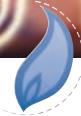


# Fire in the Ice



Vol. 9, Iss. 2

Methane Hydrate Newsletter



## CONTENTS

Expedition Underway .....	1
Molecular Level Modeling .....	7
Methane Fluxes and Gas Hydrates in the Sea Of Okhotsk.....	11
The Methane Hydrate Fellowship.....	16
The Next Generation .....	17
<b>Announcements .....</b>	<b>27</b>
• AAPG Convention	
• Postdoctoral Fellowship	
<b>Spotlight on Research .....</b>	<b>28</b>
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# Gulf of Mexico Gas Hydrate Drilling and Logging Expedition Underway

On April 16, 2009 the Gulf of Mexico Gas Hydrate Joint Industry Project ("The Gulf of Mexico JIP") initiated its second field program aboard the semi-submersible Helix Q4000 (Figure 1). This three-week expedition will conduct logging-while-drilling (LWD) operations at multiple sites to test a variety of geologic/geophysical models for the occurrence of gas hydrate in sand reservoirs in the deepwater Gulf of Mexico.



- *Figure 1: Helix's semi-submersible Q4000. The rig features dynamic positioning, 51,000 ft<sup>2</sup> deck, transit speed of 10 knots or more, 150 HP ROV, and is capable of handling double-length stands of drill pipe ("doubles").*

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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 281-494-2560.  
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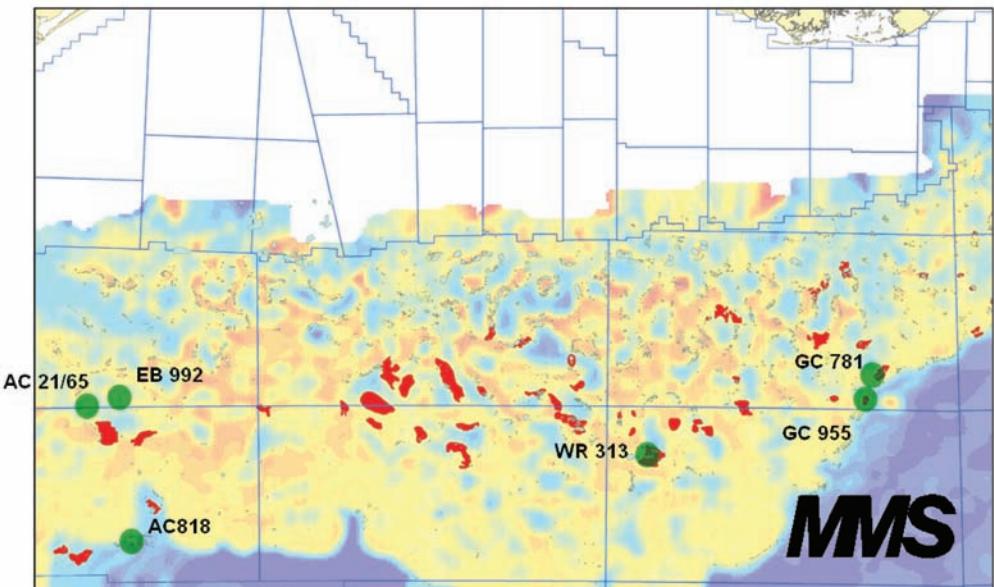
The primary goal of the Gulf of Mexico JIP is to evaluate the occurrence, nature, and implications of gas hydrates in the Gulf of Mexico. Prior work by the JIP has contributed significantly to the development of remote sensing and field sampling technologies, wellbore stability modeling, and an extensive database of experimental data on the impact of gas hydrate on the physical properties of sediments of various grain sizes. In 2005, the JIP completed Leg I drilling, logging, and coring operations designed primarily to assess hazards related to drilling through gas hydrate within the clay-dominated sediments that typify the shallow sub-seafloor in the deepwater Gulf of Mexico (see Ruppel *et al.*, 2008.). The current Leg II program is designed to extend our understanding of sand-dominated hydrate systems, and evaluate their resource and hazard potential. Leg II results will then be used to assess the best sites for additional data acquisition (through both conventional and pressure coring) in Leg III (currently planned to occur as early as 2010).

### Leg II Preparations

In preparation for Leg II, the JIP and its collaborators (see sidebar pages 4 & 5) in 2006 began detailed geologic and geophysical evaluations of numerous potential sites, seeking evidence for active petroleum systems (gas sources and migration pathways) co-located with sand-prone lithologies (see Hutchinson *et al.*, 2008). By 2008, the JIP had developed geologic interpretations; conducted pre-stack, full-waveform 3-D inversions for gas hydrate saturation; delineated and prioritized specific drilling targets; assessed drilling hazards; and developed operational plans for sites in Alaminos Canyon (AC) 818, Green Canyon (GC) 955, and Walker Ridge (WR) 313. Leg II LWD operations were originally planned for spring 2008, but drilling was postponed when delivery of the contracted drill rig was delayed until after the start of the hurricane season.

The delay in delivery of the rig allowed additional site selection and evaluation activities to continue through the rest of 2008 and early 2009. In addition to wellbore modeling within the JIP, several controlled source electromagnetic (CSEM) surveys were conducted by Scripps Institute of Oceanography over the planned drill sites in AC818, GC955, and WR 313 in Fall 2008 (see Weitemeyer *et al.*, 2009). The JIP effort also benefitted greatly from continuing work within the Minerals Management Service's ongoing assessment of Gulf of Mexico resources (see Frye, 2008) that revealed additional opportunities to target gas hydrates in coarse-grained sediments in East Breaks (EB) 992, GC 781/825, and AC 21/65. The USGS continued to coordinate the site selection process and develop additional interpretations of gas hydrate occurrence at selected existing drill holes. All sites were then fully reviewed by the site selection team in order to refine and prioritize the final drilling targets.

Throughout early 2009, the JIP has pursued permitting and hazards analysis for five sites (AC21/65; EB 955, GC 992; WR 313; GC 781/825; Figure 2). The site in AC 818 had earlier been deemed too risky for Leg II drilling due to expected reservoir overpressure and was dropped from the Leg II program. However, because of preexisting data the site remains a candidate for GoM JIP Leg III coring activities if the drilling hazard issues can be addressed. As of this writing, ongoing industry activity at two of the locations (EB 992 and GC 781) renders the JIP's ability to drill at those locations uncertain.



*Figure 2: Locations of six sites evaluated as possible targets for JIP Leg II drilling. Background colors indicate depth to salt, with areas of shallow salt in yellow/orange and small circular areas of blue representing salt-withdrawal mini-basins. Areas in red indicate seismic indications of base of gas hydrate stability.*

Other issues, including weather, ocean currents, and unexpected operational complications, may further affect which sites will be visited during the program. However, the site selection team has proposed a total of 23 potential drill holes amongst the five sites, allowing for flexibility in dealing with these unknowns.

### **Leg II Operations**

During Leg II, operations place a high priority on drilling safety and adherence to budget constraints. All sites have undergone extensive hazards review by the AOA Geophysics team (see sidebar page 4) and will be drilled only to those depths that are deemed free of safety and operational hazards, particularly free gas accumulations. The budget for the Leg II field program is approximately \$11.2 million with 80% of the cost associated with operating the rig and the remainder primarily committed to use of the LWD tools. At roughly \$500,000 per day, the expedition will be limited to ~22 days of operational time, which will include initial mobilization, transit between holes and between sites, and final demobilization. Both mobilization and demobilization will occur at sea.

GoM JIP Leg II will feature a state-of-the-art LWD tool combination (Figure 3) that will provide unprecedented information on the nature of the sediments and their pore fill constituents. The program will feature



*Figure 3: The JIP Leg II bottom hole assembly. Notable is the presence of a full suite of LWD tools, including the 6.5" MP3 sonic tool just above the bit, followed by an 8.5" hole opener, and then the GeoVision, EcoScope, TeleScope, PeriScope, and SonicVision tools. The SonicVision tool is ~160 feet above the drill bit.*

## JIP LEG II CONTRIBUTORS

### ***JIP Executive Board***

- Emrys Jones – Chevron
- James Howard – ConocoPhillips
- Dr. Espen Sletten Andersen – StatoilHydro ASA
- Dr. Lewis Norman – Halliburton Energy Services
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- Matt Frye – Minerals Management Service
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- Tim Collett – USGS

• full research-level LWD data on formation lithology and porosity, and will include Schlumberger's MP3 (quadrupole sonic tool) and PeriScope (3-D high-resolution resistivity) tools. These tools will provide full 3-D information on the acoustic (both compressional and shear wave) and electrical properties of the sediment, enabling the improved evaluation of gas hydrate in both pore filling and fracture-filling modes.

• Given the different (smaller) diameter of the MP3 tool compared to the rest of the tool string, the JIP Leg II bottom hole assembly will feature a second "hole opener" located above the MP3 tool. This innovation will enlarge the hole to allow logging with the other tools after the passage of the MP3.

• Current plans call for Leg II to proceed first to WR 313, where five holes have been permitted. The initial LWD run will target the hole judged by the site selection team, the JIP, and geohazards specialists as having the greatest potential for success in finding gas hydrates within coarse-grained lithologies with the lowest drilling risk. The Helix and JIP teams will then drill and collect LWD data from this first site in "high resolution" mode, which is characterized by reduced drilling penetration rates.

• Select LWD data will be analyzed by the onboard science team in real time, and that information will be used to evaluate the hole being drilled and inform decisions regarding the location and drilling parameters for the next hole. Once the first WR well is drilled, the drill string will be raised to clear the seafloor, and the ship will move a short distance to the next hole location. After completion of two or three holes at the WR site, the full drill string will be retrieved and layed down on deck, and the ship will steam to the next site. Under optimal conditions, it is believed that up to three sites, with up to three holes at each site, could be drilled during Leg II.

### **The Sites**

Walker Ridge 313 is characterized by an inferred ponded sand delivery system within the Terrebonne "mini-basin". Evidence for gas hydrates in the stratigraphic section include a series of anomalous, shingled seismic reflections indicative of stratal-bound free gas ("bright spots") that closely align with the predicted depth of gas hydrate stability. These anomalous features include both increased amplitude anomalies indicative of free gas below the base of gas hydrate stability (BGHS), as well as reversed polarity of those reflections above the BGHS occur. Because of low thermal gradients within the mini-basin these drilling targets occur at about 2,700 feet below the seafloor. GC781/825 targets a geologic setting similar to WR313, but is located just landward of the Sigsbee Escarpment, refer to map (Figure 2).

Green Canyon 955 features a well established and persistent sand delivery system through the Green Canyon channel at the Sigsbee Escarpment. Wells drilled previously in the lease block show significant sand development within the GHSZ and minor indications of gas hydrate. The primary target for Leg II is a large closed structure with abundant seismic evidence of gas and migration pathways into a suspected sand-rich lithofacies near the BGHS. Additional potential targets in GC955 include areas proximal to the primary paleo-channel-levee system (Figure 5).

## JIP LEG II CONTRIBUTORS CONTINUED

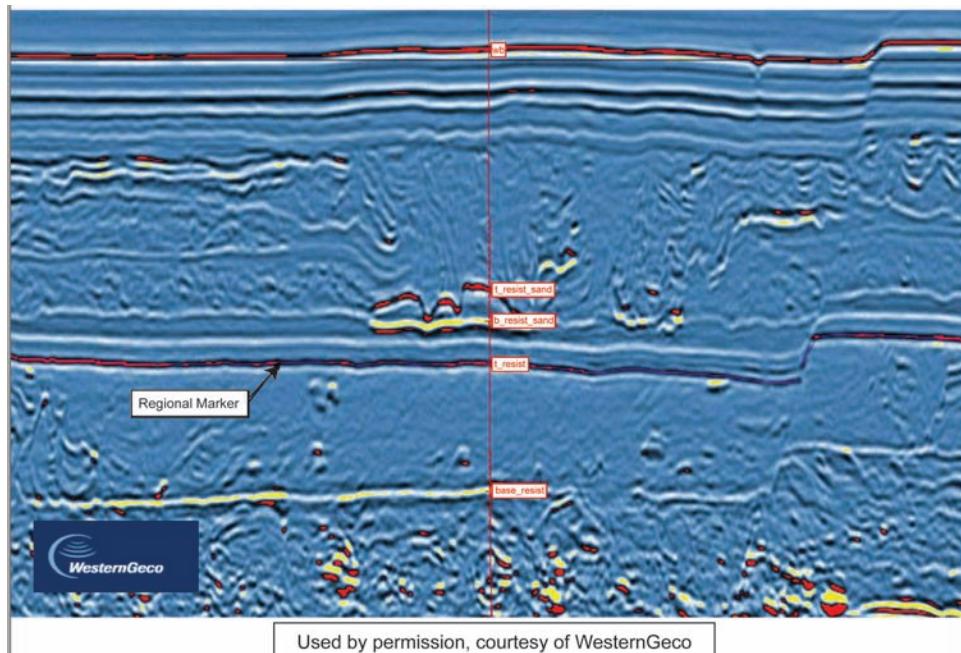
### **Site Selection Team**

Debbie Hutchinson, Carolyn Ruppel, Tim Collett, Myung Lee – US Geological Survey  
Bill Shedd, Matt Frye – US Minerals Management Service  
Dan McConnell – AOA Geophysics  
Dianna Shelander, Jianchun Dai – Schlumberger  
Ray Boswell, Kelly Rose – US DOE/NETL  
Warren Wood – Naval Research Laboratory  
Tom Latham – Chevron  
Brandon Dugan – Rice University

### **Onboard Science Team**

Tim Collett – USGS  
Ray Boswell – US DOE/NETL  
Gilles Guerin, Stefan Mrozewski, Ann Cook – Lamont Doherty Earth Observatory  
Matt Frye, Bill Shedd, Rebecca Dufrene, Paul Godfriaux – MMS  
Dan McConnell - AOA Geophysics

- East Breaks 992 wells target anomalous seismic reflections that occur well above the interpreted BGHS within the Diana sub-Basin. These anomalies coincide with the top and base of a 130'-thick, resistive sand logged in an existing well (Figure 4). The Alaminos Canyon 21/65 sites provide additional targets in the Diana Basin within a large area of seismic anomalies analogous to those targets in the EB992 wells.
- Each site evaluated for Leg II drilling has indications of (1) the existence of gas in reservoirs below the base of gas hydrate stability or visible in the shallow stratigraphic sections; (2) conduits for gas migration from potential sources and into the hydrate stability zone, through either faults or high-permeability lithologies like sands; and (3) the presence of coarse-grained sediments that could serve as reservoirs for high concentrations of gas hydrate.



• Figure 4: West-to-east seismic section through the EB992 area. Red line denotes location of an 1995 exploration well that encountered a 130'-thick resistive sand. The top and base of that sand, and the correlation of that sand to the seismic anomalies, are noted. Data courtesy WesternGeco.

## RECOMMENDED READING

Hutchinson, et al., 2008, Site selection for DOE/JIP gas hydrate drilling in the Northern Gulf of Mexico; Proceedings, 6th International Conference on Gas Hydrates.

Jones, et al., 2008, Scientific objectives of the Gulf of Mexico gas hydrate JIP Leg II drilling, Offshore Technology Conference, OTC 19501.

Ruppel, C., Boswell, R., Jones, E., eds., 2008, Thematic Set on Scientific Results of 2005 US DOE-Chevron JIP Drilling for Methane Hydrates Objectives in the Gulf of Mexico, *Mar. Petr. Geol.*, 25 (9), pp. 819-988.

Frye, M., et al., 2008, MMS releases preliminary results of Gulf of Mexico in-place natural gas hydrate assessment, *Fire in the Ice* Newsletter, Spring 2008.

Frye, M., 2008, Preliminary Evaluation of In-Place Gas Hydrate Resources: Gulf of Mexico Outer Continental Shelf, OCS Report, MMS 2008-004, 2008 <http://www.mms.gov/revaldiv/GasHydrateFiles/MMS2008-004.pdf>

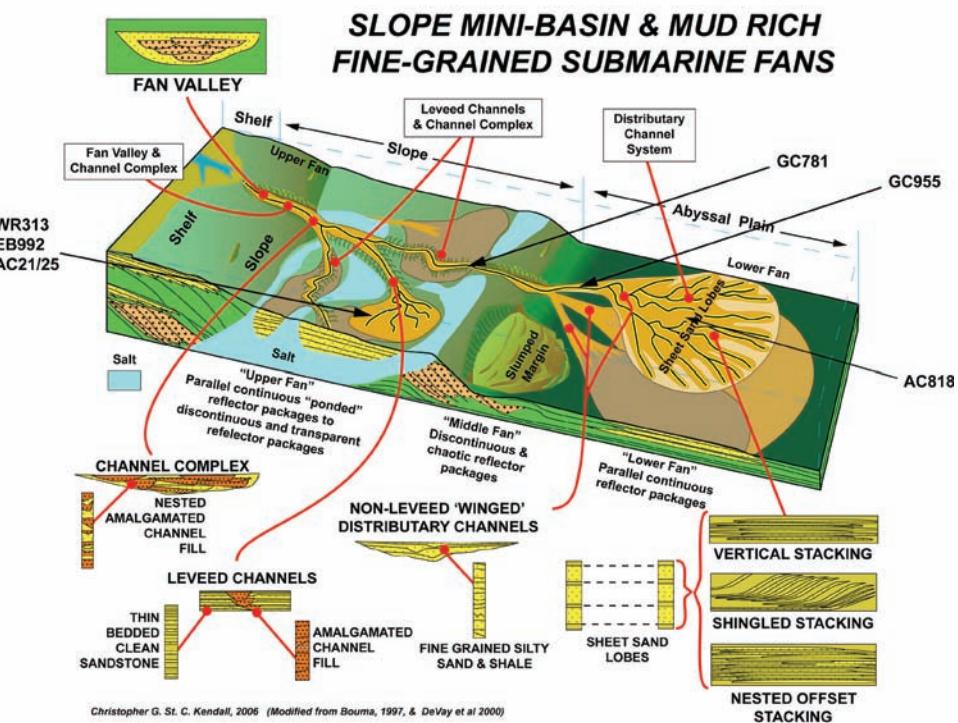
Weitemeyer, et al., 2009, Cruise report: Imaging natural gas hydrate in the Gulf of Mexico using marine electromagnetic methods. *Fire in the Ice* Newsletter, Winter 2009.

- In addition, the sites represent a variety of Gulf of Mexico geologic settings (Figure 5): if Leg II drills its planned complement of sites, the expedition will provide a good test of current concepts for the occurrence of gas-hydrate-bearing sands in the Gulf of Mexico.

Gulf of Mexico gas hydrates JIP Leg II is enabled by the contributions of dozens of scientists within the JIP and in collaborating federal agencies. The sidebar on page 4 lists the contributors. Please look for initial operational and science reports to be posted regularly on both the JIP and NETL websites. Additional data, including final drilling and logging reports, and site evaluations will be also be posted and announced in *Fire in the Ice*.

NETL website: <http://www.netl.doe.gov/technologies/oil-gas/futuresupply/methanehydrates/2009gomjip/index.html>

JIP website: <http://gomhydratejip.ucsd.edu/>



- Figure 5: Diagrammatic depiction of sand depositional environments in the deepwater Gulf of Mexico (Courtesy G. St. C. Kendall). WR313, EB992, and AC21/25 target sands within the interiors of mini-basins formed on the Gulf of Mexico shelf by salt tectonics. GC955 focuses on leveed channels on the abyssal plain just beyond the Sigsbee Escarpment. The setting for GC781 is not as well defined, although the targets sit just landward of the Escarpment.

## The Role of Molecular Level Modeling in Gas Hydrate Studies

by Brian Anderson, West Virginia University and Kenneth Jordon, University of Pittsburgh

For decades, researchers have been able to model and simulate systems of different scales independent of each other; however, the ability to bridge multiple time and length scales between such models has only recently begun to be intensively investigated. Natural gas hydrates systems are ideal for developing multiscale modeling techniques. The formation properties of hydrates are governed by molecular-level interactions between the gas and water molecules as well as the host media, yet hydrate reservoirs in nature can span tens of meters vertically and kilometers horizontally (Figure 1). Over the past few decades, many studies using Molecular-Level Modeling (MLM) have been conducted on gas hydrates and molecular dynamics (MD) simulations have been shown to correlate with experimental data in many areas such as phase equilibria, inhibition, cage occupancy, diffusion, and vibrational spectra to name a few examples.

Many successful research programs have been based on the constant integration of accurate theoretical modeling and laboratory studies. Concepts developed through simulations can enable a fundamental understanding of the processes in the laboratory while the lab can expose gaps in the fundamental knowledge eager for computational enlightenment. The following are a few examples of how researchers at NETL, The University of Pittsburgh, and West Virginia University are using MLM for hydrate systems and their connection to hydrates, and their recoverability, in nature. This work was performed as part of NETL's Institute for Advanced Energy Solutions (NETL-IAES).

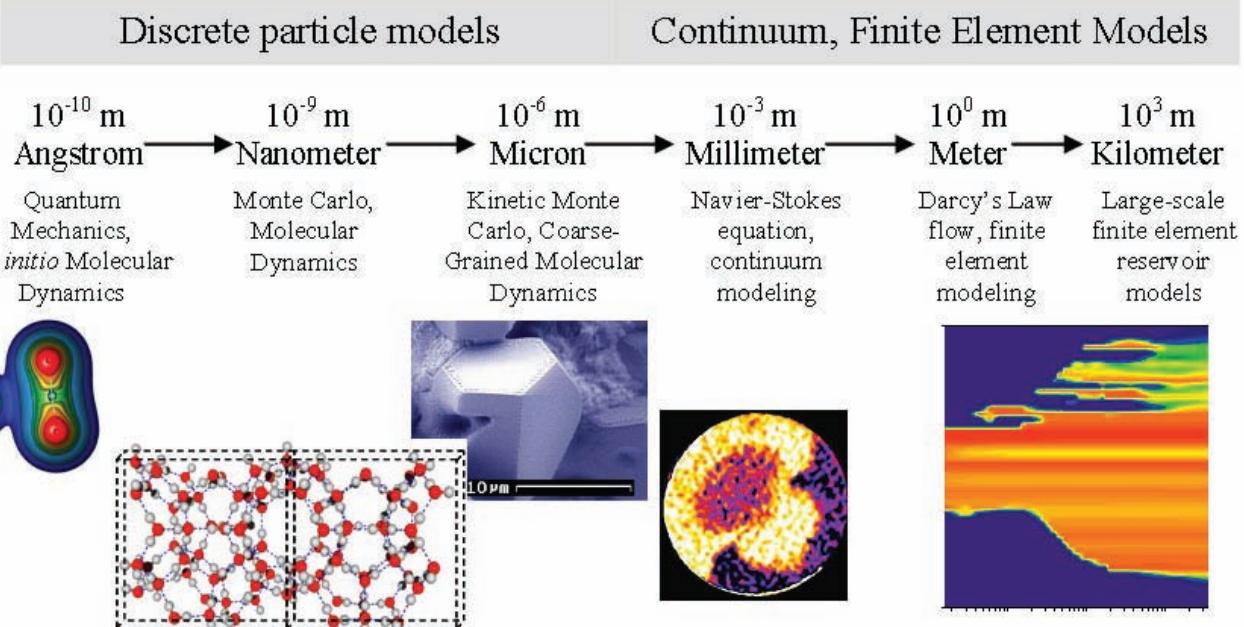


Figure 1: The multi-scale modeling continuum

- **Lattice Distortion Simulations**
- Small changes in the physical dimensions of the gas hydrate lattice degrees can create enormous physical pressures in porous media. Models of gas hydrate response to production stimulation do not include expansion due to either thermal effects or guest effects for gas hydrates. Currently, the compressibility and thermal expansivity of ice are used in the absence of any data on the subject. To address this problem, NETL, Pitt, and WVU have examined the temperature, pressure, and compositional dependence of the crystal lattice distortion of gas hydrates using molecular dynamics.<sup>1</sup>
- MD simulations were used to study the lattice dimensions (or lattice constant) of various sl and sII hydrates at different temperatures and pressures. Temperature and guest size have a large influence on the lattice dimensions while pressure and guest-guest interaction energy have a relatively smaller but significant effect. The lattice constant,  $l$ , is shown to be a function of hydrate guest composition, the fractional occupancy of the cavities and the repulsive nature of the guest molecule. The dissociation pressure variation associated with the various volume changes caused by molecular properties and temperature has been calculated using John and Holder's model and is significant in many instances (Figure 2).
- Figure 3 illustrates the effect of temperature on the lattice parameters of methane, carbon dioxide, and ethane hydrates and shows not only differences in the absolute value of the lattice parameter, but differences in the slope of the temperature dependence. These differences can be translated into variations in the coefficients of thermal expansion for hydrates of varying guests. This work highlights the importance of precise lattice dimensions in calculating hydrate equilibria and demonstrates the role that molecular dynamic simulations can play in determining the effect of temperature, pressure and guest size on  $l$ . The primary function of such calculations is to create better thermodynamic models for hydrate equilibria, but the calculations can also provide a way to determine the lattice expansion or contraction that occurs during production methods that involve, for example, temperature change or gas exchange ( $\text{CO}_2$  for  $\text{CH}_4$ ).

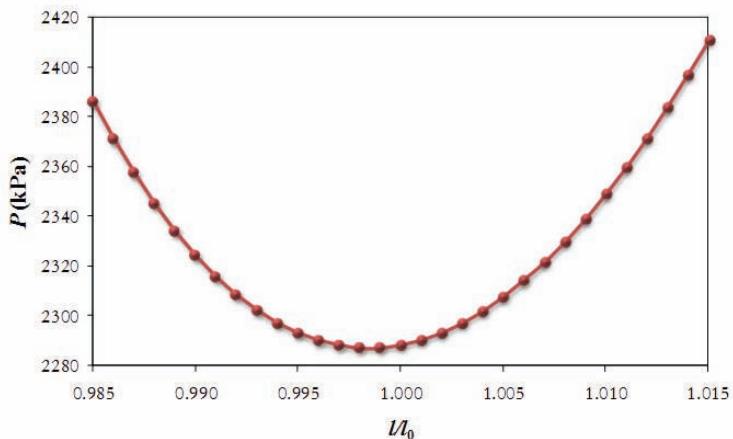


Figure 2: The dependence of the predicted dissociation pressure on the normalized lattice constant for pure methane hydrate at 270 K.

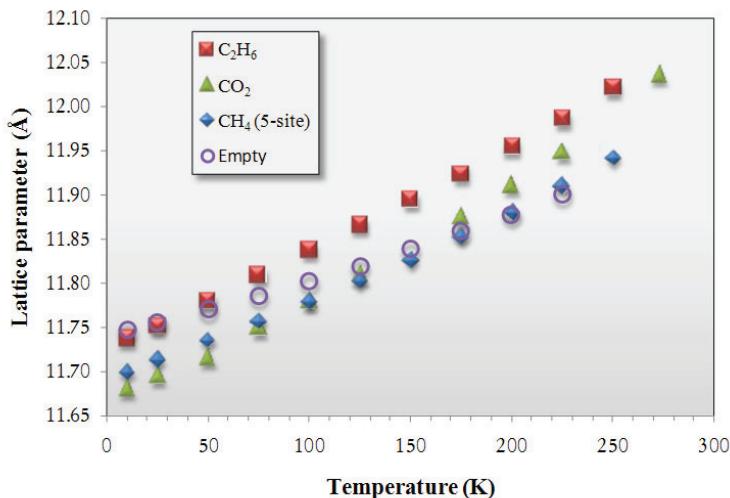


Figure 3: The dependence of the lattice constant on temperature for pure methane,  $\text{CO}_2$ , and ethane hydrates.

## REFERENCES

- (1) Zhang, M.; Anderson, B. J.; Warzinski, R. P.; Holder, G. D. "Molecular dynamics simulation of hydrate lattice distortion"; Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem., 2009, Salt Lake City, UT.
- (2) Jiang, H.; Myshakin, E. M.; Jordan, K. D.; Warzinski, R. P. *The Journal of Physical Chemistry B* 2008, 112, 10207.
- (3) Klauda, J. B.; Sandler, S. I. *Chemical Engineering Science* 2003, 58, 27.
- (4) Sloan, E. D.; Koh, C. A. *Clathrate hydrates of natural gases*, 3rd ed.; CRC Press: Boca Raton, FL, 2008.
- (5) Anderson, B. J. *Fluid Phase Equilibria* 2007, 254, 144.
- (6) Velaga, S.; Anderson, B. J. "Phase equilibrium and cage occupancy calculations of hydrates using an ab initio intermolecular potential"; Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem., 2009, Salt Lake City, UT.
- (7) Ripmeester, J. A.; Ratcliffe, C. I. *Energy & Fuels* 1998, 12, 197.
- (8) Nihous, G. C.; Masutani, S. M. *Chemical Engineering Science* 2006, 61, 7827.

## Thermal Conductivity

The thermal behavior of hydrates has attracted considerable attention since the discovery that the thermal conductivities of hydrates are very different from that of ice. In addition, gas hydrate thermal conductivity is anomalously low, and general thermal properties are relatively insensitive to temperature, in contrast to the behavior expected for crystalline materials.<sup>2</sup>

NETL and the University of Pittsburgh have recently carried out non-equilibrium MD (NEMD) simulations of the thermal conductivity of methane hydrate and for the empty hydrate cage. They have found that, except at low ( $T \lesssim 50$  K) temperatures, the calculated thermal conductivities of methane hydrate and the empty cage system are nearly the same, ruling out host-guest coupling as a dominant factor for the anomalous thermal conductivity of methane hydrate.<sup>2</sup> This finding is remarkable in that although the thermal conductivity of methane hydrate can differ from ice Ih by as much as 15 times, the difference in thermal conductivity between an empty and a methane-filled hydrate is not significant.

In recent work at NETL, Jordan *et al.* have extended these studies to Xe hydrate and to CO<sub>2</sub> hydrate, obtaining for a wide range of temperatures remarkably similar thermal conductivities to those of methane hydrate as seen from Figure 4. Whereas the productivity of many naturally-occurring gas hydrate reservoirs would be thermally-limited, understanding and quantifying the thermal conductivity of the hydrate crystal is of the utmost importance.

## Mixed Hydrates

Recent work at NETL and WVU on the equilibrium of mixed CO<sub>2</sub>-CH<sub>4</sub> hydrates has illustrated that molecular-level processes result in macroscopic properties. Previous methods such as those incorporated by Klauda and Sandler<sup>3</sup> and Sloan and Koh<sup>4</sup> result in systematic underpredictions of the dissociation pressure for the mixed hydrate system, while the errors for the pure CO<sub>2</sub> and pure CH<sub>4</sub> errors were normally distributed around zero. The systematic error was due to lattice strain caused by the incorporation of two guests of varying size and guest-host interactions into the same hydrate lattice. This phenomena was originally described by Anderson, 2007 for the case of the propane-argon mixed hydrates. While the propane-argon mixture<sup>5</sup> would not be encountered in nature, systems such as CH<sub>4</sub>-C<sub>2</sub>H<sub>6</sub> and CH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub> could be common in thermogenically-

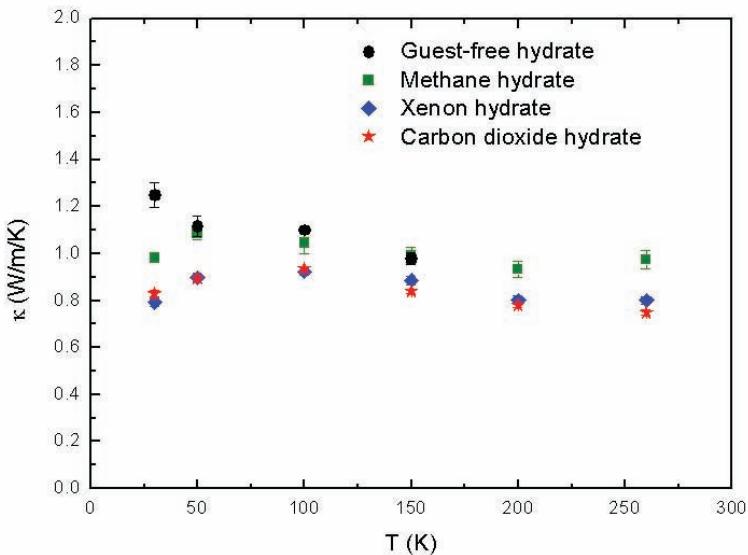


Figure 4:  
Calculated thermal conductivities of Xe, methane, and CO<sub>2</sub> hydrate, as well as for the empty hydrate cage. These preliminary results were obtained using the SPC/E two-body force field.

- produced hydrate deposits and  $\text{CO}_2\text{-CH}_4$  is being suggested as a methane recovery process. This phenomenon of the mixed hydrate lattice strain is a perfect example of a phenomenon in which macroscopic properties are governed by molecular-level events, and can be studied carefully using molecular-level modeling. In the case of  $\text{CO}_2\text{-CH}_4$  hydrate equilibrium, these equilibrium pressure errors could lead to large differences in predictions of  $\text{CO}_2\text{-CH}_4$  exchange processes and should be incorporated into reservoir simulation algorithms. As recently reported by Anderson and Velaga<sup>6</sup>, most thermodynamic models for hydrate dissociation pressure drastically overpredict the occupancy of  $\text{CO}_2$  in the small cage of the hydrate lattice compared to NMR data obtained near the hydrate equilibrium pressure.<sup>7</sup> Through the use of *ab initio* calculations (Figure 5), we have been able to develop a  $\text{CO}_2\text{-H}_2\text{O}$  potential that results in improved accuracy of  $\text{CO}_2$  and  $\text{CO}_2\text{-CH}_4$  thermodynamic predictions.<sup>6</sup>

### Hydrate Dissolution Simulations

- Currently, MD simulations are being performed at NETL and WVU to determine the dissolution rate and mechanism for  $\text{CH}_4$  and  $\text{CO}_2$  hydrates. In 2006, Nihous and Masutani<sup>8</sup> suggested that the concentration of the hydrate guest species at the interface between the desorption film and diffusive boundary layer may be much lower than ambient solubility. Preliminary MD simulations support this conclusion. Additionally, in the area near the hydrate-water interface, an increase in the solubility of  $\text{CO}_2$  may aid in increasing the rate of  $\text{CO}_2$  dissolution compared to  $\text{CH}_4$ . An understanding of the dissolution of gas hydrates in contact with undersaturated water is important to determining the long-term stability of gas hydrate reservoirs.

### Concluding Remarks

- At the nano or molecular scale, molecular modeling can be utilized to estimate key parameters such as thermal expansion, isothermal compressibility, thermal conductivity, and dissolution rates necessary for larger-scale models. These models can be extended to include relevant real-world conditions such as sediment composition and porosity and integrated into the reservoir simulation models at various degrees of detail, allowing the reservoir models to compute methane hydrate production scenarios over decade time scales.

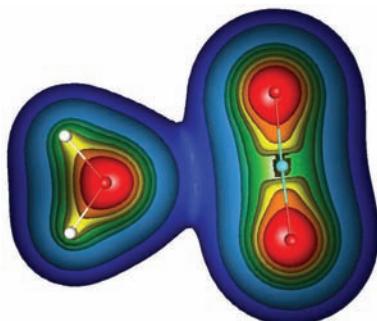


Figure 5: Electron density plot for the  $\text{CO}_2\text{-H}_2\text{O}$  pair interaction from *ab initio* calculations

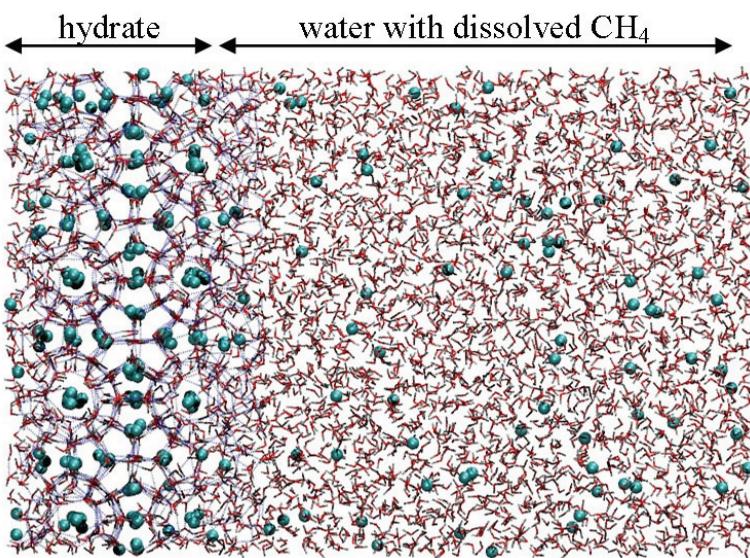


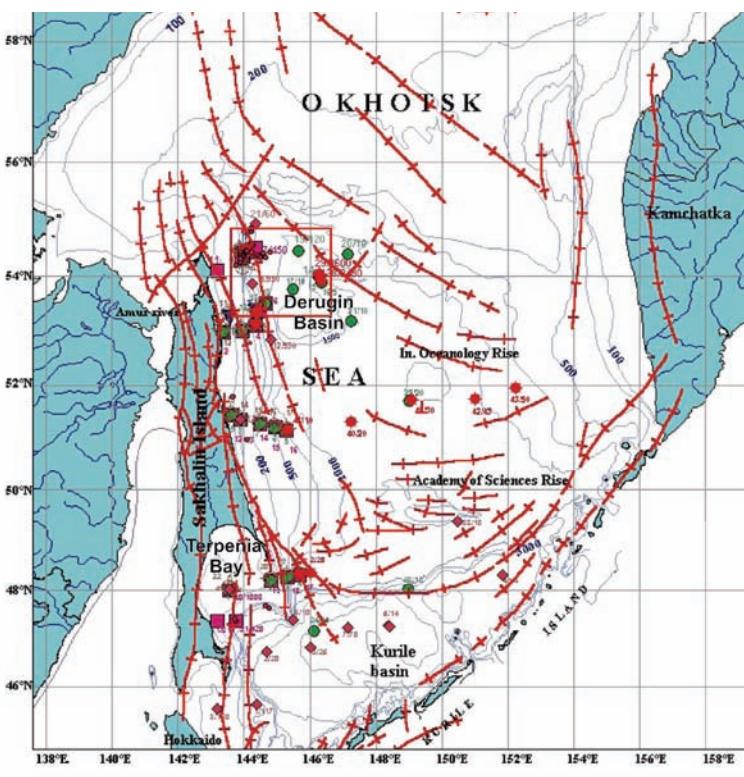
Figure 6: Snapshot of a molecular simulation of a dissolving methane hydrate

# Methane Fluxes and Gas Hydrates in the Sea Of Okhotsk

By Anatoly Obzhirov, Pacific Oceanological Institute FEB RAS, Vladivostok, Russia

It is widely accepted that methane contributes to the greenhouse effect driving global climate change, with the atmospheric methane concentration growing about 1% per year. The methane distribution found in water and sediment columns has been studied on the shelf, slope and in the deep part of the Sea of Okhotsk since 1984 (Obzhirov *et al.*, 1989, Obzhirov, 1993). Water column methane was measured on nine expeditions (from 1998 to 2004) within the framework of the Russian-German KOMEX-project (GEOMAR Reports 82, 88 and 110) and during five expeditions (2003, 2005-2007) of the Russian-Japanese-Korean project CHAOS. Background methane concentrations in the water column were monitored over the years and methane anomalies were found on all expeditions. Prior to 1988, background methane concentrations found in bottom water were ca. 20-30 nl/l, with methane anomalies coming to about 300-400 nl/l, usually above oil/gas deposits. After 1988, on the Sakhalin shelf and slope, background concentrations in the water column had increased to 70-80 nl/l and methane anomalies had risen to more than 10,000 nl/l, especially around the period of the Neftegorsk (May 1995) and Hokkaido earthquakes (September 2003). In this article we will look at the methane distributions in the water column and sediment, hydroacoustic bubble detection in the water column (referred to here as "flares" but also known as "plumes") and the relation of gas hydrate to methane fluxes.

Figure 1: Map of the Sea of Okhotsk with major faults, CTD and sediment core sample locations as well as areas named throughout the text.



- reach 1000-3000 nl/l. Methane concentrations in the sediment around these flares come to 5-10 ml/l. Methane monitoring showed that the surface water in shallow areas is oversaturated with values >1000 nl/l in the autumn and the spring. In these seasons, the methane flux is more intensive and will emanate from the surface water and into the atmosphere.

### Increasing Number of Methane Flares

During the LV29 Cruise in 2002, many new flares were found, with very few exceptions, along one single line - the fault zone that spreads from the northeastern shelf to the slope and to the bottom of the Derugin Basin. Some flares were found in fissures which cross the main fault (Figure 2). Significant methane anomalies in the water column accompanied the flares (5000-10,000 nl/l and more). The methane distribution in the water column shows that a large volume of methane exists in the sediment. The methane sources are the oil/gas deposits in the shelf area and gas hydrates located in the deep part of the slope.

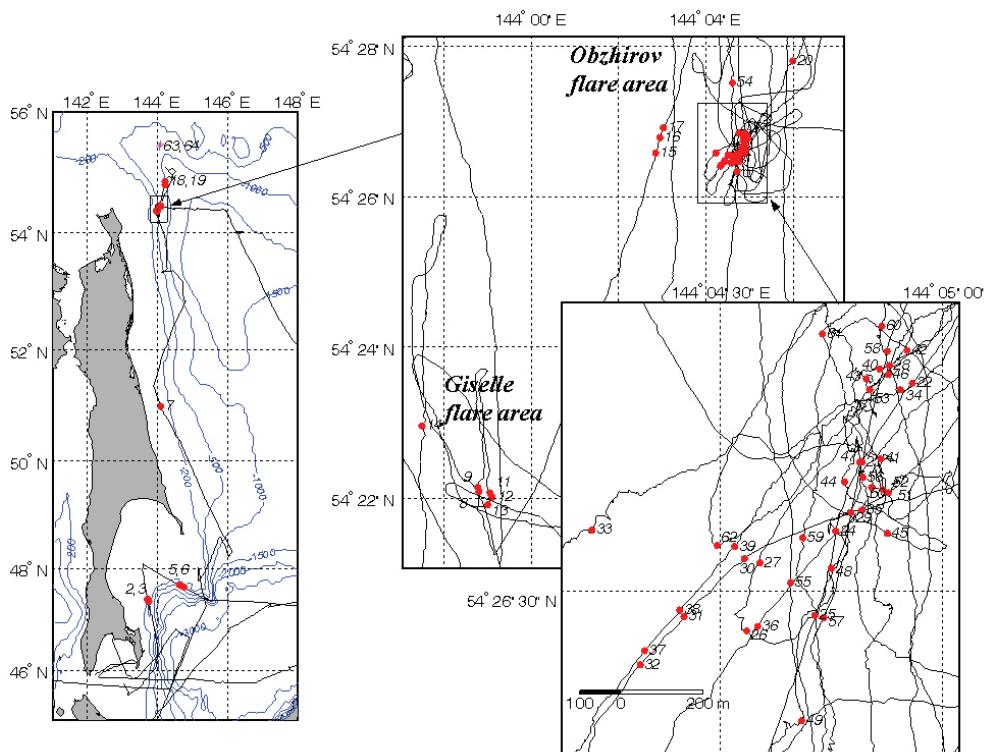
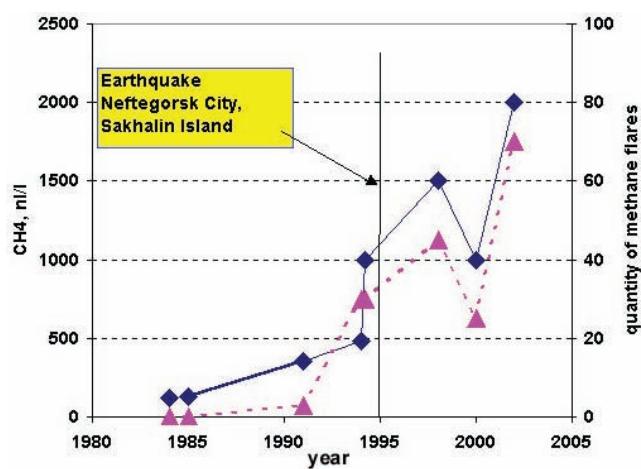


Figure 2: The northeastern Sakhalin shelf and slope of the Sea of Okhotsk. The square shows a region where detailed gas geochemical investigations have been carried out. Many new flares were found along the line of the flares Gisella and Obzhirov on the Sakhalin North-East slope of the Okhotsk Sea. Red circles indicate flare positions.

At the time of the cruise (June 2002), seismic activity connected to an earthquake in Sakhalin was registered (Figure 3). A large volume of methane escaped from the sediment and into the water column and the atmosphere from the northeastern Sakhalin shelf and slope area. In a deeper part of the Derugin Basin, water column methane concentrations did decrease to background volume levels due to the sediment thickness there being less. Oil/gas bearing sediments and gas hydrate layers were also not present at this location.

Figure 3: Variations in methane concentrations in the water column and the number of flares on the Sakhalin North-East shelf and slope. Triangles show the number of flares, squares depict methane concentrations in bottom water. The increase in the number of flares after 1995 is suggested to be caused by the major earthquake in Neftgorsk (magnitude 7.6).



## Gas Hydrate and Methane Fluxes

- Gas hydrates were found in the Sea of Okhotsk near Paramushir Island in 1986 (Zonenshain *et al.*, 1987). This area has gas hydrate fields in near-surface sediments (1-5 m below the seafloor). The BSR (Gaedicke *et al.*, 1997) shows that the thickness of the gas hydrate layer is about 200 m.
- Gas hydrate was discovered through the gas vents that form where gas hydrate decomposes in fault zones. Gas bubbles (mostly methane) from decomposing hydrates rose through the seafloor and into the water column. These bubbles create strong backscattering in echograms recorded by echosounders that look like flares when visualized and are as tall as 200-300 m (Figures 4 A,B,C,D).
- Methane concentrations inside the flare were >1000 nl/l. The concentration decreases sharply outside the flare and at the fault zone. The methane flux is directly related to the gas hydrate. In the area of the gas hydrate field, the methane concentration found in the bottom water was near background levels, about 40-50 nl/l. It is supposed that the methane anomalies are created by decomposing gas hydrate and the flux of methane from under the gas hydrate layers (Figure 5).

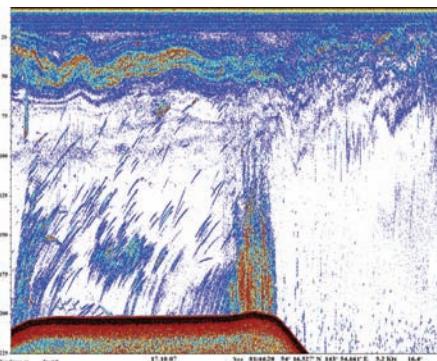


Figure 4A: Hydro-acoustic image of single beam echosounders (echograms) are commonly used to detect gas bubbles in the water column. Due to their shape in echograms these features are called "flare". The images shows a gas flare on the northeastern Sakhalin shelf. Y-axis provides depth in m (flare from 200 m to 80 m water depth).

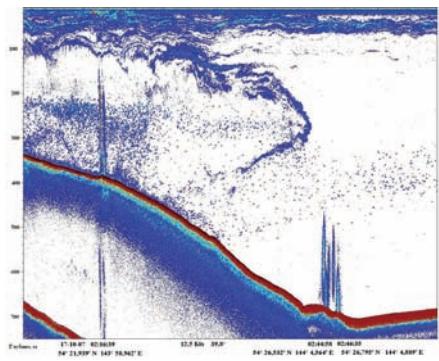


Figure 4B: Gas flares on the northeastern Sakhalin slope. Y-axis provides depth (left flare from 430 m to 130 m water depth; Gizella flare area; right flare from 680 m to 420 m water depth).

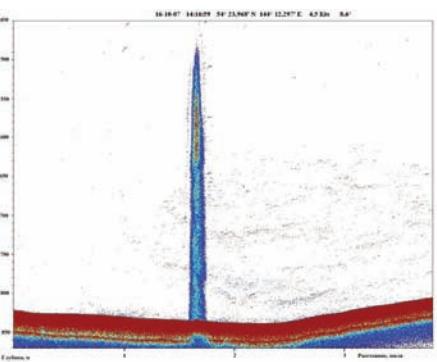


Figure 4C: Gas flare at the bottom of the Derugin basin (flare reaches from 820 m to 480 m water depth). Y-axis reads depth in m.

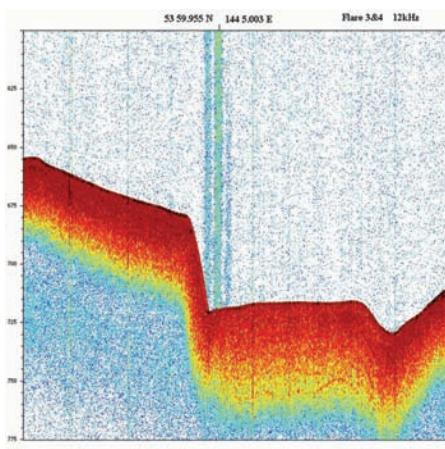


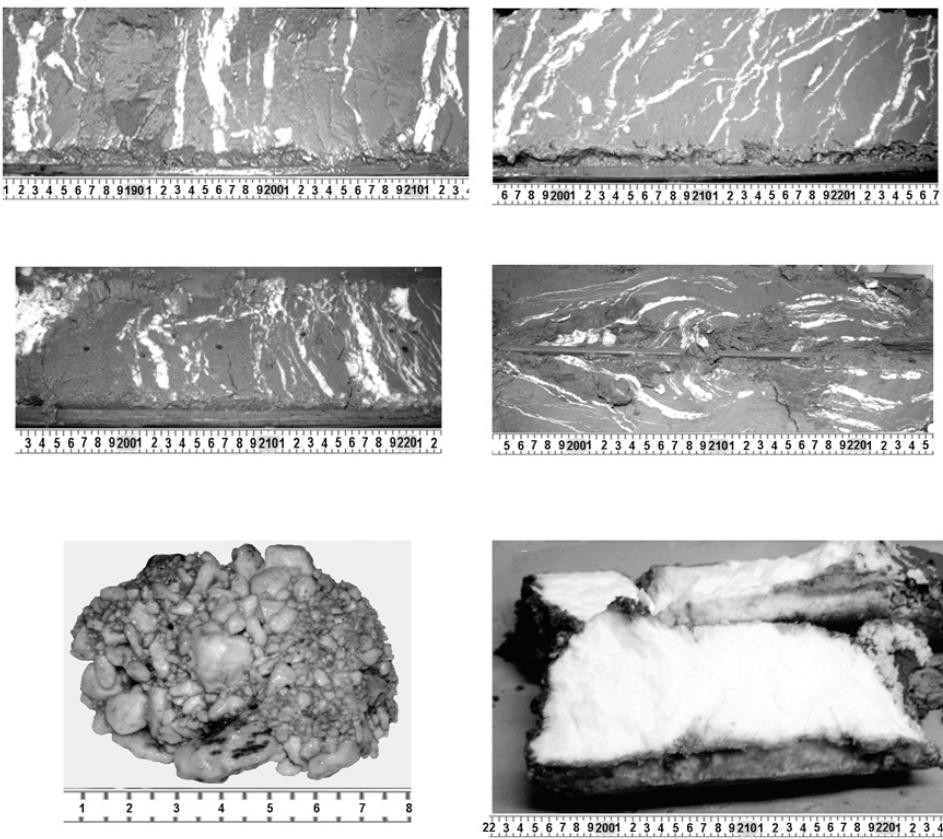
Figure 4D: Flare site "Lavrentiev" with almost vertically rising gas bubbles that are released at the foot of a steep, fault-induced escarpment. Y-axis gives depth in m.

- This regularity was used for identifying gas hydrate on the northeastern Sakhalin shelf and slope (Obzhirov *et al.*, 2002; Obzhirov *et al.*, 2004). In 1989 (Obzhirov *et al.*, 1989), flares were found very similar to those observed in the Paramushir area, where in 1991 gas hydrates were found (Ginsburg *et al.*, 1993) in a water depth from 400 to 800 m and in near-surface sediments (0.5-6 m below the seafloor). The gas content of the gas hydrate was mostly methane. Sediment cores decomposed within half an hour due to the gas hydrate degassing. The methane content of those gas hydrate-bearing sediments was usually more than 10 ml/l, which is 1000 times the background value.
- More methane anomalies were found in the bottom water (2000-5000 nl/l) in the Barite Hill area. Sediments between 2 to 6 m below the seafloor show the same methane anomalies. On the strength of this, we may conclude that gas hydrates probably exist in this area. Anomalies were also found in the slope area about 40 miles from Terpenia Bay in a southeaastern direction. Here, significant methane concentrations (2791 nl/l) were found in intermediate water depth (137 m), the surface, water (963 nl/l, depth 50 m) and the bottom water layer (337 nl/l, depth 719 m). A possible explanation for the very high concentrations in the intermediate water layer is that this water mass is a intrusion from the shelf area of Terpenia Bay. The methane anomaly in the bottom water are caused by bubble release indicating that gas hydrates may occur in this area.

### **Summary**

The main results of our investigations are summarized below:

- We discovered methane flares on the eastern Sakhalin slope and shelf. Methane concentrations in the water column inside and near the flares usually ranged from 1000 to more than 20,000 nl/l. Methane bubbles emanate from the sea floor via the fault zone and spread 300-400 m upwards in the slope area to the surface.



*Figure 5: Different morphological manifestations of gas hydrate, Sea of Okhotsk.*

## REFERENCES

- Ginsburg G.D., Soloviev V.A., Cranston R.E., Lorenson T.D., Kvenvolden K.A. (1993) Gas hydrates from the continental slope, offshore Sakhalin Island, Okhotsk Sea//*Geo-Marine Letters*, 13, 41-48.
- Gaedicke Ch., Baranov B. et al. (1997) Seismic stratigraphy, BSR distribution and venting of methane-rich fluids west off Paramushir and Onecutan Island, Northern Kurils//*Marine Geology*, V.116.3.
- Obzhirov A.I., Kazansky B.A., and Melnichenko Yu.I. (1989): Effect of the sound scattering in water of the Okhotsk Sea. // *Pacific Geology*, N2: 119-121 (in Russian).
- Obzhirov A.I. (1993): Gas geochemical fields in bottom water of seas and oceans; *Science Publ.*, Moscow: 139 pp. (in Russian).
- Obzhirov A.I. et al., (2002) *Methane monitoring in the Sea of Okhotsk. Dalnauka, Vladivostok*, 250 p. (in Russian).
- Obzhirov A., Shakirov R., Salyuk A., Suess E., Biebow N., Salomatin A. (2004). Relations between methane venting, geological structure and seismo-tectonics in the Okhotsk Sea// *Geo-Marine Letter*. Vol. 24 № 3., p. 135–139.
- Zonenshain L.P., Murdmaa I.O., Baranov B.V., et al, 1987, Submarine gas vent in the Sea of Okhotsk to the west from Paramushir Island: *Oceanology*, 27, 795-800 (in Russian).
- The methane source are oil/gas-bearing sediments, methane discharge of decomposing gas hydrate and bacteria-generated methane production. Methane anomalies exceed background values by about 10-10000 times.
- The methane flux goes from the sediment through the water column and to the sea surface further into the atmosphere, mostly in shelf and slope areas. The methane values increase in the spring and autumn.
- The methane flux from the seafloor increases in periods of seismo-tectonic activity.
- Water layers that show methane anomalies from shelf intrude into the water column in the slope area.
- Methane anomalies in the bottom water layer reach 70-100 m in thickness in the Barite Hill area of the Derugin Basin. Many new flares were found (more than 100) in the area of the formerly discovered Erwin, Gisella and Obzhirov flares. They create acoustic anomalies in echograms (flares) reaching a height of 200-300 m when visualized. Inside the flares, the methane concentrations reach about 5000-20,000 nl/l, outside they are still about 500-3000 nl/l.
- New flares appeared between 2000 and 2007; none had been observed in this area prior to 1999 (see GEOMAR Report 88, cruise Ge99, 1999). This means that in this period (1988-2007) seismo-tectonic activity opened a fault zone for gas (methane) to come to the seafloor surface. This fits very well with the documented episodes of the Sakhalin earthquakes in 1994, 1995, 2000, 2001, 2003 and 2007.
- Methane anomalies in the water column (500-2500 nl/l) were found in the shelf and slope area of Terpenia Bay in a southeastern direction. Here, the methane sources are oil/gas-bearing sediments on the shelf and may be gas hydrates on the slope.
- The methane distribution measured in sediment cores with gas hydrate from Sakhalin Slope and Barite Hill is very similar. The sediment cores from those regions show huge methane anomalies (about 1-3 mM/kg). It looks as if gas hydrate is distributed in the sediments of the Barite Hill area in a similar way as in the area of the Sakhalin slope.
- Outside the gas hydrate and barite bearing areas, the sediment methane concentrations are on background levels (0.0001-0.0003 mM/kg).

## Conclusion

The increasing quantities of methane flares and in methane concentration since 1988 are connected with seismo-tectonic activation of the faults in the Sea of Okhotsk. This concept fits well with data from mud volcanoes in the eastern Sakhalin area. Their activity seems to be connected to the growing seismo-tectonic oscillations that lead to the opening of fault zones and gas/fluid migration. Moreover, a new mud volcano formed. The average methane flux from the sediment into the water column and to the atmosphere in the shelf and slope area is 1,000,000 m<sup>3</sup> per year. It can thus be stated that the methane flux from the Sea of Okhotsk will increase the atmospheric methane concentration, adding to the greenhouse effect. Furthermore, the fluxes will increase in periods of seismo-tectonic activity

## The Methane Hydrate Fellowship

- In response to the Methane Hydrate Research and Development Act of 2000 that authorizes the Secretary of the U.S. Department of Energy (DOE) to “promote education and training in methane hydrate resource research and resource development,” the DOE’s National Energy Technology Laboratory (NETL) launched the Methane Hydrates Fellowship in the spring of 2006. The Fellowship provides financial support to post-graduate and post-doctoral students for self-directed, methane hydrate research projects.
- The Fellowship program, in cooperation with sponsoring federal laboratories, research organizations and accredited universities, is implemented by the National Research Council (NRC) in the selection of worthy M. Sc., Ph. D., and post-doctoral level candidates through a national competition. Applications are evaluated by a group of panelists who are chosen on the basis of their stature and experience in the field of methane hydrates. Their evaluations are the basis from which final awards are made on the behalf of NETL.
- An applicant’s election criteria includes their degree, training, professional experience, and research experience in any appropriate discipline or combination of disciplines required for their proposed project. Applicants must submit a detailed research proposal describing the methane hydrate research that they intend to pursue at their university or laboratory. The proposal must be the original work of the applicant and be approved by their proposed advisor.
- Currently, the Fellowship, which has supported three excellent geochemistry and microbiology researchers to date, is looking to broaden the disciplines and scope of projects supported under the program. This includes research focused on utilizing and developing advanced geological and geophysical tools and techniques for *in situ* detection, characterization and distribution of naturally occurring gas hydrate accumulations. Projects that improve understanding of processes that lead to the formation and dissociation of hydrate in the natural environment, thus addressing key issues related to methane hydrates as a potential resource as well as their potential role in global climate change, are also of interest.
- Application deadlines for the 2009 Fellowship program are February 1 and August 1. Fellowship opportunities are open to all citizens of the United States.
- For more information on the DOE/NETL Methane Hydrate Fellowship Program, please visit <http://nrc58.nas.edu/pgasurvey/data/aobooks/rapbooks.asp?mode=frntmtr&progctr=AH&seq=20/>. For more information on the research projects and research fellows, please visit <http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/GradFellowship.html/>.

## Hydrate Researchers: The Next Generation

- To study methane hydrates is to be a student of all types of sciences, much in the same way that a master chef is always on the lookout for new flavor combinations from different cultural cuisines. As for those students currently toiling away on methane hydrate research projects in the field and in labs across the United States, they are the apprentices. Working with and learning from their teachers, these students bring their own special blend of ingenuity, innovation and insight to the prep table. Facing the serious issues of global climate change, energy security, and seafloor stability, these "masters" and "apprentices" of hydrate research contribute to further developments in the science of methane hydrate.
- To this end the Department of Energy's National Energy Technology Laboratory (DOE/NETL) supports both the teachers and the students who contribute to our growing understanding of methane hydrates through projects supported under the National Methane Hydrate Research and Development Program.
- Students contribute to the research process through opportunities currently available at over 40 universities participating in the Program. In the spring of 2005, there were over 100 undergraduate, graduate, and post-doctoral students involved in methane hydrate research. Today, that number has grown to over 180, with 23 students participating in research at national laboratories, where they are gaining a wealth of experience.
- In the pages that follow, you will meet a few members of the next generation of methane hydrate scientists. In one story, you will find a father of three that realized a career as a pharmacist was not the path for him, and through volunteer work in a microbiology lab found what would become his life's work. You will also meet a student who found geophysics more fascinating than veterinary medicine and now utilizes marine electromagnetic methods to remotely image methane hydrates.
- These are just two of the varied and interesting tales that our future scientists have shared with us. Coming from points as distant as Korea and India and as close as Canada and the United States, these students are supporting methane hydrate research through their many contributions. They are the future innovators whose efforts are, in part supported by the National Methane Hydrate Research and Development Program.

### Kaushik Bandyopadhyay

**Geology (B. Sc. 1999), Jadavpur University, Calcutta, India**

**Geophysics (M. Sc. 2001), Indian Institute of Technology, Kharagpur, India**

**Geophysics (Ph. D. expected 2009), Stanford University**

Armed with degrees in Geology from Jadavpur University, and Geophysics from the Indian Institute of Technology, Kharagpur, India, Kaushik Bandyopadhyay moved to the United States to pursue his Ph. D. in Geophysics from Stanford University in Stanford, California. While at Stanford, Kaushik attended a lecture by Dr. Amos Nur that introduced the resource potential of methane hydrate.

According to Kaushik, it was a different Stanford professor that helped solidify his interest in methane hydrates, "My research interests lie in



- rock physics and Dr. Jack Dvorkin showed me an interesting property of methane hydrate-bearing sediments having a high seismic velocity, yet an unexpectedly high attenuation."
- Kaushik uses geophysical measurements (seismic or electromagnetic) to infer different rock properties such as lithology, porosity, and pore fluids. "My main research focus is to improve theoretical rock physics models for anisotropic and attenuative rocks through an understanding of their geological origin," says Kaushik. "A part of my research is applying these models to methane hydrate reservoirs in order to gain a better understanding of their seismic behavior."
- Currently, Kaushik measures the ultrasonic velocity anisotropy in pure clay minerals. "Elastic properties of clay minerals are important, but largely unknown parameters needed to interpret the seismic signatures from clay-bearing rocks," says Kaushik.
- As for the future, Kaushik plans to continue his research to develop a greater understanding of elastic properties of rocks relevant to conventional and unconventional energy resources. For now though, Kaushik says that, "Guidance from my advisor Dr. Gary Mavko and inspiration from my wife, Tania Dutta, help to keep me motivated in my studies."
- Kaushik is supported under NETL Project DE-FC26-05NT42663. Please see [http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH\\_42663RockPhysics.html](http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH_42663RockPhysics.html) for more information regarding this project.
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### **Gaurav Bhatnagar**

**Chemical Engineering (B. Sc. 2002 and M. Sc. 2003), Indian Institute of Technology, Delhi, India**

**Chemical Engineering (Ph. D. 2008), Rice University**

Prior to coming to the United States, Gaurav Bhatnagar knew of methane hydrate research that was being pursued in his native India. But with his background in chemical engineering, Gaurav felt that natural gas hydrate research was a very different field of study requiring a very different set of skills. After obtaining his Bachelor's and Master's in Chemical Engineering from the Indian Institute of Technology in Delhi, Gaurav moved to Houston, Texas to pursue his Ph.D. at Rice University, where he found that his chemical engineering training had better prepared him for gas hydrate research than he thought.

It was through his work with Ph.D. advisor Dr. George Hirasaki that Gaurav was first encouraged to pursue gas hydrate research. "Dr. Hirasaki helped me realize how conventional chemical engineering knowledge could be applied to study natural gas hydrate systems," says Gaurav. "It was Dr. Hirasaki's enthusiasm to explore new fields of study that motivated me to apply my strengths in modeling and simulation in a very different area, such as hydrates." While at Rice, Gaurav also worked in close collaboration with Dr. Jerry Dickens and Dr. Brandon Dugan, which "was very helpful in jumpstarting my research and allowed me to learn various aspects of earth science that I never fully appreciated as a chemical engineer," adds Gaurav.

His work at Rice focused on modeling gas hydrate accumulations over geologic timescales, which helped develop an understanding of different hydrate systems through a unified perspective. "We were trying to identify



- how much hydrate can form at a given site and what controls this distribution," notes Gaurav. "To this end, we identified key dimensionless groups and parameters that control gas hydrate saturation at different geologic sites. This helped us to predict the conditions suitable for finding hydrate 'sweet spots' that might be feasible to exploit economically," he adds.
- To assist in accomplishing this feat, Gaurav and others developed their own "relatively complex numerical models and codes to study the temporal evolution of dynamic gas hydrate systems. We came up with special scaling schemes that helped condense the data from hundreds of simulations into simple hydrate maps. We also identified new proxies for quantifying gas hydrate saturation and showed how lithology can dominate local gas hydrate distribution," says Gaurav.
- After successfully defending his thesis in February 2008, Gaurav accepted a position with Shell Global Solutions as a gas hydrate researcher focused on flow assurance issues related to hydrates and geohazards associated with drilling through shallow hydrated systems. From his days as a student, Gaurav holds fond memories of winning the Society of Petroleum Engineers (SPE) student paper contests (both regional and international) in 2006, as well as a best student paper award at the American Geophysical Union (AGU) 2006 Fall Meeting for his work on hydrates. "It was especially rewarding to be recognized by both the industrial and the academic community. I was glad I was able to communicate the importance of our work and ideas to very different audiences," he adds. When he is not working, Gaurav enjoys playing cricket and racquetball, travelling and listening to classical Hindustani music.
- Gaurav was supported under NETL Project DE-FC26-06NT42960. Please see [http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH\\_42960DetectProd.html](http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH_42960DetectProd.html) for more information regarding this project

### **Brandon Briggs**

- **Biology (B. Sc. 2003) and Microbiology (M. Sc. 2007), Idaho State University**
- **Oceanography (Ph. D. expected 2011), Oregon State University**
- If Brandon Briggs had followed his original plan, one would be able to find him behind the pharmacist's counter filling prescriptions. "When I started college at Idaho State University (ISU), I wanted to be a pharmacist, but I quickly realized that it was not the right choice for me," says Brandon. "I began volunteering in a microbiology lab, where I helped to develop a technique to concentrate DNA from an aquifer."
- Brandon pursued his interest in microbiology which eventually led him to his current work in hydrate research. "After completing my Bachelor's of Science in Biology from ISU, I stayed on there to complete my Master's of Science in Microbiology. For my master's work, I grew a bacterium that reduced iron at a pH of 3," says Brandon. "It was during a quick presentation by Dr. Frederick Colwell of Oregon State University (OSU) that I first learned of the importance microbial influences in methane hydrates."
- When he is not chasing his three kids (ages 4 years, 2 years, and 2 months) around or performing science experiments for his oldest on "Science Saturdays," Brandon can be found working on his Ph. D. with Dr. Colwell, studying the microbial distributions of methane charged sediments.



- Using techniques that extract the DNA and RNA from microbes within the sediment, Brandon is able to use DNA measurements like terminal restriction length polymorphism (t-RFLP) to determine the microbial diversity. “I can also do a more detailed analysis and sequence specific parts of the DNA to determine what type of taxa are found below the seafloor,” notes Brandon. “Usually the microbes that I find have not been previously described, so the only way to identify the microbes is to infer an identity from related DNA sequences.”
- Even though getting enough samples to work with is a frustrating limitation, Brandon feels that, “the interdisciplinary nature of hydrates makes the work most rewarding. It will take geologists, chemists, modelers, and microbiologists to unlock the mysteries of hydrates,” says Brandon. “Knowing that what I am studying will someday help mankind is pretty motivating. My research adds a piece to the puzzle that someone else can use to further us along even more.”
- Brandon is supported under NETL Project FLU5A425/100400. Please see [http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH\\_FLU5A425Methanogen.html](http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH_FLU5A425Methanogen.html) for more information regarding this project.
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### **Michael Eaton**

- **Chemical Engineering (B. Sc. 2002) and Petroleum Refining (M. Sc. 2003), Colorado School of Mines**
- **Materials Science (Ph. D. 2007), State University of New York**
- Michael Eaton received his introduction to methane hydrates as a grad student working in the lab for Dr. Dendy Sloan at the Colorado School of Mines (CSM) in Golden, CO. Michael was pursuing his Master’s Degree in Petroleum Refining when fate stepped in, “Going into graduate school, I had very little knowledge of what a hydrate was, or just how interesting they are. I knew I wanted an advanced degree, but had no particular gravitation towards hydrates,” says Michael. “Dendy Sloan, a giant in the hydrates world, offered me a research position in his lab, and the rest is history.”
- After completing his Master’s at CSM, Michael enrolled at the State University of New York in Stony Brook, NY to pursue his Ph.D. in materials science, “My advisor at Stony Brook, Dr. Devinder Mahajan, provided the opportunity for me to continue studying hydrates. I have been incredibly fortunate to have worked with many world-class researchers and in general some great people along the way in my studies,” says Michael. “Each has shown me a different aspect of what it means to be a scientist.”
- His research while at CSM used neutron and X-ray diffraction to study the cage occupancy of both xenon and methane hydrates as a function of temperature and pressure. “Using a technique known as Rietveld analysis, I analyzed the diffraction patterns and numerically extracted such values,” he says. “For my Ph.D., I constructed a reactor to study the formation and decomposition kinetics, morphology, and distribution of hydrates in different types of sediments. In order to extract such data from simple pressure and temperature measurements within the reactor, I wrote a computer program to model the 2-Dimensional transient thermal behavior of the reactor.”
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- Michael's experiences in the lab provided some unique opportunities to obtain his data. "One of my favorite memories was being able to perform some of my master's work at Oak Ridge National Laboratory with guidance from Claudia Rawn and Bryan Chakoumakos," says Michael. "I learned more in a week about X-ray diffraction from Claudia and Bryan than I did the rest of the time on my master's -- they were incredibly patient with me."
- After obtaining his Ph.D., Michael accepted a full-time position in the oil and gas industry. When he is not at work, he can be found spending his free time with his wife Erin or out hitting the pavement, "I run quite a bit. It helps me burn off stress, and I also find that I get most of my best thinking done then."
- Michael was supported under NETL Project EST-380-NEDA. Please see [http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/EST-380-NEDA\\_SubsurfaceMimic.html](http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/EST-380-NEDA_SubsurfaceMimic.html) for more information regarding this project.
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## Alex Hangsterfer

- **Chemical Oceanography and Biology (B. Sc. 2004), Roger Williams University**
- **Chemical Oceanography (M.Sc. expected 2009), Scripps Institution of Oceanography**

After completing her undergraduate studies as an ocean-based environmental chemistry and biology student at Roger Williams University in Bristol, RI, Alex Hangsterfer first became interested in methane hydrates while working as a visiting researcher at Woods Hole Oceanographic Institution (WHOI). It was there that she first saw live, videotaped footage of methane bubbling to the ocean's surface. "I was working with Chris Reddy, who does a lot of work with oil spills, and at the time and there were these seeps that were generating visible oil slicks on the sea surface," says Alex. "...once I saw this footage, it sparked my interest in what was really going on with sub-seafloor methane and if there is a way that we can harness its energy potential if we know more about the subseafloor hydrological systems associated with methane hydrate deposits."

Currently finishing her Masters at Scripps Institution of Oceanography, Alex's focus is on the geological settings, geochemical signatures, and microbial communities associated with sub-seafloor gas hydrate-bearing sediments. "My focus while here has been to determine how these different parameters are interconnected and how they influence one another in gas hydrate-bearing sediments and what effect the interaction between the parameters has on gas hydrate occurrence," she notes. "For example, how does a microbial community structure vary with changes in depth and geochemical horizons; which microbes present in the sediments contribute to the production of the observed geochemical signatures, or how does permeability act to constrain gas hydrate occurrence?"

To help answer these questions, Alex had been working on extracting bacterial and archaeal DNA from sediment samples taken from cores drilled in the Krishna-Godavari Basin in the Indian Ocean. "This can be a challenge due to the extremely low abundance of microbes deep within the sediment column," she says. Alex has also worked with scientists from Lawrence Berkeley National Laboratory to apply extracted DNA to a phylochip. This DNA microarray can identify a multitude of archaeal and



- bacterial groups present in the sediment sample. "This analysis allows scientists to track how microbial community structure is changing from sample to sample, encountering varying depths, geochemical horizons and geological settings, as in the case of my samples" notes Alex.
- Using her innate creativity that is bolstered by encouragement and support from a host of teachers and professors, Alex is motivated by the possibility of making new connections between the biological, chemical and geological systems associated with gas hydrate occurrences. Some favorite memories involve being at sea and experiencing first hand how methane hydrates and seeps are investigated. One of her greatest experiences was "...the opportunity to go to the bottom of the ocean in the *DSV Alvin* to investigate and recover samples from methane-rich sediments off the coast of Costa Rica, and experience what the deep ocean is truly like for myself," Alex recalls. "It will never cease to amaze me how life has adapted to thrive in these deep, dark and cold conditions; it is truly an honor to experience it so closely. I hope to take many more trips to continue to explore the bottom of the ocean in my lifetime!"
- Alex is supported under NETL Project FLU5A425/100400. Please see [http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH\\_FLU5A425Methanogen.html](http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH_FLU5A425Methanogen.html) for more information regarding this project.
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### **Antone Jain**

**Environmental Engineering (B. Sc. 2007, M. Sc. expected 2009),  
Massachusetts Institute of Technology**

As an environmental engineering undergrad at Massachusetts Institute of Technology (MIT) in Cambridge, MA, Antone Jain found in methane hydrates a perfect way to combine his interest in the ocean with finding quantitative approaches to the problems found in energy and the environment. "Dr. Ruben Juanes joined my department during the summer before my senior year and I found his methane hydrate research to be a perfect match for me," notes Antone. Equipped with the idea of what he wanted to pursue, Antone completed his degree and chose to stay at MIT to pursue his M. Sc. degree in hydrology.

His current work with Dr. Juanes involves looking at, "Methane fluxes in the Hydrate Stability Zone (HSZ), which are dynamic processes, as evidenced by the observations of co-existence of gas and hydrate, diverse hydrate morphologies and active gas venting on the seafloor," says Antone. "Our computational modeling explores how the interplay of multiphase flow, geomechanics, and hydrate formation/dissociation dynamics cause distinct methane flux paths in the HSZ. In our coupled grain-scale model, we use the discrete element method to simulate the soil mechanics and a two-phase flow pore network to simulate free gas and brine."

Through his work with Dr. Juanes, Antone has found that with enough capillary pressure, free gas migration occurs by one of two modes: capillary invasion or by fracture opening and propagation. The results of Dr. Juanes's and his work imply that in very fine sediments, hydrate will tend to form in veins along a fracture network. In coarser sediments the hydrates will fill the pore space more uniformly. Their next steps involve incorporating hydrate formation into the grain-scale model and validation



- with laboratory experiments. After validation and using their grain scale knowledge, the plan is to model gas migration at the geologic scale.
- Motivated by his interests in science and furthering our understanding of methane hydrate, Jain believes that the work he is involved with today will contribute to the rapidly growing body of knowledge on methane hydrates, and that this body of knowledge will enable accurate assessments of hydrates as a prospective energy resource and component in the global carbon cycle. He sums it up best, "I hope that the application of this knowledge will improve the quality of life for people. There are so many scientists who have worked for many years on understanding geologically occurring methane hydrates, that I view myself as one young contributor in a huge and growing research community. The collective work of the methane hydrates research community can have a great impact on people's lives."
- Antone is supported under NETL Project DE-FC26-06NT43067. Please see [http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH\\_43067GasHydSediments.html](http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH_43067GasHydSediments.html) for more information regarding this project.



### **Jongwon Jung**

- Civil and Environmental Engineering (B. Sc. 1999 and M. Sc. 2004)  
Korea University**
- Civil and Environmental Engineering (Ph. D. expected 2009), Georgia Institute of Technology**
- Since 2006, Jongwon Jung has pursued his Ph. D. in Civil and Environmental Engineering from Georgia Institute of Technology in Atlanta, Georgia. There he is researching methane production from hydrate-bearing sediments with his advisor, Dr. Carlos Santamaria. "He showed me the path to becoming a scientist and provided me an opportunity to study methane hydrates," says Jongwon.
- Prior to working with Dr. Santamaria at Georgia Tech, Jongwon completed both his bachelor's and master's degrees in Civil and Environmental Engineering from Korea University located in Seoul, South Korea.
- Currently Jongwon's research is focused on understanding the pore scale interaction between hydrate and sediment particles during formation and dissociation. "I measure temperature, pressure, electrical conductivity, mechanical impedance, bonding and tensile strength," says Jongwon. "I am also finalizing several studies on hydrate properties at small scales during formation and dissociation. In the mean time, I work on advancing numerical models to process data received from one-dimensional experiments on gas production during hydrate dissociation and formation."
- His research has created very many memorable moments, with his favorite being, "the first time I made hydrate in the lab. After several weeks of keeping the system within the stability field and after many previous frustrations with heat loss from the chamber, the experience was made all the more memorable," says Jongwon.
- For Jongwon, the study of hydrate bearing sediments requires "deep knowledge in many different areas, including chemistry, geology, physics,

- and geomechanics," he says. "It is both stimulating and challenging!" While his research and studies keep him busy, when Jongwon does find time to relax a little he enjoys playing tennis or swimming, but above all, "I love playing with my son."
- Jongwon is supported under NETL Project DE-FC26-06NT42963. Please see [http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH\\_42963MethaneRecov.html](http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH_42963MethaneRecov.html) for more information regarding this project.
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### **Peter Kannberg**

**Geological Sciences (B. Sc. 2004), University of Rochester  
Geophysics (M. Sc. expected 2009), Oregon State University**

As an undergrad at the University of Rochester in Rochester, NY, Peter Kannberg spent a summer working as an intern at Pacific Northwest National Laboratory (PNNL) in Richland, WA, imaging clastic dikes using an infrared (IR) camera. As a result of this experience, use of IR imaging for the identification and quantification of gas hydrates in sediment cores was proposed to the Ocean Drilling Program (ODP). Peter, "gave a presentation to Dr. Frank Rack of ODP demonstrating the use of infrared cameras on a simulated hydrate core." This led to the use of IR imaging onboard the *R/V JOIDES Resolution* (JR) during ODP's Leg 204 Expedition on Hydrate Ridge. "The fast paced nature of studying something as ephemeral as hydrates made for a very exciting first experience," recalls Peter who participated as a shipboard technician.

Peter's experience during Leg 204 led to his eventual acceptance of a position as a full-time marine technician, a position that provided Peter a front-row seat to a wide-variety of research opportunities that very few are fortunate to experience. "Being a part of ODP and IODP (Integrated Ocean Drilling Program) was an incredible experience. The opportunity to participate in research and work with leading scientists from such a wide range of oceanographic disciplines was invaluable," says Peter. "Phil Long, my advisor at PNNL, was instrumental in exposing me to hydrate research, and getting my foot in the door at ODP, an opening that has allowed me to sail on three hydrate expeditions aboard the *JOIDES Resolution*."

Peter is now at Oregon State University pursuing his Master's in marine geology and geophysics. His work there with Dr. Anne Tréhu involves using temperature data taken during India's National Gas Hydrate Program (NGHP) Expedition 01 to map heat flow in hydrate-bearing sediments on the Indian margin. "I was fortunate to sail as the downhole tools technician during the expedition, not knowing at the time that a couple of years later I would be using the temperature data collected by those tools in my master's research," says Peter. "I am currently reviewing the temperature data from that expedition. By comparing the geothermal gradient derived from those temperature measurements to the depth of the Bottom Simulating Reflector found in seismic data, we will be able to map the heat flow of the region."

Where he sees himself in ten years is difficult to say, but Peter notes that, "wherever my career takes me, the research I will conduct will be applicable to societal problems. I see energy research as having increasing importance as nations continue to develop, and gas hydrate could provide abundant

- energy for those countries putting forth the effort to better understand these deposits.”
- Peter is supported under NETL Project DE-NT0005669. Please see [http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH\\_05669HydratesIndia.html](http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH_05669HydratesIndia.html) for more information regarding this project.
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### **Frank Kinnaman**

**Chemistry (B. Sc. 2003), University of California – Santa Barbara**

**Marine Science (Ph. D. 2008), University of California – Santa Barbara**

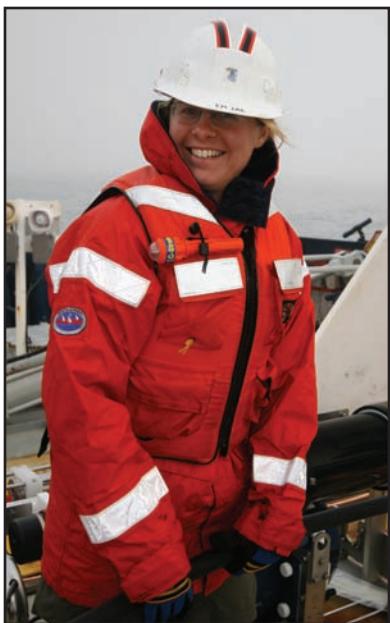
Frank Kinnaman, who in 2008 received his Ph. D. in Marine Science from the University of California in Santa Barbara, CA (UCSB), first became interested in methane hydrates while working as an undergraduate intern. This interest led to his graduate work studying microbial oxidation of methane and hydrocarbon seep sediments of the Coal Oil Point seep field, which is located directly offshore UCSB. “In my current work, I am focusing on methane concentrations and oxidation in the water column of the Santa Barbara Basin,” says Frank. “I am also advising an undergraduate who is examining propane consumption in seep sediments.”

As part of his Ph. D. studies, Frank studied the patterns and extent of microbial degradation of methane and other gases in sediments around seep vents found not only in shallow and hydrate free-seeps but also in the deep, hydrate-rich environments of the Santa Monica Basin. “Thus far, laboratory incubations of sediment with and without  $^{14}\text{C}$ - $\text{CH}_4$  as a tracer and studying the natural abundance of  $^{13}\text{C}$  have been key methods,” he says. These results “demonstrated approximately ten-fold more methane oxidation at seeps situated at 80 and 800 m depth than seeps at 10 and 20 m depth, with the microbial communities at the shallower sites heavily impacted by benthic disturbances, and starved of methane by the action of intense bubble discharge,” he notes. “Examination of a relatively shallow and intense seep at 20 m depth resulted in the observation of consistent spatial patterns of methane oxidation, which probably results from the interplay between diffusive and advective processes around individual gas vents.” Frank also designed and constructed novel *in-situ* equilibration samplers (peepers) in the course of his research.

Frank’s methane hydrate research has provided multiple opportunities to see methane seeps up close. He participated in *Alvin* dives in 2007 and sample collection trips to the shallow portions of the Coal Oil Point seep field using SCUBA. Frank said, “Diving through ascending bubbles of natural gas at these seeps is hauntingly beautiful – visually fascinating – but a little spooky too!”

What helps to keep Frank focused on his research is the belief that even minute advances in this field will have global implications. The most rewarding aspect of studying methane-dominated systems is the, “diverse skill set and broad background gained during the course of study.” When he is not advising undergrads or researching methane hydrates, Frank Kinnaman likes to garden, a fitting hobby when one considers that all three activities require infinite patience and perseverance, to obtain success.

Frank is supported under NETL Project DE-NT0005667. Please see [http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH\\_05667Methanotropic.html](http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH_05667Methanotropic.html) for more information regarding this project.



## ● **Karen Weitemeyer**

● **Geophysics (B. Sc. 2003), University of British Columbia**

● **Earth Sciences (Ph. D. 2008), University of California – San Diego**

The path to methane hydrate research was a winding one for Karen Weitemeyer, currently a post-doc researcher at Scripps Institution of Oceanography in La Jolla, CA. With an interest in both veterinarian science and geophysics, it was the excitement brought to the table by her geophysics professors at the University of British Columbia (UBC) in Vancouver, BC, Canada that convinced her that geophysics was the right field for her. "I was fortunate to be introduced to geophysics by the exceptional professors and teaching assistants at UBC. Their excellent instruction and interest in geophysics convinced me," says Karen.

Karen was introduced to methane hydrates as an undergraduate through her work on a model of the climatic effects from the release of methane due to hydrate dissociation below the Laurentide and Cascadia ice sheets. "Dr. Bruce Buffett opened a whole new world for me. When I presented my work at the UBC Science open house and at the American Geophysical Union (AGU) annual meeting, I was surprised at how much interest people had in listening to the hydrate story," she says.

It was a three-month exchange program with the Australian National University in Canberra, working with Dr. F.E.M. Lilley that introduced her to research in electromagnetic studies. Karen's specific area of research uses marine electromagnetic methods to remotely image methane hydrates in the field. When compared against the surrounding water-saturated sediment, gas hydrates are electrically resistive. "I am able to find resistors with controlled source electromagnetic (CSEM) techniques," notes Karen. "CSEM is one of two marine-based techniques used for oil and gas exploration. We have adapted the technique to be more sensitive to shallow sediments in which hydrates are found."

It was her Ph. D. advisor, Dr. Steven Constable, who helped to make it possible to use these electromagnetic techniques to image gas hydrates in a pilot study along Hydrate Ridge. "I am currently processing a recently collected controlled source electromagnetic data set from four sites in the Gulf of Mexico: Alaminos Canyon 818, Walker Ridge 313, Green Canyon 955, and Mississippi Canyon 118. This project will later involve laboratory studies on the electrical conductivity of hydrates," notes Karen. "A new field for me, but I am excited to learn about it!"

The interdisciplinary nature of hydrates research interests Karen considerably, "What I find most rewarding is that this field of study integrates physics, chemistry, biology and geology together," she says. "It allows you to meet many different people and scientists. Studying gas hydrates is also interesting because of the social, economic, and environmental implications that surround gas hydrates. My particular field of interest is breaking new ground, which makes it exciting."

Karen is supported under NETL Project DE-NT0005668. Please see [http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH\\_5668EMCharGOM.html](http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH_5668EMCharGOM.html) for more information regarding this project.

## • Anouncements

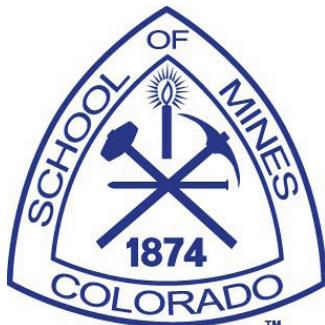


### AAPG Convention to Include Two Sessions on Gas Hydrates

The AAPG Annual Convention and Exhibition to be held June 7-10, 2009 in Denver, Colorado, will include two sessions titled "Hydrates - Sedimentology and Resources I and II." The sessions are sponsored by the Energy Minerals Division (EMD) of the AAPG. The two sessions will feature 19 poster presentations on a wide range of gas hydrate related permafrost and marine research and development issues.

The AAPG-EMD Gas Hydrate Research Committee will also host an informal "Friends of Gas Hydrate" meeting on Tuesday night, June 9th, at 5:00 p.m. (location to be announced). This year's AAPG-EMD Gas Hydrate Research Committee meeting will feature updates and reviews of various ongoing international gas hydrate research programs.

For more information about the meeting see: <http://www.aapg.org/denver/>



### Postdoctoral Fellowship

Applications are invited for Postdoctoral Fellowships at the Colorado School of Mines, Center for Hydrate Research in the Chemical Engineering Department. The Center for Hydrate Research is a global leader in the field of gas hydrates, with a funding level in excess of \$1.3 million per year. The Center houses an industrial consortium composed of twelve major energy companies, and leads several national and international collaborative programs.

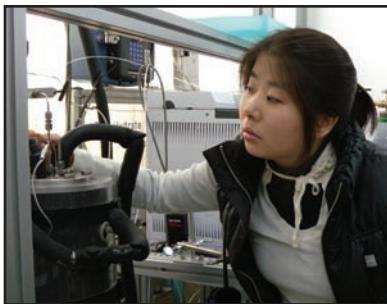
The Chemical Engineering Department and Center for Hydrate Research also have close links with the National Institute of Standards and Technology (NIST) in Boulder, CO, and the US Geological Survey (USGS) in Golden, CO.

The postdoctoral fellowships are in two research areas:

- Hydrogen storage in clathrate materials
- Gas hydrates in flow assurance

To obtain additional information regarding fellowship responsibilities and qualifications, as well as instructions on how to apply, please visit <http://hydrates.mines.edu/CHR/Positions.html>.

## • Spotlight on Research



### JOO-YONG LEE

Researcher

Korean Institute of Geoscience & Mineral Resources

When asked for what advice she would give to students considering gas hydrate research, Joo-yong said: *Studying hydrates, especially performing experimental study, really requires patience and passion for the research as gas hydrate is not an easy material to work with.*

*One will face every different aspect of frustration in different degrees that one must cope with, every month, every week, or every day, which is something that probably applies to all researchers.*

*Every time I face frustration, I try not to focus on the fact that I am stuck, since that will only make me even more frustrated. Instead, I think about what I should do at that current stage or about things that I should have done but haven't done so far, instead of worrying about "what if it doesn't work even after I've done this?" Sometimes it may become a long detour to my goal, but I always believe that I'll get there eventually and also by some reasonable deadline.*

*My advisor used to say, "Good things happen to good people." I agree with his comment very much. The only thing one should worry about is whether he or she tries hard enough to deserve the final triumph.*

## Joo-yong Lee

Joo-yong Lee has an appreciation for the phrase *Carpe Diem*, "Seize the day." While defending her Ph. D. dissertation, researchers from the Korean Institute of Geoscience and Mineral Resources (KIGAM) group had discovered methane hydrates in the East Sea. At the same time they had also contacted Joo-yong regarding her plans after graduation. So the day after graduating from the Georgia Institute of Technology with her Ph.D. in Civil Engineering, Joo-yong was on a plane headed for Seoul, South Korea, "I thought that I had no time to lose in joining the research group," says Joo-yong. "I flew to Korea the day after my graduation ceremony to be a part of the UBGHO1 hydrate research cruise, which was the first gas hydrate deep drilling cruise in Korea."

While a student at Georgia Tech, Joo-yong had her first experience with gas hydrate when she joined the particulate media research lab. "Dr. Carlos Santamaria was my advisor at that time, and he fostered my interest in geophysical methods in geotechnical study," says Joo-yong. "He introduced me to gas hydrates. At the time Dr. Carolyn Ruppel was at Georgia Tech and she also helped me get started in gas hydrates research."

Her work with Drs. Santamaria and Ruppel involved examining the hydrate formation and dissociation mechanism in sediments and determining the geophysical properties of hydrate-bearing sediment. "I was very fortunate to have Dr. Santamaria as my advisor," says Joo-yong. "I truly enjoyed working with him at Georgia Tech both as his Ph. D. student and his friend. Working with Dr. Ruppel was also enjoyable as she inspired me to continue my work as a female scientist in the gas hydrate research arena."

After completing the research cruise that brought her home to Korea, Joo-yong continued her work as researcher for KIGAM in their department of gas hydrate research. There her focus is on the production of natural gas from gas hydrate in sediments, "I am now focused on the mechanical behavior of hydrate-bearing sediments during production using geophysical tools," says Joo-yong. "Last year, I performed lab-scale production tests with natural gas hydrate-bearing sediments from the East Sea in Korea. The experiment was monitored with geophysical instrumentation and X-ray CT scanning devices. The experimental results provided crucial insights on the production of gas hydrate in marine sediments. I am very excited and can't wait to present the results to my colleagues from around the world."

Joo-yong believes that the most rewarding thing about studying hydrate is, "That I can research what I am most currently interested in. Gas hydrate research is very popular in Korea as it is one of the potential new energy resources. It also includes many aspects of geophysical and geotechnical resources, which allow for study of the various aspects of natural phenomena related to gas hydrates, which really thrills me."

In her off-time, Joo-yong enjoys watching movies, listening to music and reading books. When she wants to do something active, meeting friends for all-day shopping excursion is at the top of her list.