Winter 2003

Fire in the Ice

THE NATIONAL ENERGY TECHNOLOGY LABORATORY METHANE HYDRATE NEWSLETTER

CONTENTS

ANNOUNCEMENTS

Preliminary Report Published—The preliminary report for Leg 204 of the Ocean Drilling Program has been published online at http://www-odp.tamu.edu/publications/prelim/204_prel/204toc.html

The international expedition Leg 204, aboard the research vessel *JOIDES Resolution*, recovered large amounts of gas hydrates from the Hydrate Ridge area off the coast of Washington and Oregon. The cruise was featured in the Fall 2002 issue of *Fire in the Ice*.

GHOSTS AND MOSQUITOS IN THE GULF OF MEXICO

The GHOSTS in question are not scary white things that go bump in the night, and the MOSQUITOs are not annoying insects. They are acronyms associated with a 2-year program to characterize naturally occurring gas hydrates in the Gulf of Mexico.

The Gas Hydrate Observation, Sampling, and Tracer Study[1] (GHOSTS) is designed to further the understanding of the potential impacts of gas hydrate instability on the seafloor and the effects of the release of methane into the ocean and atmosphere. The principal investigators for GHOSTS are Ian MacDonald of Texas A&M University and Miriam Kastner of Scripps Institution of Oceanography (SIO). Together they are collaborating on a 2-year field monitoring and laboratory program in the Gulf of Mexico (GOM) under a cooperative agreement with U.S. DOE NETL.

Ian R. MacDonald and Harbor Branch submersible pilot Phil Santos are descending in the Johnson-Sea-Link.

Acknowledgement

The photo of the ice worm appearing with the article, Twenty Days Studying Life in Extreme Environments, in the Fall 2002 issue of *Fire in the Ice* should have been credited to **Greg Boland** of the Minerals Management Service. He took the photo in July 1997 when ice worms were first discovered during a submersible dive. He was on a cruise as a contracted scientist for Texas A&M University at the time.

This is Your Newsletter

Fire in the Ice is the newsletter for the entire hydrate community. It is challenging to bring together such a diverse group of researchers and devise a newsletter that will be interesting to all of you. If you have or know of something you'd like to see published in *Fire in the Ice*, or ideas for how to improve the newsletter, please contact us.

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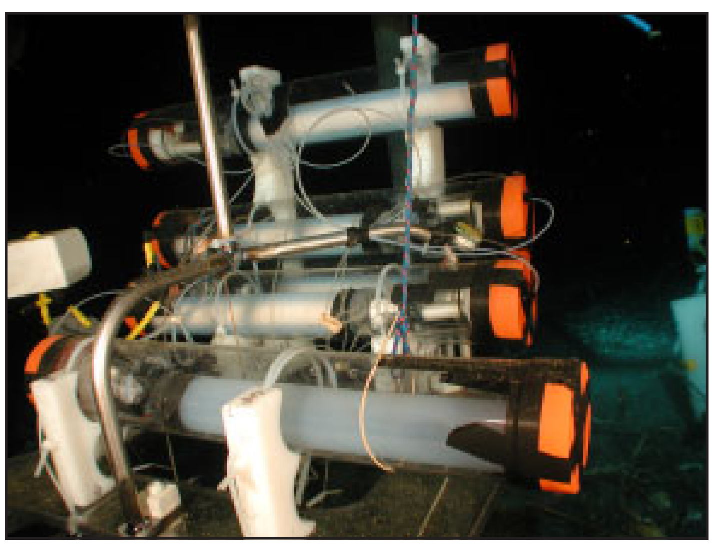
Be sure to visit our website at http://www.netl.doe.gov/scng/hydrate

The scientific program combines quantitative field monitoring and laboratory study to determine the physical and chemical effects of in situ environmental perturbations on seafloor gas hydrate stability in the northern GOM. The study should yield a better understanding of the dynamics of marine gas hydrate formation and dissociation and their impact on the near seafloor biochemical environment. Previous observations at the GOM field sites suggest that gas hydrates on the seafloor form and dissociate in cycles over periods of several weeks to several months. Biochemistry, subsurface hydrology, and temperature play a role in these cycles. Much of our understanding of the kinetics of gas hydrate behavior comes from laboratory studies on synthetic gas hydrates (e.g., structure I). However, data on the kinetics of natural gas hydrate formation and dissociation in the marine environment are lacking and the major and minor controls have not been monitored. Miriam Kastner is in charge of the geochemical, hydrological, and sedimentological investigations and Ian MacDonald is overseeing the field-monitoring program.

GHOSTS 2002 Cruise

The first of two research cruises took place June 6-14, 2002 aboard the Research Vessel (R/V) *Seward Johnson II*. Two sites GC185—Bush Hill, and GC234 (which are so-designated by their Minerals Management Service lease block numbers) were selected because they had the best mapped and characterized shallow gas hydrate outcrops in the Gulf of Mexico. The sites are colonized by chemosynthetic tube worms, mussels, and free-living bacteria.

Using the submersible *Johnson-Sea-Link*, the scientists took core and water samples, installed time-lapse video and temperature recorders, and deployed geochemical and hydrological monitoring equipment on the seafloor. The monitoring instruments will operate continuously and collect data for an entire year. They are designed to monitor fluid and methane fluxes that influence the dynamics of gas hydrate formation and dissociation on areas of the seafloor that are vulnerable to environmental changes. The instruments will give the scientists a record of pore fluid and bottom-water chemical and isotopic compositions, seafloor temperatures, and sediment fluid flow rates. The instruments will also provide a visual record of hydrate responses and changes on the sea floor that occur as a result of environmental variations.



This photo shows a closeup of the capillary tubing in one of the MOSQUITOs deployed at Bush Hill.

MOSQUITOs—The innovative, new, and tested MOSQUITO (multiple orifice sampler and quantitative injection tracer observer) is being used to collect geochemical samples and fluid-flux data. The MOSQUITO operates using the principles of osmotic pumping and tracer dilution. The novel design allows the MOSQUITO to continuously monitor, in three-dimensions, for months to years, the vertical and horizontal fluid flow in sediments and to obtain an accurate record of the fluid geochemistry.

Three MOSQUITO samplers were deployed adjacent to the Bush Hill hydrate mound—one each in a mussel field, a bacterial mat, and a tubeworm field. The fourth MOSQUITO was positioned a short distance southwest of the mound to record baseline background conditions. At the end of the year-long deployment, fluids collected by the four MOSQUITOs will be analyzed for tracer concentrations, methane, and other hydrocarbon concentrations. Samples from the coils will provide fluids for geochemical and isotopic analysis, data from which fluid flow rates can be calculated within a 1- to 2-day resolution.

Principal Investigator Miriam Kastner, scientist Yishai Weinstein and graduate student Evan Solomon, (right to left) oversee deployment of a MOSQUITO sampler from the Johnson-Sea-Link.

Because the Bush Hill region is rich in gas, a specially-designed T-Bar (an osmotically-driven sampling device that pulls samples into a capillary tube) was deployed to collect a time series of large gas samples. Four T-Bars were emplaced adjacent to the MOSQUITOs and a fifth was deployed on the hydrate mound in the space vacated by the hydrate drill core.

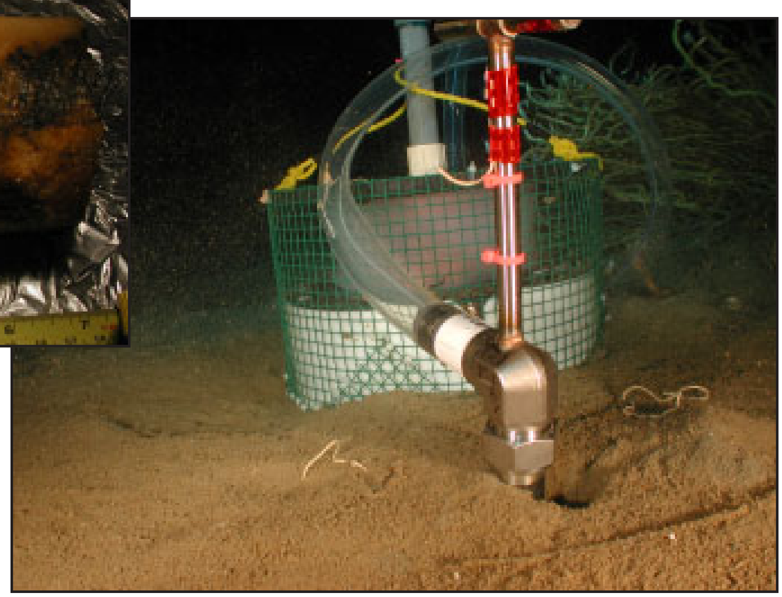
Gas Hydrate Samples—Samples of gas hydrates exposed on the seabed were collected during the cruise. The challenge with hydrate sampling is to transport the hydrates to the laboratory with minimum disturbance and contamination. Core samples were taken with a newly designed hydrate corer, a manipulator-operated drill with a detachable core bit. *Sea-Link*'s manipulator arm held the drill during drilling; the bit containing the hydrate core was then detached and placed in a specially designed hydrate recovery chamber prior to being hauled to the surface. The insulated recovery chamber preserves the sample at 90 percent of the bottom pressure and over 95 percent of the bottom temperatures. After minor problems with the hydrate drill not being able to break off the core, and some adjustments to the drill's hydraulic system, a 6-inch (15 centimeters) core was successfully recovered.

Twenty-seven push cores were collected during the cruise, providing a wealth of information about near-seafloor gas hydrates. Of particular interest is how the formation of hydrates changes the porosity and integrity of the sediment. The cores also provide a record of initial, in-situ, sediment-pore fluid chemistry. Pore fluids were sampled and sectioned in the cold room aboard the ship. Using standard wet chemistry techniques, the fluids were immediately analyzed for alkalinity, pH, and ammonium, and sulfide was precipitated. The remaining fluids were then stored for later shore-based analyses.

Water Column Samples—Water column profile samples were successfully acquired using a Nisken bottle rosette sampler. Nine high-resolution samples, including those from a gas-plume and from background sites, were collected for comprehensive solute and dissolved gas analyses, including chlorofluorocarbon (CFC). Deep samples will help document the chemical effects of gas venting on seawater chemistry. Samples from shallower depths will document if and how much methane is presently reaching the atmosphere at Bush Hill. The CFC data provide an apparent age of the hydrate mound.

A 9- by 22-centimeter core of gas hydrates is collected with the hydrate drill.

The intake of a T-Bar sampler is shown inserted into a drill hole that remains after a hydrate core was taken.

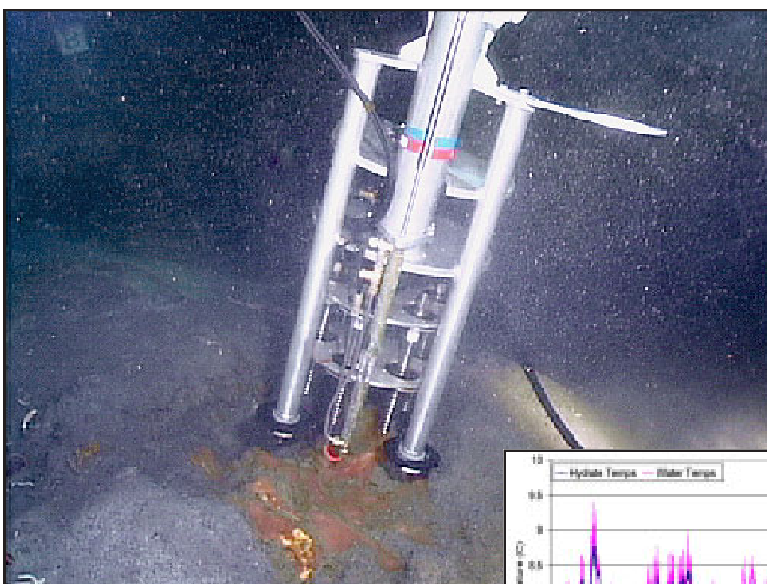


Video—Augmenting the hydrologic program at Bush Hill is the photographic record from a time-lapse digital camera assembly installed on the seafloor. This rig is recording hourly images of the growth or dissolution of an exposed gas hydrate deposit and is equipped with a synoptic temperature recorder.

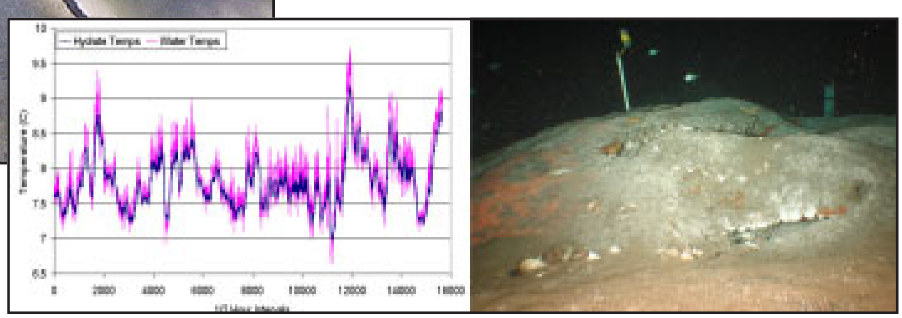
Analyses—The fluids and samples collected during the summer cruise now reside at the shore-based laboratory at SIO. Miriam Kastner is conducting an extensive array of geochemical, isotopic, mineralogical, and structural analyses of the gas hydrate, vent water, pore fluid, and sediment samples. Kastner is working on determining the carbon and hydrogen isotope ratios of the methane and other low molecular weight hydrocarbons (C1-C3), and the isotope ratios for sulfur and hydrogen if hydrogen sulfide is present. In addition, the percent gas occupancy in the hydrates is being measured by decomposing clean hydrate samples and measuring the methane to water ratios. These latter analyses are being carried out on clean samples of large gas hydrate pieces sectioned from the hydrate core in a freezer. By taking time series samples, geochemical zonation in the hydrates can be assessed. Hydrate dissociated water is also being analyzed for oxygen and hydrogen isotopic ratios as well as chloride, the latter being a good indicator of porosity and dilution. Vent water samples taken on the cruise are also being analyzed for carbon and hydrogen isotopes of the methane. Other chemical species of interest in the fluids include sulfate, calcium, magnesium, silicon, and lithium.

Analyses of petroleum and other high carbon number organic compounds are being conducted at Texas A&M. Of particular interest will be concentrations of methane and other longer chain hydrocarbons, as well as any petroleum associated with these deposits.

The collective geochemical data from this cruise will provide essential information on the coupling of the ocean and sub-seafloor thermal regime, on heat transfer between the ocean and the sub-seafloor, and on the amount of methane and other low-carbon number organic species that are required to form additional gas hydrates or stabilize existing deposits.



The hydrate drill collects a core from an exposed deposit of gas hydrates at a depth of 550 meters. The gas hydrates is the yellow material at the base of the drill.



Detailed records of water temperature and the internal temperature of a hydrate deposit were measured during a 327-day deployment. Temperatures inside the gas hydrate deposit fluctuated with changes in bottom water temperature (left), but because heat transfer must pass through the mass of the hydrate sample, the interior temperature has a lesser amplitude of variation. The hydrate deposit and the thermal probe are shown in one of the timelapse images collected four times per day during a 96 day interval (right).

GHOSTS PROGRAM STUDY OBJECTIVES

Monitor, characterize, and ***quantify*** the rates of formation and dissociation of methane gas hydrates at and near the seafloor in the northern Gulf of Mexico, and *determine* linkages between physical and chemical parameters of the deposits over the course of a year.

Monitor, in situ, the stability and response of shallow gas hydrates to temperature and chemical perturbations, and *characterize* seafloor and water column environmental impacts of hydrate formation and dissociation.

Determine equilibrium/steady state conditions for structure II methane gas hydrates at the field sites; *examine* if this system is in dynamic equilibrium and whether the local hydrology is characterized by steady state episodic fluid flow; and *determine* how fluid fluxes and fluid composition work together to dynamically influence gas hydrate stability.

GHOSTS 2003 Cruise

Additional water and sediment sampling and the retrieval of monitoring equipment are scheduled for the summer 2003 cruise. Data for comparison will be collected at site GC234. Analyses of the collected information will begin immediately on shipboard. This second phase of the program will include data analysis, comparison, and synthesis.

Finding the Answers

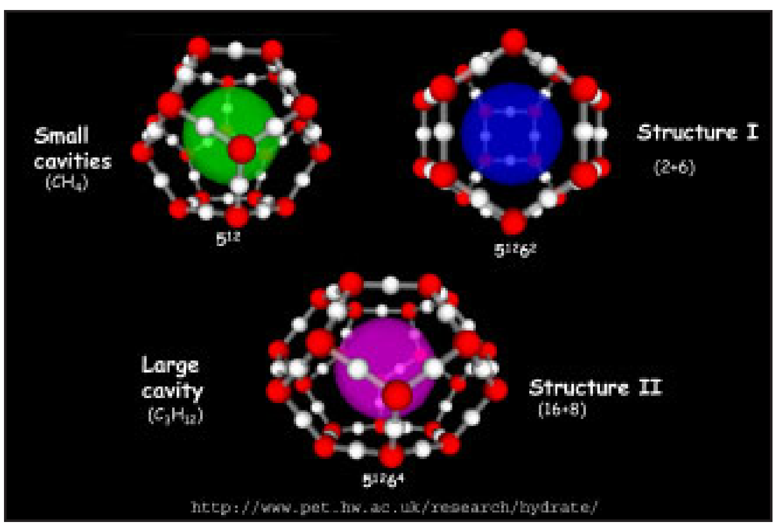
Methane hydrates are particularly vulnerable to becoming unstable where they occur near the sediment-water interface (where pressure and temperature conditions are near the hydrate three-phase boundary curve). Natural fluctuations in bottom water temperature may drive gas hydrate deposits above and below this stability horizon. Harry Roberts of Louisiana State University recently observed that the methane flow rate (i.e., rate of bubbling) at a seafloor methane vent doubled in response to a 1°C increase in temperature.

Hydrate dissociation potentially poses risks to drilling safety as well as to the local seafloor environment. Hydrate formation and dissociation is also thought to affect global climate, yet its role is still not well understood. The two-year GHOSTS research program is designed to provide a much better understanding of the stability field of marine gas hydrates, their kinetics of formation, and their dissociation in response to natural seafloor chemical and thermal changes. Scientists can use this understanding to interpret the potential risks of hydrate-initiated slope instability and create possible mitigation strategies. In addition to phase and seafloor stability, the GHOSTS program seeks to evaluate the full range of the potential environmental impacts of gas hydrate formation, dissociation, and dynamics.

[1] 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."

Structure I and Structure II Hydrates

At sufficiently high pressure, cooling water molecules form complex solid structures at temperatures significantly above the normal freezing point. But (unlike ice) these structures are characterized by networks of large open cavities and are inherently unstable. As cooling continues, the normally compact and stable ice structure will form, unless some guest molecules of



Hydrate lattice structures

appropriate size enter the structure and support the cavities. Methane is the most common guest molecule and forms the stable, solid compound called methane hydrates.

Two primary types of naturally occurring hydrate structures are known to exist commonly: structure I and structure II. These structures represent different arrangements of water molecules and result in slightly different shapes, sizes, and assortment of cavities. Which structure forms depends on the available guest gas. Methane preferentially forms structure I.

Dendy Sloan found in 1990 that the addition of a small amount of propane to the available guest gas causes a change from structure I to structure II, and leads to a pronounced shift of the hydrate stability phase diagram towards higher temperatures. Less than half the pressure is required at a given temperature to stabilize structure II hydrates than structure I hydrates.

The structure I hydrate consists of 46 water molecules surrounding 2 small cavities and 6 medium-sized cavities. The structure II hydrate consists of 138 water molecules creating 16 small cavities and 8 large cavities.

For more information on the chemistry of naturally occurring methane hydrates, go to http://www.netl.doe.gov/scng/hydrate/

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Highlighting Hydrate Heterogeneities in the Gulf of Mexico

A team of scientists led by Carolyn Ruppel of the Georgia Institute of Technology embarked on a cruise in October 2002 aboard the research vessel (R/V) *Seward Johnson*. Their goal was to examine in detail the physical and chemical characteristics of the seafloor in the Gulf of Mexico (GOM). Three sites were scheduled for study:

- Bush Hill (lease block GC185) at a water depth of approximately 1770 feet (540 meters), where gas hydrates had been observed on the seafloor.
- A mud volcano site (GB425) at a water depth of approximately 1970 feet (600 meters), where sub-seafloor fluids are being expelled.
- A Mississippi Canyon vent site (MC852/853) at a water depth of 3,500 feet (1,070 meters), where gas hydrate has previously been recovered close to the seafloor.

The sites are of interest because they represent the range of hydrogeologic regimes associated with gas hydrates and fluid flow in the GOM, and because they have been proposed for possible academic drilling under the auspices of the international Ocean Drilling Program (ODP) www.oceandrilling.org.

Undergraduate student Audrey Hucks (Rice), co-investigator Gerald Dickens, and Georgia middle school teacher Kathryn Henderson, who participated as part of K-12 outreach efforts, measure a piston core.

The research, sponsored by the National Science Foundation, focused on imaging fluid pathways and measuring fluid flow, gas transport, and sediment temperatures at each site. From October 18 to 30, 2002, researchers acquired overlapping seismic, piston coring, and heat flow data.

Seismic images were acquired with an Edgetech 512 swept frequency system, which provides better resolution than conventional multichannel seismic sensors. The seismic data revealed features associated with seafloor gas venting, gas migration in the sediments, fine-scale faulting, and mudflows. The data also provided enough resolution to permit researchers to link chemical and thermal signatures to specific faults that act as conduits for the movement of fluid and gas.

The scientists took advantage of the dynamic positioning capabilities of the *R/V Seward Johnson* to gather heat-flow measurements and piston and gravity cores. Heat-flow data were acquired with instruments having up to 39 thermistors penetrating to depths of up to 15 feet (5 meters). When possible, the heat-flow data were collected within a few meters of the piston core sites. This strategy enabled precise correlation of chemical and stratigraphic information from cores with the thermal data. Heat-flow data were also

Graduate student Grace Castellini (Rice) gives hand signals to the crane operator during deployment of the gravity corer at the Bush Hill site.

Heat flow technicians Chris LeBlanc and Walter Judge, both of Dalhousie University, service the short heat-flow instrument after recovery. The yellow instrument in the background is the Edgetech seismic fish used to obtain images of the shallow sub seafloor.

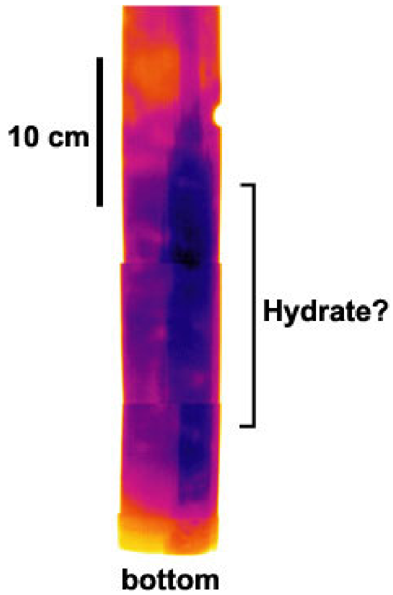
collected at spacing as close as 160 feet (50 meters) along transects that crossed such seafloor features as mud volcanoes, hydrate outcrops, and seafloor vents. The high lateral spatial resolution of the heat-flow measurements meant the researchers could begin mapping the thermal perturbations associated with the GOM's highly heterogeneous flow systems.

Many of the recovered cores were scanned for cold regions that reflect local endothermic dissociation of gas hydrates, using the FLIR (forward looking infrared radar) Thermcam 2000 thermal infrared camera. The camera was acquired by Joint Oceanographic Institutions through a cooperative agreement with U.S. DOE NETL. Graduate student Jill Weinberger (Scripps) obtained images from a core recovered from near the center of the seafloor vent at the deepwater Mississippi Canyon site.

Preliminary analyses of pore water salinities and thermal data show that fluid composition and fluid flow rates vary dramatically over length scales of even 330 feet (100 meters), underscoring the heterogeneous and dynamic nature of processes that control the location of GOM gas hydrate deposits. Preliminary results imply a complicated fluid circulation system characterized by the

The osmotic flux meters on deck with Mike Tryon (Scripps) following retrieval at Bush Hill.

Graduate student Jill Weinberger (Scripps) acquires an infrared image of the end of a recovered piston core.



This is a portion of an infrared image for a piece of a core retrieved from the Mississippi Canyon vent site. The blue areas are much colder than the surrounding core and are probably associated with dissociation of gas hydrates.

emission of hot, briny fluids at vents, and downward diffusion of seawater on the flanks. A surprising result was the recovery of gas hydrates from seafloor sediments characterized by high temperatures or salinities. Depending on their compositions, these hydrates may occur just at the edge of their stability conditions in a zone confined between the seafloor surface down through tens of meters of sediment.

During the cruise, the researchers also retrieved osmotic flux meters that had been deployed at Bush Hill in July 2002. The flux meters had been placed at seeps near hydrate mounds and chemosynthetic communities, and on normal “background” seafloor using the submersible *Johnson-Sea-Link* during a cruise led by Patricia Sobecky (Georgia Tech) as part of the National Science Foundation-sponsored Life in Extreme Environments initiative. The flux meters, built by Kevin Brown and Michael Tryon at the Scripps Institute of Oceanography, record both the rate of fluid emission and the chemical composition of fluids. Upon retrieval, Tryon noted that some of the flux meters had trapped significant amounts of gas, probably indicative of very high rates of fluid emission near faults.

In addition to Carolyn Ruppel (Georgia Tech), the scientific team included Gerald Dickens (Rice University), Kevin Brown (Scripps), and Daniel Lizarralde (Georgia Tech) as formal co-investigators. J. Carlos Santamarina (Georgia Tech) conducted geotechnical measurements on recovered sediment cores, and Stephen Macko (University of Virginia) and Patricia Sobecky (Georgia Tech) sent students who collected samples for isotopic and microbial analyses.

Carolyn Ruppel (Georgia Tech) and Gerald Dickens (Rice) plan scientific operations at the Bush Hill gas hydrate site aboard the R/V Seward Johnson.

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SPOTLIGHT ON RESEARCH

Childhood Love of Science Becomes Oceanography Career

Professor Miriam Kastner has been fascinated by science since she was a child, and now she's passing along this fascination to the next generation. But, she notes that funds for hydrates research are slipping away from academia, and says "This is unfortunate for the field, and special attention should be given to this regrettable development." Miriam is a professor and researcher, and she also goes to sea.

Early in her career, Miriam became interested in studying chemical paleoceanography as recorded in marine sediments and became involved with the Ocean Drilling Program (ODP). She has participated in nine legs—equivalent to 18 months at sea. Her first exciting encounter with hydrates was on Deep-Sea Drilling Project (DDP) Leg 112, where the scientists drilled in the Peruvian outer margin and recovered hydrates at two sites. The isotopic data indicated that the methane origin was primarily biogenic. She notes that estimates of the global significance of the enormous amounts of carbon sequestered in marine methane hydrates were just emerging then. The first publications on the impact of global warming on hydrate stability and the environmental consequences of significant methane release by G.J. MacDonald in 1982 and R.R. Revelle in 1983 also occurred about the same time.

Miriam has contributed several firsts to hydrate knowledge:

- She provided the first synthesis of methane hydrate occurrences and distributions in different lithologies in convergent margins.
- She was the first to analyze C1 concentration of decomposed marine hydrates and show the significance of the C1 concentration data.
- She was the first to measure low core temperatures and explain their significance.
- She thoroughly characterized the first observed natural mixed CH_4-H_2S hydrate sample and explained its origin.

A native of Czechoslovakia, Miriam was raised in Israel and earned bachelor's and master's degrees in geology at the Hebrew University in Jerusalem. She received both a Fulbright travel grant and a Fellowship from Harvard University, where she earned her Ph.D. degree in geology. She worked as a Research Associate at Harvard and the University of Chicago, and then joined the Scripps Institution of Oceanography as the institution's first female professor. Miriam has been a full professor since 1982. Her hobbies include music (she used to play the violin in orchestras), reading, and traveling to new, culturally interesting places.

Professor Kastner notes that the following is one of the most important significant challenges that face hydrate research: "The potential catastrophic dissociation due to global warming is high on the list of important problems, because such methane release would impact ocean chemistry, thus biology, and some of the methane would escape to the atmosphere. Resulting slope instabilities may cause other serious problems for coastal communities."