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# Fire in the Ice

THE NATIONAL ENERGY TECHNOLOGY LABORATORY METHANE HYDRATE NEWSLETTER

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## MALLIK RESULTS PRESENTED IN CHIBA, JAPAN

*by Thomas H. Mroz*

The partners of the Mallik 2002 Gas Hydrate Production Research Well Program held an international symposium on December 8 to 10, 2003 in Chiba, Japan. The purpose was to present production test results and hydrate science results from the Mallik wells that were drilled in the Canadian Arctic during January of 2002. Thirty talks and 45 posters were presented to an audience that included 250 attendees from 13 countries.

The results presented in Chiba prove for the first time that gas can be produced from naturally occurring hydrates, and that gas hydrate deposits in Canada and elsewhere have real potential as a future energy resource. Thomas Mroz, of the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL), who attended the 3-day event, said "the results were significant enough for the Japanese National Oil Company (JNOC) to propose a dedicated production test at the Mallik site next winter."

The Mallik Program partners include the Geological Survey of Canada (GSC), JNOC, GeoForschungsZentrum Potsdam (GFZ), U.S. Geological Survey (USGS), U.S. DOE, India Ministry of Petroleum and Natural Gas (GAIL/ONGC), BP-ChevronTexaco-Burlington Joint Venture Group, and the International Continental Scientific Drilling Program (ICDP).

*Left to right are: Dr. Rolf Emmerman–GeoFurshungZentrum, Mr. Thomas H. Mroz–NETL, Dr. Arun V. Sathe–Ministry of Petroleum and Natural Gas in India, Dr. Tsuji–Japan National Oil Corporation, Dr. Timothy Collett–USGS, and Dr. Scott Dallimore–Geological Survey of Canada. Right photo: they open a keg of sake and celebrate the success of the Mallik Program.*

The *Fire in the Ice* Newsletter is also available online at our website.

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## INTENT

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

The partners' exemplary collaboration took them to a remote frozen beach on Richard's Island, in the Mackenzie Delta, Northwest Territories, Canada, during the winter months of 2001-2002. Methane hydrates were known to occur at the site from previous drilling activities. The Mallik partners had a mission—to carry out the first fully integrated field study and production testing of gas hydrates.

The partners drilled three wells—the Mallik 3L-38 and 4L-38 observation wells, and the Mallik 5L-38 gas hydrate production well. Gas hydrate core was recovered from the Mallik 5L-38 well at depths of about 2,900 to 3,800 feet (880 to 1,150 m), and geophysical studies were conducted to test the extent and nature of the hydrate reservoir.

Two short-duration production tests were conducted—a depressurization test, and a thermal injection test. Both tests produced gas, as the flare in the photograph below attests. According to Mroz, the production results suggest that the hydrate reservoir is more permeable than anticipated, and that fracturing may play a role in enhancing the flow of gas to the wellbore.

DOE supported the Mallik Program through direct funding to the Mallik 2002 Program, and through additional funding of scientists and engineers at the USGS, Lawrence Berkeley National Laboratory (LBNL), Idaho National Energy and Environmental Laboratory (INEEL), and Oak Ridge National Laboratory (ORNL).

Dr. Tim Collett of the USGS played a lead role in planning and conducting the Mallik 2002 field work. Collett was on site around the clock during drilling and coring operations, to direct the intensive well logging and sampling program. DOE's Mroz worked with Collett to conduct onsite mud logging during the drilling of the Mallik 5L-38 well.

In addition, Dr. Rick Colwell of INEEL partnered with scientists from ORNL to collect biological samples to determine the influence of biogenic gas on the formation of hydrates.

In a critical effort, Dr. George Moridis of LBNL modeled potential gas production from the Mallik gas hydrate reservoir in the months prior to the production tests. He used results from the Mallik 5L-38 production tests to validate LBNL's Tough2 hydrate reservoir simulator. According to Moridis, the agreement between field observations at Mallik and model predictions from Tough2 was excellent. Moridis said the most promising production scenario for the Mallik gas hydrate reservoir involves a combination of thermal stimulation and depressurization.

The Chiba meeting provided an opportunity for the Mallik partners to share not only their technical accomplishments, but also the good will from working together as an international team. In a traditional Japanese ceremony, the main sponsors of the hydrate well program were given the honor of opening a keg of sake with a wooden sledge hammer to celebrate their shared success at Mallik.

The science and engineering results from the Mallik Program will be published by the Geological Survey of Canada in September 2004. The publication will include about 60 papers and an extensive set of digital data. In the future, the publication will be available through the GSC Mallik web site at http://gashydrate.nrcan.gc.ca/mallik2002/index.html

*The gas flare from the Mallik 5L-38 production well illustrates the success of the production tests.*

# HYDRATE DECOMPOSITION UNDER SCRUTINY

*by Stephen H. Kirby, Laura A. Stern, Susan Circone, and John Pinkston, U.S. Geological Survey, Menlo Park, CA*

Natural-gas hydrates can form and are stable under specific ranges of elevated gas pressure and temperature, conditions that depend largely on gas composition and hydrate structure. When pressures (*P*) and temperatures (*T*) are changed, placing these hydrates outside their stability field, they are prone to decompose at rates that depend on many factors, including hydrate composition and structure, the degree to which the equilibrium boundaries defining the stability field are exceeded, the *P-T*-time pathway taken to make them unstable, and the physical state and properties of the hydrate and its surroundings.

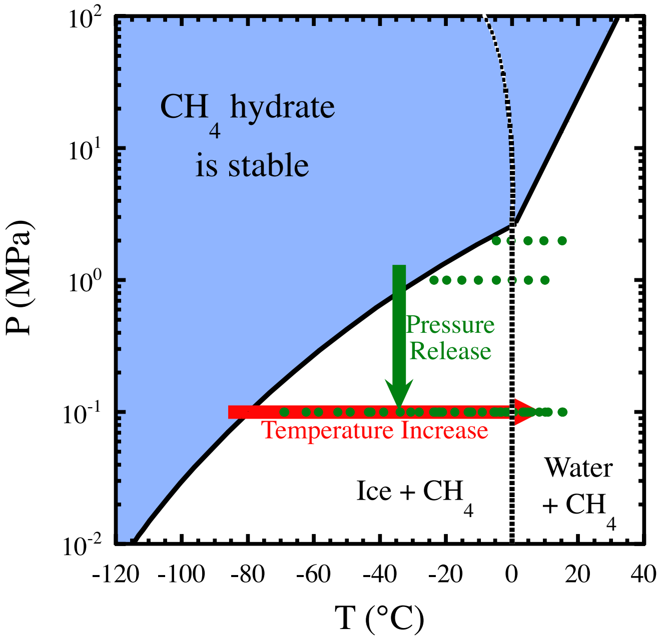
Decomposition of natural-gas hydrates can be brought on by climate-induced *P-T* changes that destabilize the hydrates. Release of this stored natural gas in marine environments could trigger submarine landslides. If large quantities of escaping gas enter the atmosphere, such releases could influence global climate through methane's role as a greenhouse gas. Moreover, understanding the physical processes governing gas release from hydrates has applications to such practical problems as clearing plugs in natural gas pipelines, optimizing hydrate recovery in drill core, evaluating the effects of deep oil and gas production on well borehole stability in shallow gas-hydrate intervals, and natural gas production from hydrate deposits through thermal stimulation and/or pressure reduction.

Quantitative assessment of hydrate decomposition rates is difficult to obtain solely from field gas-stimulation tests, however, because such measurements are often site-specific and usually cannot isolate the individual factors that control decomposition rates. In support of interpretation of field tests, much experimental and theoretical work has been done on hydrate decomposition rates.

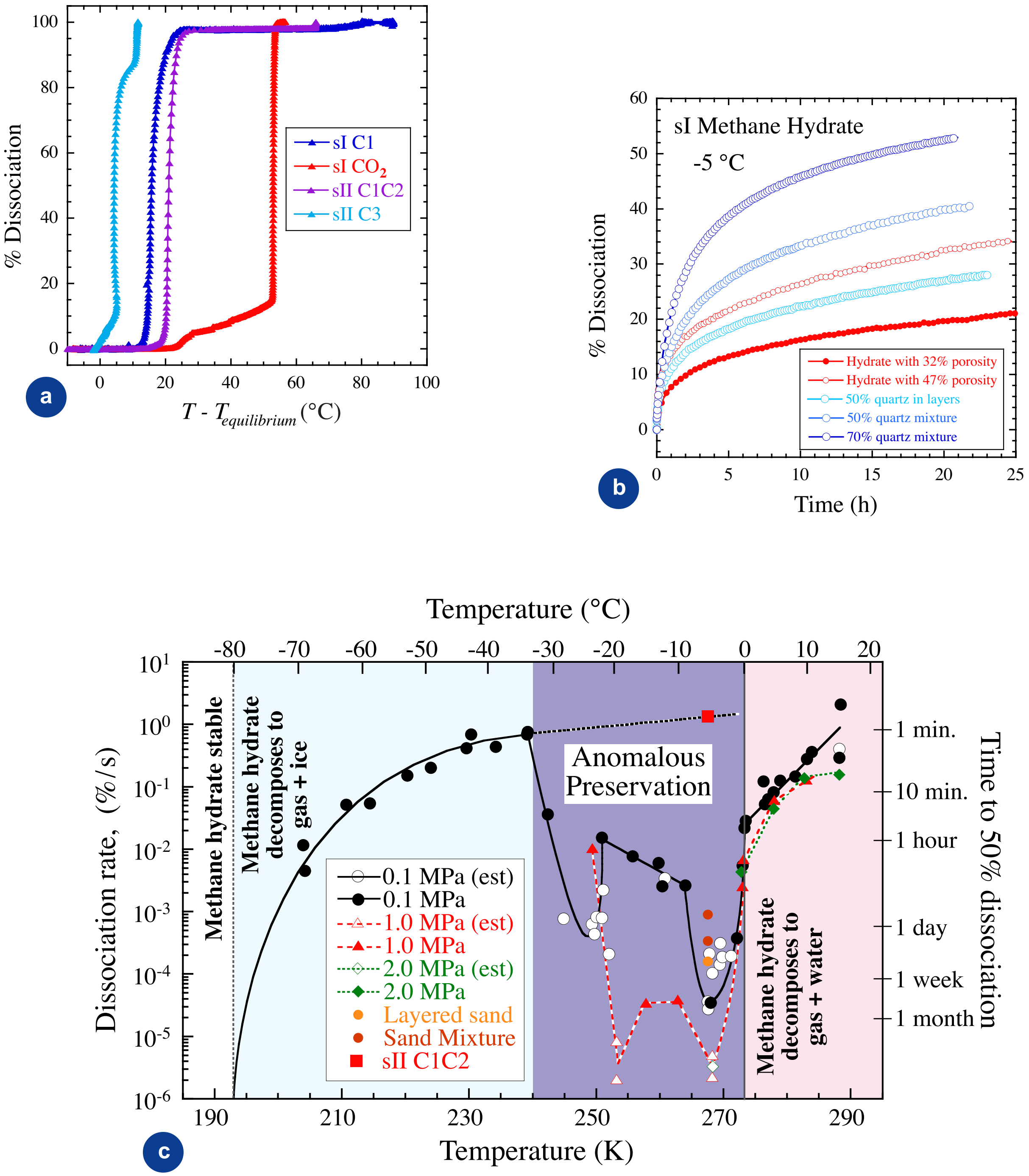
*Gas hydrate research lab team members are, left to right: Stephen Kirby, Susan Circone, Laura Stern, and John Pinkston.*

We describe the astonishing variations in the decomposition rates of porous samples of hydrocarbon hydrates that occur with differences in *P*-*T*-time pathways, sample composition, and experimental conditions. Our samples include structure I "sI" methane [C1], structure II "sII" methane-ethane [C1C2], structure II "sII" propane [C3], and structure I "sI" carbon dioxide [$CO_2$] hydrates. Our experiments, lasting from minutes to more than a month depending on the decomposition rate, were continuously monitored and maintained under controlled *P*-*T* conditions outside the hydrate stability field in the presence of the hydrate-forming gas. The series of three graphs on the next page shows variations in decomposition rate and illustrates our experiments.

Our recent work used pure, porous samples that were made under closely controlled conditions, yielding reproducible grain and pore textures. Decomposition experiments on these samples produced rate curves that were exceptionally reproducible, allowing us to identify some of the major factors that control decomposition rates. Cryogenic scanning electron microscopy (SEM) of the textures and structures of such samples also gave important clues about the processes that govern gas hydrate decomposition.



*This graph shows the methane-hydrate stability field plotted as temperature versus methane pressure. We decompose methane hydrates by two different pathways: increasing the temperature (red arrow) or decreasing the pressure (green arrow). The green data points indicate the P-T conditions of the experiments illustrated in graph (C) in the series.*



***Graph A*** *shows the decomposition behavior of gas hydrates heated at about 13 °C/hr at P = 0.1 MPa. The equilibrium boundary ($T_{eq}$) is crossed at the following temperatures for the various hydrates: -80 °C (C1), -66 °C (C1C2, estimated), -55 °C ($CO_2$), and -11 °C (C3).*

***Graph B*** *shows methane hydrate decomposition rates at -5°C, following rapid gas pressure release to 0.1 MPa. The results for methane hydrate samples with different porosities and varying amounts and distributions of quartz sand are indicated. The initial porosity of the ice + sand samples was comparable to the low-porosity, pure hydrate sample. Every10th data point has been plotted.*

***Graph C*** *shows decomposition rates of methane hydrates at various temperatures, following rapid gas pressure release to P = 0.1, 1.0, or 2.0 MPa. Each point represents a single experiment on one sample. The decomposition rate shown is the average rate calculated from the time required for the sample to release 50% of its methane content, with the time scale shown on the right axis. In experiments where the isothermal conditions were not maintained until 50% of the sample decomposed, the rate was extrapolated from the decomposition curve (open symbols, est = estimated). Note that decomposition rates vary by a factor of 10,000 at P = 0.1 MPa. The decomposition rate of sII C1C2 hydrate at -5°C is also shown (filled red square).*

## Decomposition by Heating

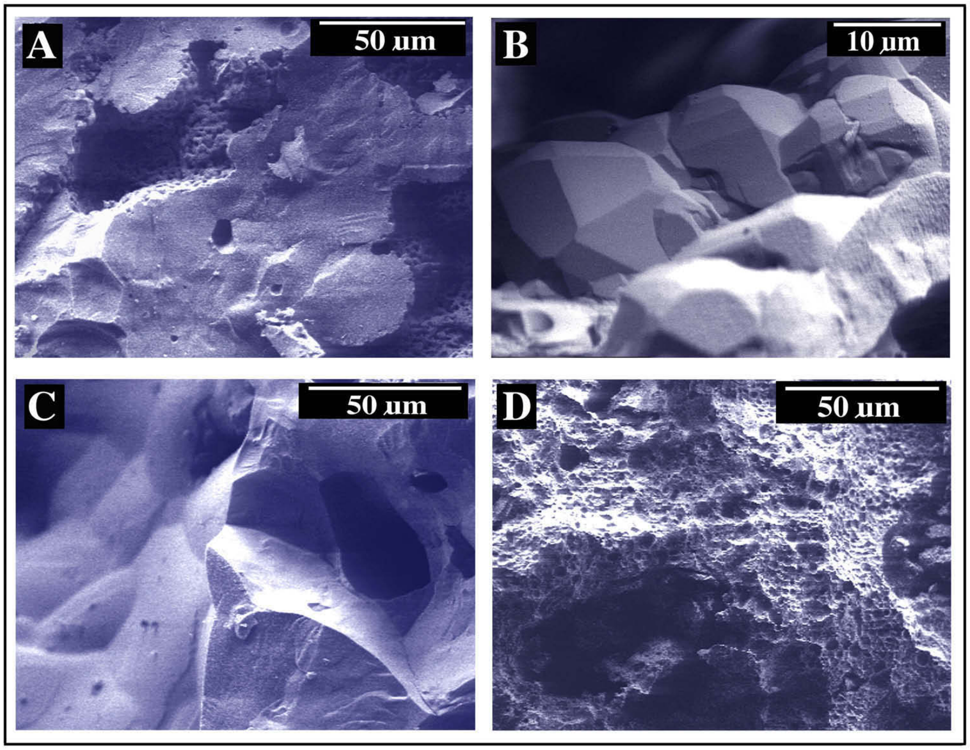
Gas hydrates decompose when warmed from conditions within the hydrate stability field to higher temperatures outside their stability field. Hydrocarbon hydrates (both sI and sII) released the bulk of their gas within about 20 °C above their respective equilibrium boundary. However, the sI $CO_2$ hydrate samples did not undergo their main decomposition event until the ice melting temperature was reached at more than 50 °C above the equilibrium boundary. X-ray tomography of our samples by our Lawrence Berkeley National Laboratory (LBNL) colleagues has been a powerful tool for imaging the decomposition front associated with heating.

## Decomposition by Pressure Reduction

Gas hydrates also decompose when gas pressure is reduced to pressure conditions below the hydrate stability field. In our experiments, temperature was externally fixed by submerging the sample pressure vessel in a temperature-controlled bath while gas pressure was rapidly reduced to 0.1, 1.0, or 2.0 megapascals ( MPa).

At 0.1 MPa and temperatures below -33 °C, decomposition behavior of methane hydrate was consistent with the results shown for warming the hydrate. Rates scale with the temperature overstep of the equilibrium boundary. However, at warmer temperatures up to the ice melting point (-31 to 0 °C), decomposition rates were markedly lower, and their relationship to temperature was complex.

Remarkably, the slowest rates measured in this “anomalous preservation” regime were at minus 5 °C, about 75 °C above the P= 0.1 MPa equilibrium boundary that defines methane hydrate stability! At temperatures above the ice



(A) Low magnification SEM micrograph of porous methane hydrates. (B) SEM micrograph showing a pore lined with methane hydrate crystals. (C) Partially decomposed middle section of a methane hydrate sample (17% of methane released), following 24 h at -5 °C, 0.1 MPa. (D) porous ice decomposition product of a methane hydrate sample after 95% of the methane was released by heating 30 °C above the equilibrium boundary.

## GAS HYDRATES MADE FROM MELTING ICE

Pure gas hydrates can be made by heating granular ice in the presence of pressurized hydrate-forming gases or liquids (i.e. the "guest" molecules). Some hydrates initially form from the reaction between ice and the hydrate former, but most hydrates form when the ice melts and reacts with the hydrate former. Subsequent heating to just below the temperature limit of hydrate stability produces well-crystallized hydrates.

This synthesis method has several big advantages:

- The reaction goes to completion overnight in most cases, producing a pure, homogeneous material with nearly all structural cages filled.
- Samples are gas-permeable.
- The method allows production of very large samples to emulate hydrate-bearing drill cores.
- Mixtures of sediment with hydrates can also be made by mixing ice with sediment grains, producing aggregates with specified hydrate distribution that bear striking similarities to naturally occurring permafrost hydrates.
- These permeable mixtures may be subsequently flooded with gas-saturated seawater.
- This general technique yields reproducible samples with closely reproducible measured properties.

To date, only simple end-member (C1, C2, C3, and $CO_2$) or binary samples (C1C2) have been synthesized and their physical properties measured.

melting point, decomposition rates increased sharply and systematically with increasing temperature.

Decomposition rates at higher pressures were slower than those measured at 0.1 MPa, as would be expected. At -5 °C, it took more than a month for half of the sample to decompose at 1 to 2 MPa. The complex trends in decomposition rates with vessel bath temperature observed at 0.1 MPa persisted to higher pressures. When either temperature or pressure was varied stepwise on a single sample, the change in decomposition rate followed the trends shown in the isothermal (and isobaric) experiments.

How does this decomposition behavior of C1 hydrate compare with other hydrates? At -5 °C, where it took about two weeks for half of a sI C1 hydrate sample to decompose, the sII C1C2 hydrate samples dissociated so rapidly that more than half of the sample was gone in one minute! Conversely, the sI $CO_2$ hydrate samples showed none of the complex temperature-dependent behavior exhibited by the sI C1 hydrate, but behavior was consistent with the results obtained for warming the $CO_2$ samples: decomposition rates were slow at fixed temperatures between -23 and -5 °C, with the remaining gas released only when samples were warmed through 0 °C.

These results indicate that at temperatures below the ice melting point, porous hydrates exhibit complex decomposition behavior that is:

- Highly dependent on the *P*-*T*-time pathway,
- Highly dependent on structure and composition, and
- Difficult to predict from one hydrate system to another.

Moreover, at warmer temperatures, hydrates dissociate completely to gas + water within hours to minutes as temperatures increase. These results suggest that it will be difficult to predict hydrate decomposition behavior based on measurements on analog systems.

*The left photo shows a full methane hydrate sample in a split metal jacket. The right photo shows mixed-sand/methane hydrate mixtures stratified with different proportions of sand and hydrates. The yellow layers are made with quartz sand and the gray layers with aluminum oxide. A translucent Teflon sheath surrounds the two samples to the right.*

## Other Important Factors

We also performed some preliminary work at -5 °C on methane hydrate samples with varying porosity and mixed with sand.

- First, increasing sample porosity (by increasing the initial porosity of the starting ice pack) increases the decomposition rate.
- Second, introducing quartz sand, first in layers (50-50 mixture by volume, 3 sand: 4 hydrate layers), then as a homogeneous mixture with the C1 hydrate (50 and 70 percent quartz by volume), systematically increases the decomposition rate.

These results suggest that, as the density of hydrate-to-hydrate grain contacts decrease, decomposition rates increase. Although relative decomposition rates are always higher with methane hydrate/sand mixtures than with pure hydrates, they are still, in absolute terms, very slow in the anomalous preservation regime.

## A Potential Practical Application of These Results

The precipitous decrease in decomposition rates from 0 to -5 °C, even when methane hydrate is mixed with sand, suggests that the recovery of methane hydrate in permafrost drill core could be improved by controlling drilling mud temperature and core handling temperature.

On the basis of these experimental results, the Maurer/Anadarko Joint Industry Program (JIP) drilling project at the Hot Ice No. 1 drilling site on the North Slope of Alaska is using a special mud-temperature control system and a lab temperature control system this winter. The purpose is to maintain $T$ near -5°C during core recovery and handling to maximize hydrate preservation. We hope results of this attempt to preserve hydrate will be known later this winter.

## Prospects for the Future

Even though our synthesis method produces pure hydrate material with simple grain and pore structure, experiments on this material show remarkable variability in decomposition rates for the effects of temperature, pressure, hydrate porosity, and the presence of sediment. The structures and textures of our synthetic hydrate/sand aggregates may be reasonable analogs for gas hydrates in permafrost sediment. However, they are likely not representative of marine gas hydrates, which are thought to grow from dissolved natural gas in seawater-filled pores in sediment.

Well-characterized gas hydrates grown from aqueous solution have not been achieved in the laboratory to date and remain a highly-desired missing link to the natural marine environment. Because of the low solubility of hydrate-forming gases in water (in particular the hydrocarbon gases), hydrate samples synthesized in this manner are difficult to characterize in terms of hydrates versus free-water content, hydrate distribution, and hydrate stoichiometry. These uncertainties create challenges for determining the chemical properties of hydrates and the physical properties that depend on them.

We are making progress, however, in understanding how synthetic gas hydrate/sediment aggregates interact in a closed system with seawater and how, in turn, seawater affects hydrate decomposition rates. These topics, together with recent experimental results on the role of liquid water in methane hydrate decomposition at high temperatures, will be the subjects of our next article in *Fire in the Ice*.

## FURTHER READING

Circone, S., L.A. Stern, S.H. Kirby, W.B. Durham, B.C. Chakoumakos, C.J. Rawn, A.J. Rondinone, and Y. Ishii. $CO_2$ hydrate: synthesis, composition, dissociation behavior, and a comparison to structure I CH4 hydrate *Journal of Physical Chemistry B*, **2003**, *107*, 5529.

Stern, L.A., S. Circone, S.H. Kirby, and W.B. Durham. Anomalous preservation of pure methane hydrate at 1 atm *Journal of Physical Chemistry B*, **2001**, *105*, 1756.

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# GHOSTS, MOSQUITOs, AND PEEPERS RETURN TO THE GULF OF MEXICO

The project's official title is "Controls on Gas Hydrate Formation and Dissociation, Gulf of Mexico: In situ field study with laboratory characterization of exposed and buried gas hydrate."

Scientists from Scripps Institution of Oceanography, Texas A&M University, University of North Carolina, and Bar Ilan University (Israel) concluded their field work for the second phase of the Gas Hydrate Observation, Sampling, and Tracer Study (GHOSTS) project in the Gulf of Mexico. For two weeks, August 12 to 24, researchers recovered fluid chemistry and flux monitoring equipment that had been emplaced in 2002, installed new monitoring equipment (peepers), and took sediment, water column, and hydrate samples from cold seep locations and where shallow gas hydrate outcrops on the seafloor.

The GHOSTS project is designed to (1) provide essential information on the thermal regime of the ocean and sub-seafloor at active gas hydrate sites, such as at Bush Hill in the Gulf of Mexico, and (2) investigate the effects of heat transfer between bottom sea-water and seafloor sediments on the stability of methane hydrates. Physical and chemical data were obtained by in situ monitoring systems deployed on the sea floor for over a year. The data will help scientists understand the potential impacts of gas hydrate dissociation on and near the sea floor in response to thermal fluctuations, and the effects of the release of methane into the ocean and atmosphere.

Phase I of the project began in June 2002 when Miriam Kastner (Scripps Institution of Oceanography, University of California, San Diego), Ian MacDonald (Texas A&M University), and their research team selected several sites for study: GC185-Bush Hill, GC234, GC232, and GB425 (Mineral Management Service lease block numbers). The researchers, aboard the research vessel *Seward Johnson II* and the submersible *Johnson-Sea-Link*, installed a time-lapse camera and temperature recorders. They also deployed

*The gas hydrate mound has a thermistor probe installed. The location is GC185 at a depth of 1800 ft (545 m). The picture was taken with the time-lapse camera deployed by the GHOSTS program.*

geochemical and hydrological monitoring equipment, known as MOSQUITOs (multiple orifice sampler and quantitative injection tracer observers) and T-Bars (osmotically driven sampling devices that pump formation fluids into copper and Teflon capillary tubes).

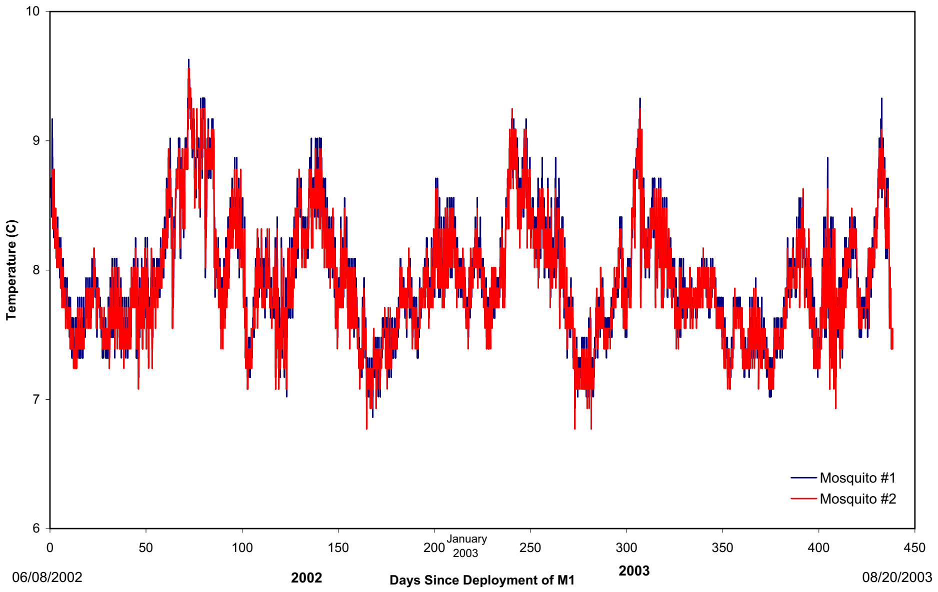
MOSQUITOs collect fluids that provide weekly fluid chemical concentration, isotopic composition, and pore fluid flux data. T-Bars collect a time series of large gas (methane and higher hydrocarbons) samples. In addition, researchers collected water column samples, especially in the methane plumes, and samples of hydrates and associated sediments, using push-cores and a specially designed hydrate drill. (See Winter 2003 *Fire in the Ice*).

In the summer of 2003, the objectives of the GHOSTS II cruise were to retrieve the monitoring equipment and, based on the results from GHOSTS I cruise, to take additional water column, gas hydrate, and sediment samples where necessary. Again aboard the *Seward Johnson II*, with the aid of the *Johnson-Sea-Link*, the team successfully recovered all four MOSQUITOs, all six T-Bars, and two bottom water-temperature probes that were attached to MOSQUITOs. Thermistor probes that monitor bottom water, sediment, and hydrate temperatures, and the time-lapse camera were also recovered.

## The Recovery

For 14 months, the MOSQUITOs and T-Bars collected fluid samples in copper and Teflon tubing. When brought aboard, the MOSQUITO tubing was sectioned into 785 sub-samples for chemistry and flux analyses. Fluids within the T-Bar tubing were frozen and transported to the shore-based laboratory for gas analyses; approximately 375 T-Bar sub-samples will be available.

Two bottom-water in situ temperature probes from two MOSQUITOs collected time-series data for nearly 14 months at a recording frequency of one reading every 40 minutes. One was deployed near the Bush Hill hydrate mound; the second was located approximately 300 meters southwest of the hydrate mound to record background conditions. Both showed almost identical bottom-water temperature fluctuations of about 5° F (3° C) over the time period, indicating thorough and rapid mixing.



*Temperature data from two MOSQUITOS show almost identical bottom-water temperature fluctuations, indicating thorough and rapid mixing.*

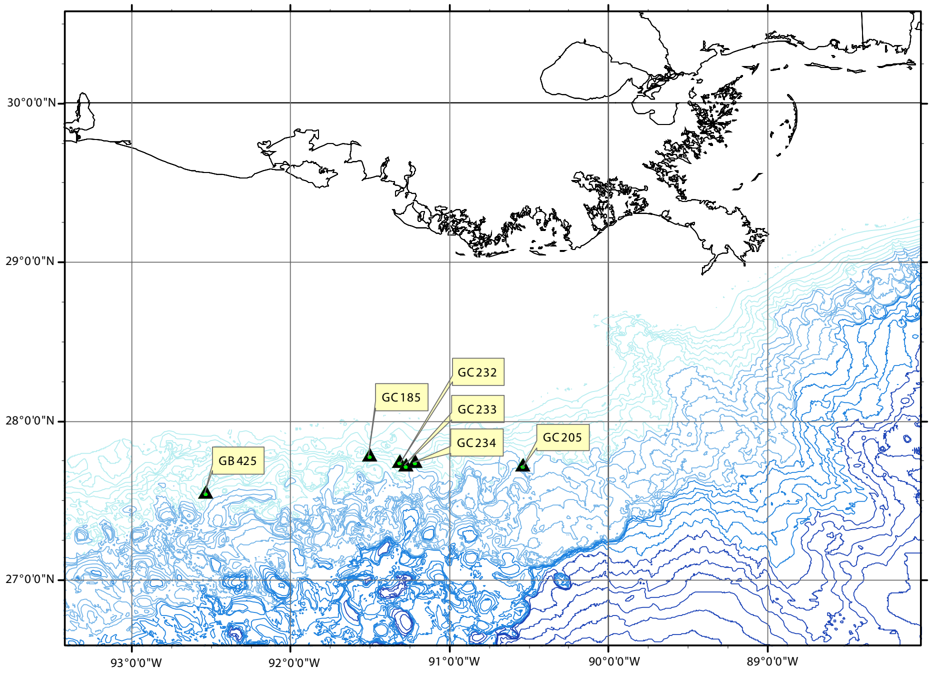
A second set of in situ thermistor probes had been installed to monitor the temperatures of the bottom water, the sediment at depths of 20 and 40 inches (50 and 100 cm), and the interior of gas hydrate masses. As expected, the bottom-water temperature data from this second set of probes showed very similar bottom-water temperature variations to those recorded on the MOSQUITO probes. The two data sets will undergo an in-depth comparative analysis.

The time-lapse video camera, which had been installed at GC185-Bush Hill, provided an important descriptive and quantitative record of the gas hydrate environment. The camera recorded six photos per day for 31 days. Unfortunately one of the light cables developed a short circuit, which prevented further photographic information from being recorded.

## New Investigations

The team of scientists also had a number of new investigations on their agenda. They deployed five "peeper" samplers, which obtain rather large volumes of uncontaminated in situ pore fluid samples at 11 depth intervals plus a bottom-water sample, at various locations in the vicinity of the GC185-Bush Hill hydrate mound. Push cores for pore-fluid chemistry and porosity were taken at Bush Hill from sites where the MOSQUITOs were recovered, as well as from the Brine Pool, GB232, GC234, and GB425.

Methane-plume profiles were collected for chemistry and dissolved methane analysis at Bush Hill, GB425, and GC234. In addition, water column sample profiles were obtained by conductivity, temperature, density (CTD) hydrocasts between the vent sites at Bush Hill and GC234. Additional bottom-water samples were taken with a Niskin bottle, attached to the submersible basket, on almost every one of the 16 submersible dives. Scientists also collected seven gas samples from bubble streams at various dive locations. On board the *Seward Johnson II*, the scientists analyzed samples for alkalinity, pH, sulfide, and sulfate. They retained the remaining pore fluids under proper storage conditions for further analyses on shore.



*This regional map shows the study sites in the northern Gulf of Mexico offshore Louisiana. Most sampling activity was concentrated at the GC185 and GC234 sites.*

## CRUISE PARTICIPANTS

**University of California, San Diego**

Miriam Kastner (co-chief scientist)

Gretchen Robertson (scientist)

Evan Solomon (student)

Wei Wei (student)

Andrew Aubrey (student)

Tabitha Hensley (student)

Lora Van Uffelen (student)

**Bar Ilan University (Israel)**

Yishai Weinstein (scientist)

**U.S. State Department**

Elizabeth Tirpak (observer)

**Texas A&M University**

Ian MacDonald (co-chief scientist)

Michael Vardaro (student)

Richard Arena (student)

**University of North Carolina, Chapel Hill**

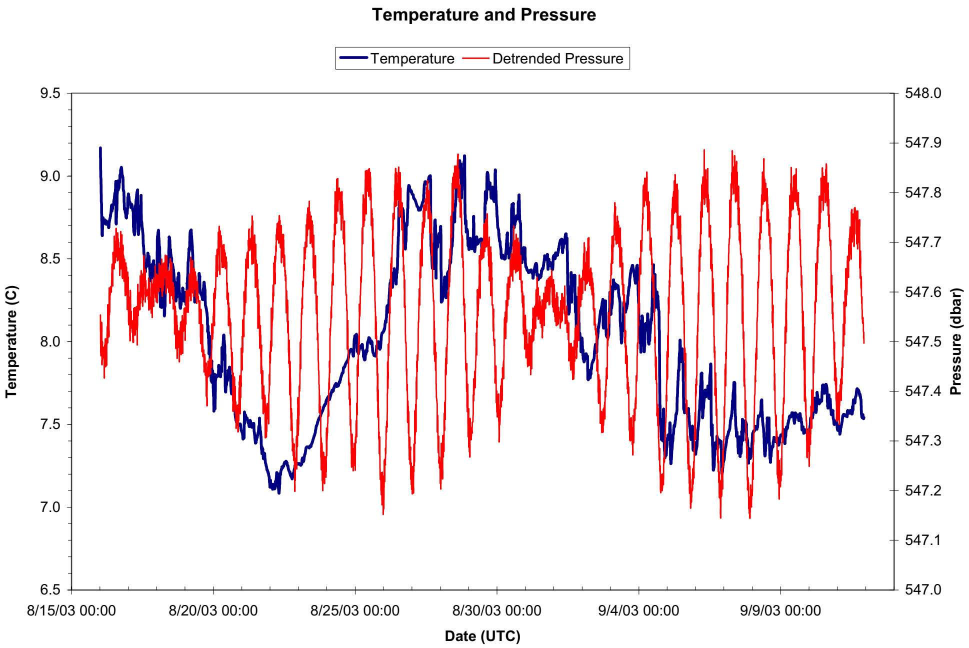
Laura Lapham (student)

At the end of several dives, the researchers sampled the water column within the bubble plumes at Bush Hill and GC 234 while ascending to the surface. Samples, collected in serum bottles, were taken with a sampling tube from inside *Sea-Link's* back chamber. The samples will undergo both gas and chemical analyses.

During the cruise, the gas hydrate drill and gas hydrate pressurized recovery system, developed with DOE support, were used to recover samples of gas hydrates and to drill holes in solid hydrate deposits to implant thermistor probes.

A short-term experiment, deploying thermal probes and a monitoring station, was undertaken during the cruise. This equipment and the peepers were recovered a month later in September 2003. The two thermal probes, deployed and recovered at GC185-Bush Hill and GC234, provided data on the thermal conductivity of gas hydrate and surface sediments. Two additional probes were left in place to continue long-term monitoring of the hydrate environment. These remaining probes are scheduled for recovery in 2004.

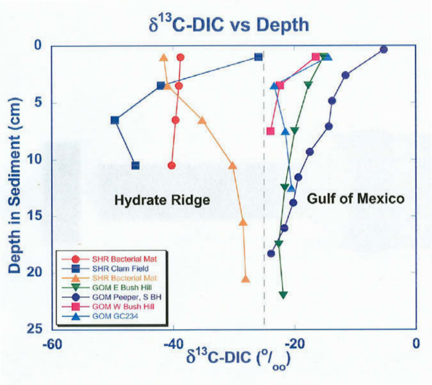
The monitoring station consisted of a CTD and passive-acoustic recorder to detect the sound of bubbling gas at vents, illustrated in the temperature/pressure graph below. The acoustic data are being analyzed at the National Oceanic and Atmospheric Administration (NOAA) Pacific Marine Environmental Laboratory. Preliminary results indicate high ambient noise from ships and other background activity, which may challenge the extraction of a signal.



*Data from the CTD show a typical variation in temperature over a range of almost 5°F (3°C) and smaller diurnal cycles are evident. The pressure data (the first such data series recorded from Bush Hill) show clear lunar cycles in tides that correlate well with temperature cycles*

## Preliminary Results

Preliminary results of GHOSTS II data analyses have uncovered some significant discoveries. Fluids in recovered MOSQUITO Osmo-Samplers indicate pervasive fluid advection. Flow rates vary greatly in time and space at Bush Hill. The highest methane, alkalinity, and sulfide concentrations and the lowest sulfate, calcium, and magnesium concentrations are observed at the seep and bacterial mat sites at both Bush Hill and GD 234. The high alkalinities induce authigenic carbonate precipitation, and thus, Ca and Mg consumption. The depletion in both Ca and Mg concentrations at a molar ratio of <1/1 suggests the presence of Mg-calcite (in addition to calcite) and most likely also dolomite, formed in situ. Chlorinites above seawater concentration are observed primarily at the deep sites and at some of the bacterial mat sites, indicating in situ formation of methane hydrates in the shallow sub-seafloor.



*Comparison of dissolved inorganic carbon isotope data from Hydrate Ridge, Cascadia, and Gulf of Mexico*

Most interesting are the dissolved inorganic carbon (DIC) isotope data. At typical cold-seep sites associated with methane hydrates, for example at Hydrate Ridge, Cascadia, DIC-C isotope values are extremely negative (between -20 to -50 permil), and more negative than the organic matter C isotope values. This indicates anaerobic oxidation of methane. In contrast, at both Bush Hill and GC 234 and at the methane seep and bacteria mats sites, the minimum DIC-C isotope values are just equal to -21 to -23 permil. This indicates that anaerobic oil oxidation, instead of anaerobic methane oxidation, is the dominant reaction controlling the DIC-C isotopes.

The data collected during the GHOSTS research program, when analyzed and released, will provide much-needed information on the stability of marine gas hydrates, their formation kinetics, and their dissociation in response to natural seafloor chemical and thermal changes. Scientists and engineers will use this information to understand the role of hydrates in slope stability and to formulate mitigation strategies.

### Dive Sites for GHOSTS II Cruise

| Site | Latitude | Longitude | Depth (m) | Comment |
|---|---|---|---|---|
| GC185 | 27°43.01' | 91°30.35' | 545 | Main MOSQUITO site, gas hydrates |
| GC234 | 27°44.75' | 91°13.22' | 545 | Thermistor & Tee Bar site, gas hydrates |
| GB425 | 27°33.22' | 92°32.40' | 550 | Thermistor and mud volcano |
| GC233 | 27°43.41' | 91°16.85' | 650 | Brine pool and gas vent |
| GC232 | 27°44.71' | 91°19.05' | 567 | Thermistor and gas hydrate site |
| GC205 | 27°43.22' | 90°32.58 | 873 | Exploration |

# MAJOR HYDRATE EXPEDITION PLANNED FOR THE GULF OF MEXICO

A 30 day cruise to study hydrates in the Gulf of Mexico will leave port in early May from Galveston, TX. The plan is to drill wells at two deep-water gas hydrate sites—Atwater Valley and Keathley Canyon—on the outer continental shelf. The project *Characterizing Natural Gas Hydrates in the Deep Water Gulf of Mexico: Applications for Safe Exploration and Production Activities* is funded by the Joint Industry Program (JIP) and the Department of Energy.

Three well pairs are planned at both the Atwater Valley and Keathley Canyon locations at a water depth of approximately 4,300 ft (1,300 m). Each pair will consist of a logging-while-drilling well and a nearby (~50 to 75 ft, or 13 to 23 m) offset cored well for correlation and instrumentation. The researchers selected the drilling sites based on maps of gas hydrate indicators and an interpretation of the geologic framework of the selected sites. This information was the result of the high-resolution multichannel seismic (MCS) data collected during Phase I, combined with three-dimensional MCS data provided by industry.

The Scripps Institute of Oceanography is organizing the cruise and shipboard scientific staff. The research team will be aboard the recently renovated *Fugro Explorer* drilling vessel. The *Fugro Explorer* was completely refitted in 2002, and now serves as one of the most technologically advanced geotechnical drilling vessels, equipped with the latest drilling, soil sampling, and in situ testing equipment. It is also fully equipped for geotechnical, geological/stratigraphic, and reservoir characterization investigations and is capable of operating in water depths up to 10,000 ft (3,000 m).

The project is a 4-year collaborative effort to develop technology and collect data to characterize naturally occurring gas hydrates in the deep-water Gulf of Mexico. JIP industry partners include ChevronTexaco, ConocoPhillips, Total E&P USA, Schlumberger, Halliburton Energy Services, the Minerals Management Service (Gulf of Mexico Region), the Japan National Oil Corporation, and India's Reliance Industries. Academic collaborators include the Georgia Institute of Technology, the Scripps Institute of Oceanography, and Texas A&M University through the Joint Oceanographic Institute.

*The Fugro Explorer*

# Announcements

AAPG ANNUAL MEETING
APRIL 18-21, 2004
DALLAS, TEXAS

## American Association of Petroleum Geologists Annual Meeting 2004

The American Association of Petroleum Geologists Annual Meeting, April 18-21, 2004 in Dallas will include two oral sessions and one poster session on methane hydrate research. More information can be found at http://www.aapg.org/meetings/dallas04/technical/index.cfm.

## AAPG Hedberg Research Conference On Gas Hydrates

The American Association of Petroleum Geologists (AAPG) is sponsoring a Hedberg Research Conference, titled "Gas Hydrates: Energy Resource Potential and Associated Geologic Hazards." This conference will be held in Vancouver, British Columbia, Canada from September 12-16, 2004.

Hedberg Research Conferences are limited to about 100 INVITED participants. To participate in this conference you must inform the AAPG of your interest through their web site at http://www.aapg.org/education/hedberg/vancouver/index.cfm under the button, Express Your Interest.

## International Geological Congress, Italia 2004, Florence, Italy

Recent developments in gas hydrates will be the subject of several Topical Symposia at the 32nd International Geological Congress (IGC), Italia 2004. The IGC will be held in Florence, Italy, August 20-28, 2004. The Gas Hydrates in Continental Margins symposium [session T15.03] will include a diverse range of issues, such as geophysical detection and characterization, modes of formation, biological mediation, mechanisms for gas release into the ocean, and interaction with climate change. Hydrate research will also appear in the Future of Energy Resources [T09.04], Deep Biosphere [T18.01], and Submarine Slope Stability [T15-04] sessions.

Information on the IGC can be found at its web site http://www.32igc.org. The deadline for submittal of abstracts was January 10, 2004.

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George Moridis is currently the Research Area Leader of the Transport Dynamics Group and a Principal Investigator in charge of gas hydrate studies. He is also responsible for the radionuclide transport studies of the proposed Yucca Mountain High Level Waste Repository, and for the development of the next generation of models for the simulation of subsurface processes. He is the author or co-author of 26 refereed publications, and of over 100 reports.

## Spotlight on Research

# FROM ATHENS TO MALLIK–IN THE NAME OF SCIENCE

George Moridis began his academic studies at the National Metsovion Technical University in Athens in his native Greece. He graduated with a B.S. (1979) and an M.S. (1980), both in chemical engineering.

George was fascinated by the subject of modeling physical systems, and had a chance to pursue this interest in his graduate studies for a second M.S. (1982) in agricultural engineering at Texas A&M University, where he worked on a model of water flow in a soil-plant system. His expanding interest in mathematical models and numerical simulation led him to pursue a PhD in reservoir engineering from Texas A&M.

Upon graduation in 1986, he joined the Food and Agriculture Organization of the United Nations (U.N.) where he was responsible for groundwater development in south and southeast Asia. In 1989 he returned to the United States and joined the faculty of the Civil Engineering Department at Texas A&M.

While at Texas A&M, he was responsible for the design and development of the largest dual-gamma attenuation system in the world (6ft x 6ft x 0.5 ft), designed for non-destructive studies of multiphase fluids in porous media while evaluating aggressive decontamination methods (such as hydraulic controls, steam injection, and the use of surfactants). In addition, he developed the Laplace Transform Finite Difference method, a new numerical method for solving of the equations of flow and transport in the subsurface.

George joined the Berkeley Lab in 1991. He has developed new analytical, semi-analytical, and numerical methods and new solvers for matrix equations that arise in numerical analysis. He has worked on geothermal and environmental restoration problems, and he has developed new technologies to isolate contaminants in the subsurface using a new generation of barrier fluids.

He received a patent for his Liquid Barrier Technology. This technology won the 1996 Best of What is New award in environmental technology (organized by *Popular Science* magazine). The technology was used to isolate radionuclides in the subsurface at Brookhaven National Laboratory. He received another patent for the development and use of magnetic fluids to guide and emplace liquids in the subsurface.

George has been working on hydrates since 1998, using a numerical model he developed (1) to evaluate a wide range of natural hydrate deposits in geologic systems, and (2) to develop appropriate production strategies.

He has used this numerical model for scoping calculations and the design of the first field test of gas production from hydrates at the Mallik site well (see “Mallik Partners…” story, this issue). The numerical model has also been used to design planned field experiments in the North Slope, Alaska, in DOE-funded projects led by Maurer/Anadarko and British Petroleum. He is using the field data from a North Slope test, conducted in early 2002, to validate the numerical model and to determine the values of important parameters. Along with colleagues Barry Freifeld, Tim Kneafsey, Liviu Tomutsa, and Yongkoo Seol, George is also involved in laboratory projects focusing on new techniques for the preparation of large-scale samples of hydrates (both pure and produced in situ within porous media), and on the use of X-ray computed tomography to non-destructively study hydrate dissociation and flow processes under controlled conditions.

George cannot hide his excitement about the opportunity to work on the cutting edge of hydrate research, and to be involved in the study of this challenging frontier resource.