively involved in Consortium-funded hydrate research at any given time. Bob was instrumental in securing federal funding for the Consortium largely because he was passionate as well as knowledgeable about every aspect of the project. He was proud of every achievement and especially proud of the student efforts whose innovation he fueled with his own enthusiasm and encouragement. He never tired of making opportunities for new research and researchers, always making room in his own repertoire for new ideas, new ways to look at problems, and innovative solutions.

Bob was indeed a classroom professor but his real teaching talent came to the fore when he was in the field. He was always looking to get outside – to get going, to get to the outcrop, to get the ship moving, to find out more about why things were the way they were – to know more about them. With a love for both geology and people, Bob immersed himself in the local geology as well as local people.

He always left a project knowing more about the people and the place. He never tired of collecting stories and those who knew him know that he loved to tell stories – and that he had an impressive trove of them. That's partly because in addition to being a gifted storyteller, he was a gifted listener. This trait endeared him to his students and kept him a student his entire life. Whether it was in the local climes of Mississippi or Georgia, or far off places like Alaska, Belize, Brazil, Burma, the Congo, Ghana, Nova Scotia, or Russia, Bob had a story appropriate to the locale. He would often take more stories home, collected from the locals, co-workers, and co-travelers.

"He was an old-style geologist, the kind that is hard to find these days; his experiences took him around the world, and because of his broad range of expertise, he could talk with anybody," said Terry Panhorst, University of Mississippi Associate Professor of Geology.

More than anything, Bob wanted to know more about you. He was a most talented mentor and would talk you through a problem or a project and draw more out of you than you thought you had. Before you knew it, you had defined your immediate objective and you had a plan to reach it.

Jesse Hunt, who has known Bob since they were in graduate school together at the University of Georgia in the mid-1960s, puts it this way, "He was an incredible person. There wasn't anything he couldn't do. I've never met anyone more knowledgeable and flexible than Bob. He touched thousands of people and I've never heard anybody say a bad word about him."

Going to the field or to sea with Bob was like a holiday and a homecoming at the same time. You would never work harder than with Bob, you would never be asked to do anything he wasn't willing or able to do himself but you would have the opportunity to pursue your own investigations and you could count on his support and input.

When the job was done, you were proud that you were part of a team that could be counted on to do the best job possible under the circumstances. "He had an extraordinary ability in bringing people together to address important problems," said Alice Clark, University of Mississippi vice chancellor for research and sponsored programs. "It was obvious to all who knew him that he loved his work and the people he worked with. He was a delightful man who will be deeply missed."

Memorial contributions can be made to the J.R. Woolsey Geology and Geological Engineering Memorial Scholarship, c/o University of Mississippi Foundation, P.O. Box 249, University, MS 38677.