Fall 2002

Fire in the Ice

THE NATIONAL ENERGY TECHNOLOGY LABORATORY METHANE HYDRATE NEWSLETTER

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R/V *JOIDES Resolution* Docks With a Payload of Hydrate Samples

Dr. Frank Rack, Assistant Director of the Ocean Drilling Program and Staff Scientist, during Leg 204 of the Ocean Drilling Program, handles the ODP Pressure Core Sampler on the deck of the R/V JOIDES Resolution. It contains gas hydrates in an ice bath awaiting controlled degassing in the lab.

After two months in the Pacific Ocean off the Oregon coast, the research vessel (R/V) *JOIDES Resolution* docked in Victoria, British Columbia, with a precious payload of methane hydrate samples, the largest amount ever recovered for scientific study.

The international expedition, known as Leg 204 of the Ocean Drilling Program, spent the summer approximately 50 miles offshore collecting and preserving hydrate samples in pressure vessels for study by scientists around the globe. The area of interest is Hydrate Ridge, where two tectonic plates converge, and where scientific surveys indicate massive accumulations of hydrates.

The cruise, dedicated to investigating the origin and distribution of gas hydrates, was primarily funded by the National Science Foundation. The Department of Energy (DOE) Office of Fossil Energy through the National Energy Technology Laboratory contributed more than $1 million and several pieces of research equipment to the Hydrate Ridge expedition. Frank Rack, Assistant Director of the Ocean Drilling Program held the position of Staff Scientist during the cruise. Gerhard Bohrman of the German Research Center for Marine Geosciences (GEOMAR) and Anne Tréhu of the University of Oregon were Co-Chief Scientists.

Using the latest in pressure-coring devices, scientists for the first time were able to maintain the samples at sub-seafloor pressures after they were brought to the surface. The objective was to maintain in-situ pressure so that scientists might analyze the methane gas trapped inside the frozen ice crystals. Using specially designed pressure vessels, each six feet

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

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.

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(two meters) long and four inches (10 centimeters) in diameter, nearly two miles (over 3,000 meters) of core were recovered from the ocean floor. Ice cores in 34 of the vessels will be preserved and stored at Texas A&M University for post-cruise investigations.

A major goal was to physically verify the presence of hydrates within the sediments in the cores. Many of the cores were used for controlled degassing experiments. In addition, an x-ray linear scanner, developed just a month before the cruise, was utilized to detect density contrasts in the cores, a prime indicator of hydrate occurrence. Infrared thermal imaging and a nuclear magnetic resonance logging-while-drilling tool were among other instruments used to evaluate the occurrence of hydrates in ocean sediments and in the cores.

Another first for the scientists was the ability to acquire core samples simultaneously with logging-while-drilling data. This allows a direct comparison of the logging data with the core samples. Core data and the logging-while-drilling data will also be compared with a variety of conventional wire line and seismic information to more accurately correlate ocean bottom layers.

The photo shows the graduated cylinder filling with gas as the ODP Pressure Core Sampler undergoes controlled degassing in the lab aboard the R/V JOIDES Resolution. A maximum of 27.6 gallons (97 liters) of methane from gas hydrates was recovered during Leg 204, a record for this tool.

The *JOIDES Resolution* spent from July 6 to September 2, 2002 in the Hydrate Ridge area. Scientists from many nations, including the United States, Japan, Canada, Spain, Norway, the United Kingdom, Taiwan, the People's Republic of China and the Republic of Korea participated in various research and recovery activities. The scientists had specific research objectives planned for each site, for example:

- Investigating variations in the distribution, composition and concentration of gas hydrates laterally and with depth;
- Sampling the sediments, fluids, gases and gas hydrates for correlation, modeling, geochemical, geophysical and historical research; and
- Figuring out what causes variations in the seismic character of bottom simulating reflectors (BSRs), and how BSRs and hydrate occurrence are related.

Data, photographs and core samples from the cruise are available for research. The database includes paleontological, lithostratigraphic, chemical, physical, sedimentological and geophysical data for ocean sediments and hard rocks. Information on requesting data and core samples can be found at http://www-odp.tamu.edu

For more information on the *Joides Resolution* Hydrate Ridge cruise, contact Frank Rack at frack@joiscience.org, (202) 232-3900 x216;or Bill Gwilliam at wgwill@netl.doe.gov, (304) 285-4401.

Anne Tréhu (Co-Chief Scientist; USA) and Brad Julson (Laboratory Officer) discuss one of the first sediment cores recovered during Leg 204.

The R/V JOIDES Resolution

Cross Sections of Methane Hydrate Core Samples

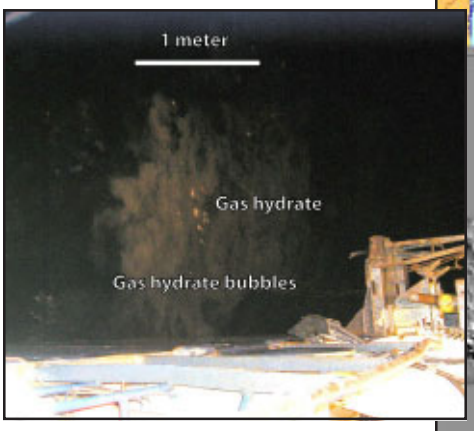
Multinational Team Recovers Sub-Bottom Gulf-of-Mexico Hydrate Cores

It was an impressive, dramatic show.

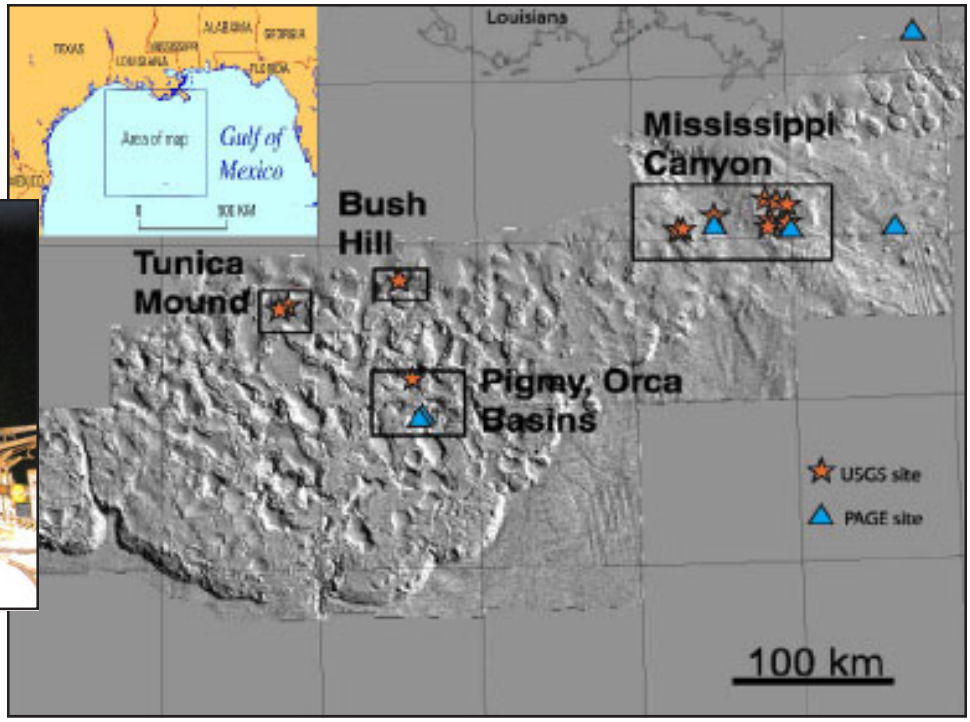
Hydrate dissociation was spectacularly demonstrated when several meters of a core blew vertically out of the end of the core barrel, flew at least 33 feet (10 meters) into the air, and landed in the water next to the giant piston-coring cruise ship. The gas hydrate specimen remained on the surface (because of its low density), and floated away as it dissociated.

Scientists from the United States, France, Germany, the Netherlands, Canada, Japan, Greece, Russia and Mexico set out from Cancún, Mexico in the Gulf of Mexico (GOM) aboard the 400-foot (120-meter) long French research vessel (R/V) *Marion Dufresne*. The cruise, scheduled from July 1 though July 18, 2002, was partially funded by the U.S. Department of Energy, and was conducted jointly by the Institut Polaire Français, Paul-Émile Victor (IPEV) and the U.S. Geological Survey (USGS).

The focus of the cruise was to determine whether gas hydrates exist away from obvious seafloor hydrate mounds into adjacent sedimentary basins and, if so, whether significant deposits occur deep within these basins. The GOM is unique in that it contains numerous, aerially extensive, occurrences of both biogenic and thermogenic hydrates. Gas hydrates are relatively common on the GOM seafloor, but there is a lack of bottom simulating reflections on seismic records.



"Ballistic" Hydrate Sample Dissociating Over the Sea Surface



Site Map for R/V Marion Dufresne Research Cruise

Unlike any U.S. research vessel, the *Marion Dufresne* has an unobstructed starboard main deck where IPEV's "Calypso" corer is deployed and recovered. During the 17-day cruise, the piston-coring system collected 17 cores, some as long as 125 feet (38 meters), under the direction of the chief of operations, Yvon Balut (IPEV). USGS scientists also collected 17 deep (46 to 69 feet or 4 to 21 meters) heat-flow profiles near the piston-core sites. The scientists found that widely varying geothermal gradients exist across the northern GOM. This observation will help define the sub-bottom extent of gas-hydrate stability.

Cores were taken from the Tunica Mound, Bush Hill and the east and west flanks of the Mississippi Canyon. Gas hydrates were recovered in four different cores at a maximum depth of about 27 feet (8 meters) below the seafloor. The hydrates in one core were disseminated within fine-grained sediment associated with the presence of nearby hydrocarbons. In another core, hydrates formed massive veins that filled the entire cross section of the core liner. These samples imply that continuous layers of gas hydrates of some unknown lateral extent exist.

As gas and oil exploration and production move into deeper water—where hydrate mounds are found and where hydrates are stable in the sediments—the potential hazards of drilling increase. Preliminary results confirm the existence of gas hydrates in the sub-bottom in the vicinity of the vents, although their presence is not common in the adjacent sedimentary basins. The scientists will use geochemical analyses, physical properties and biological associations to study the pore water and gas samples. Results will also be correlated with seismic records to assess the potential for using such records to locate sub-seafloor gas hydrates.

For more information on the R/V *Marion Dufresne* cruise, contact Deborah Hutchinson at dhutchinson@usgs.gov, 508-457-2263; or Bill Gwilliam at wgwill@netl.doe.gov, (304) 285-4401.

Gas Hydrate Chunks Recovered From a Giant Piston Core

R/V Marion Dufresne

Gulf of Mexico Hydrate Research Consortium Cruise Locates New Hydrate Site, Tests Pore-Water Sampler and Recovers Seafloor Probe

Researchers aboard the cruise ship research vessel (R/V) *Seward Johnson* and the submersible *Johnson Sea-Link* collected valuable gas hydrate data during dives conducted from May 28 through June 5, 2002. The cruise was dedicated to studying the near-seafloor hydrocarbon system within the hydrate stability zone of the northern Gulf of Mexico (GOM), and specifically at locations in the Green, Mississippi and Desoto canyons. Mother Nature favored them with perfect weather and sea conditions, yielding 14 successful dives.

The Research Crew for the Johnson Sea Link Cruise Sponsored by the Gulf of Mexico Hydrate Research Consortium

The primary research team was composed of scientists from the GOM Hydrates Research Consortium (HRC). The consortium is part of the Center for Marine Resources and Environmental Technology (CMRET) at the University of Mississippi, and is supported by the Mineral Management Service (MMS), the National Oceanic and Atmospheric Administration (NOAA), and the Department of Energy's National Energy Technology Laboratory. Members are from academia, federal institutions and the U.S. Navy. Dive planning and selection of study locations were based on information from proprietary data provided by MMS, represented by Jesse Hunt. The HRC site selection team consisted of Harry Roberts and Roger Sassen. J.R. (Bob) Woolsey and Tom McGee of the CMRET had overall responsibility for the DOE leg of the cruise.

New Hydrate Site. The huge amount of data accumulated from the cruise is now being analyzed. Scientists collected samples of vent gas and gas hydrates from a newly discovered gas hydrate mound in the deeper water of the Mississippi Canyon, making this the easternmost gas hydrate site

identified in the GOM Salt Basin. Preliminary data show that the molecular properties of the gas hydrates are unusual, because the main hydrocarbons are methane and ethane. Only trace amounts of other hydrocarbons were present. Little is known about the occurrence or origin of natural methane-ethane gas hydrates, so the newly discovered mound is a significant find.

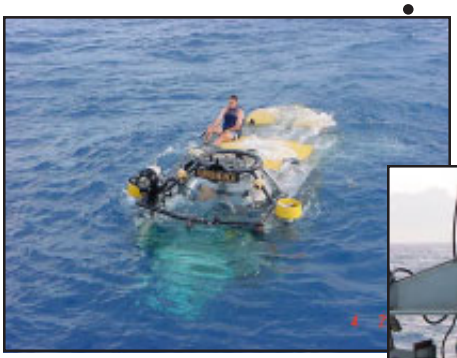
Pore-Water Sampler. A new in-situ pressurized pore-water sampler was deployed and successfully tested. Developed by the Florida State University (FSU)/University of North Carolina (UNC) geochemistry group, the sampler can collect interstitial water samples at various depths and deliver the samples to the surface without degassing. The samples collected during the cruise yielded the highest dissolved hydrocarbon concentrations thus far reported for a gas hydrate environment. FSU/UNC researchers are attempting to determine the relative importance of petroleum and dissolved methane in supporting microbial respiration.

Dr. Bob Woolsey admires the FSU/UNC in-situ pressurized pore-water sampler.

Seafloor Probe. Researchers succeeded in recovering a 3.3-foot (1-meter) long seafloor temperature probe that had been in place at a depth of 1,870 feet (570 meters) for more than three years. The data recorded by the probe was still intact, and suggests transient thermal effects of a significant loop current over a period of several months. Satellite remote sensing data and other evidence seem to corroborate the existence of this loop current. If verified, loop currents perturb the temperature of seafloor sediments in deeper water than previously supposed.

Other Studies. The Geotechnical and Environmental Research Group at Texas A&M University is analyzing light hydrocarbon gases and gas hydrates, particularly the molecular distribution (methane through propane) of gases that vent naturally from the seafloor to the water column. The composition of the vent gas controls the crystal structure of gas hydrates and is an indicator of the gas hydrate origin. Scientists at the National Center for Natural Products Research at the University of Mississippi are analyzing biological samples, and have begun isolating specific microorganisms. The microbes will be extracted and filtered through biomedical screens that include antimicrobial, anticancer and antiviral targets. The ecological role of these microbes will also be examined, and biosurfactants produced by several of the more characteristic microbial communities (e.g., vent sites, hydrate outcrops) will be collected and separated for further studies.

For more information on the DOE segment of the cruise, contact J. Robert Woolsey at inst@mmri.olemiss.edu, (662) 915-7320; or Joseph Renk at Joseph.Renk@netl.doe.gov, (412) 386-6406.



Johnson Sea-Link Submersible Ready for Pickup

Dr. Harry Roberts Back From the Depths

This thermister probe was found to be in good condition with more than three years of thermal recordings. A thermal record captures loop current transit as corroborated by satellite imagery. The event coincided with an increase/decrease of gas vent bubble stream activity in the vicinity of the hydrate mound.

LEXEN02 CRUISE PERSONNEL

Joseph P. Montoya Ga. Tech PI Scientist
Chris Payne Ga. Tech Technician
Kim Rathbun Ga. Tech Technician
Patricia A. Sobecky Ga. Tech Chief Scientist
Heath Mills Ga. Tech Graduate Student
Cassie Hodges Ga. Tech Technician
Rob Martinez Ga. Tech Graduate Student
Samantha B. Joye UGA co-Chief Scientist
Matt Erickson UGA Technician
Vladimir Samarkin UGA Post-doctoral Fellow
Beth Orcutt UGA Graduate Student
Karin Kalentra UC Santa Barbara Graduate Student
Ian MacDonald Texas A&M PI Scientist
Debekeauler TAMU Graduate Student
Mik Vadaro TAMU Graduate Student
John Murray Side-scan Sonar Technician
Kevin Brown Scripps Scientist
Mike Tryon Scripps Post-doctoral Fellow

Twenty Days Studying Life in Extreme Environments

Scientists aboard the research vessel (R/V) *Seward Johnson II* spent twenty days in the Gulf of Mexico (GOM) this summer studying the life forms and conditions in the extreme environments associated with gas hydrates and brines. As part of the National Science Foundation (NSF) Life in Extreme Environments project, the group collected hydrate samples, sediments, brine and animals from four locations (two brine and two hydrate sites) in the deep waters and seafloor of the GOM.

The physical and chemical conditions of the sites approach or exceed the tolerances for life, and researchers are trying to understand the life processes that occur there. Microbial life forms are of particular interest, and the samples were subjected to extensive molecular, microbiological and geochemical assays to characterize microbial community composition and activity in brine and hydrate extreme environments. The cruise was a major success in terms of sample collections despite the cancellation of seven dives because of weather conditions and a mechanical problem.

Funding for the July 2 to 22, 2002 cruise was provided by NSF, National Oceanic and Atmospheric Association/National Undersea Research Program (NOAA/NURP), NOAA/Ocean Exploration and the U.S. Department of Energy, National Energy Technology Laboratory. Results of the research will be published in six to eight months.

For more information, contact Dr. Patricia A. Sobecky at patricia.sobecky@biology.gatech.edu.

Hydrate-Ice Worm

SCIENTISTS ON THE CRUISE

Miriam Kastner, Chief Scientist, University of California San Diego, SIO
Gretchen Robertson, University of California San Diego, SIO
Wei-Wei, University of California San Diego, SIO
Christian Solem, University of California San Diego, SIO
Evan Solomon, University of California San Diego, SIO
Tabitha Hensley, University of California San Diego, SIO
Patrick Rafter, University of California San Diego, SIO
Joseph Bone, volunteer
Chelsea Richardson, volunteer
Nicolas Grijalva y Ortiz, CICESE, academic observer
Doug Bartlett, University of California San Diego, SIO
Tessa Hill, University of California, Santa Barbara
Mr. George D. Wardlaw, III, University of California San Diego, SIO
Dr. David Valentine, University of California San Diego, SIO
Ms. Alexandra Elizabeth Purdy, University of California San Diego, SIO
Dr. David Ridgway Boone, Portland State University
Ms. Melissa Mary Kendall, Portland State University

Alvin Explores the Juan de Fuca Seafloor

During late July 2002, researchers aboard the research vessel (R/V) *Atlantis* explored the Pacific seafloor in search of methane and methane hydrates. The area of interest was the Juan de Fuca microplate off the coast of the Pacific Northwest of the United States and southern British Columbia. Utilizing the submersible *Alvin*, the scientists searched for fresh sediment samples from anaerobic methane oxidation (AMO) marine sediment environments and, if possible, methane hydrate samples for use in laboratory-maintained bioreactor studies of AMO.

The cruise was highly successful. During each of the four allotted *Alvin* dives, scientists observed active methane vents and expansive fields of microbial mats and clams, which are bioindicators of AMO. Large numbers of push-core sediment samples were taken from which subcores were prepared for pore fluid chemistry, methane (and higher hydrocarbons) measurements, microbiology, molecular biology and the bioreactor inoculum, an apparatus containing a medium for growing organisms. One sample of each core was archived.

The scientists were also able to produce gas hydrate in situ by holding an inverted Plexiglas collection chamber over an actively venting cold seep. The sample gas was recovered using a pressure-retaining sampler and will be used for subsequent chemical and isotopic studies. A grid of Nisken seawater samples for water column measurements of methane concentration and isotope ratios and dissolved inorganic carbon (DIC) was also collected. Cold seep plumes were sampled for gas chemistry and isotopic compositions.

Results of the experimental laboratory work will be published in approximately 12 months. Funding for this project was provided by the National Science Foundation. For more information, contact Dr. Miriam Kastner at jrs_kastner@odpemail.tamu.edu.

Research Vessel (R/V) Atlantis

German Researchers Study Hydrate Ridge Aboard the R/V *Sonne*

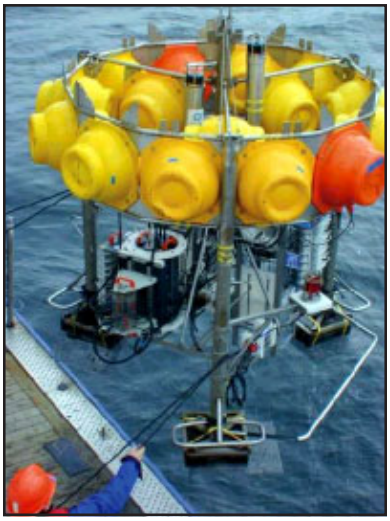
The research vessel (R/V) *Sonne*, carrying a crew of German scientists, cruised the Pacific Ocean for two months last summer collecting data to better understand gas hydrates in the geosystem. The SO165/ OTEGA cruise was a joint expedition of LOTUS[1] and OMEGA[2] (specializing in marine gas hydrates projects in the Pacific subduction zone), and MUMM[3] (specializing in microorganisms and their turnover rates in gas hydrate-bearing sediments).

The *Sonne* followed in the footsteps of the R/V *JOIDES Resolution*, exploring the hydrate province located off the shore of Oregon. During Leg 1, the area of Hydrate Ridge was mapped along a dense grid with a high resolution side-scan sonar, which allowed a resolution of decimeters to centimeters. Long-term benthic observatories were deployed to monitor mechanisms that control the formation and dissociation of gas hydrates over longer periods of time to more accurately reflect natural conditions. Scientists are also interested in investigating biological turnover and the occurrence of benthic organisms associated with hydrates, the geochemical character of sediments and the composition and concentration of gases in the hydrates.

Leg 2 focused on sampling and processing the gas hydrates. Scientists tested a newly developed MultiAutoclavCorer (MAC), which allows the preservation of sediment cores under in-situ pressures. This technology allows hydrates to be preserved within the sediment structure and will permit the internal structure of the hydrates to be imaged through computer tomography. Another new technology, a SwordFish system developed by Christian Situ of Vancouver, Canada, was used to determine the physical properties of sediment containing gas hydrate.

Funding for the cruise was solely provided by the German Ministry of Education and Research under the topic, Geotechnologies. The cruise report will appear in approximately two months and will be available from Geomar. Initial results in international journals will appear next year.

More information is available at *http://www.gashydrate.de/projekte/omega/otega/*.



Benthic Long-Term Observatory

Deep-Towed Side-Scan Sonar and Sub-Bottom Profiler

Photos courtesy of the GEOMAR Research Center, Germany

[1]Langzeit-Observatorien zur Untersuchung der Steuermechanismen bei der Bildung und Rückbildung von Gashydraten (Collaborative Research Project on Marine Gas Hydrates)

[2]Oberflächennahe Marine Gashydrate

[3]Methan in Marinen Gashydrathaltigen Sedimenten – Umsatzraten und Microorganismen (Methane in Gas Hydrate Bearing Sediments – Turnover Rates and Microorganisms)

First Dedicated Hydrate Well in Alaska Scheduled for Early 2003

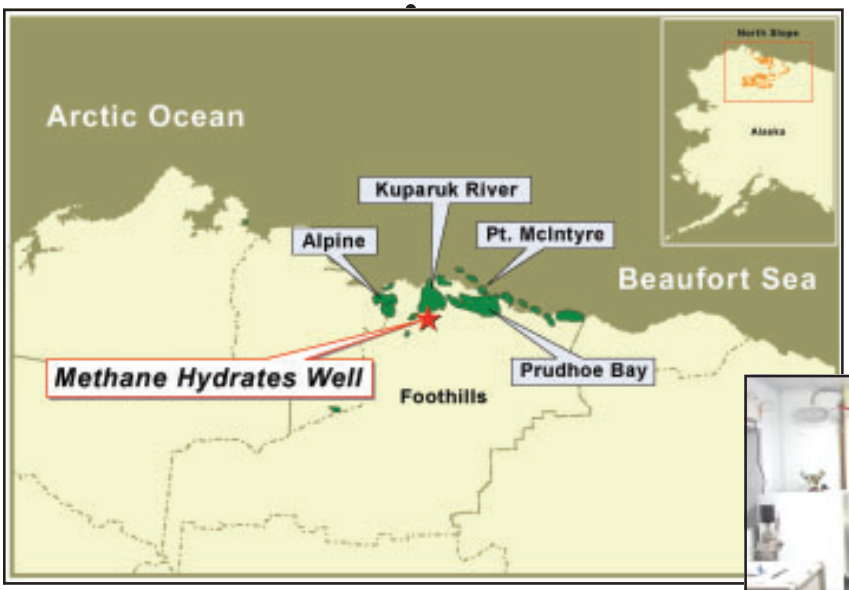
DOE and industry partners Anadarko Petroleum Corporation, Maurer Technology Incorporated and Noble Engineering and Development are making plans to drill and core the entire hydrate stability zone in a North Slope location southwest of the Kuparuk River Oil Field and adjacent to the Tarn-Cirque hydrate occurrence. It will be the first dedicated hydrate well in Alaska and is intended to test the reservoir characteristics and concentrations of hydrates in the North Slope hydrate resource.

The 3,500-foot (1,000-meter) well is scheduled to be spudded in early March 2003. It will deploy the latest Arctic technology, including Anadarko's Arctic Platform, a modular raised platform that is anchored into the permafrost, and a specialized Mobile Core Characterization System, designed for measuring and testing core samples on site. Also making its debut is a new system from Noble Engineering and Development called Drill Smart that will allow monitoring of the entire operation and transmission of the live data to Houston. The well will be drilled and cored with a hard-rock mining rig to allow continuous coring through the hydrate stability zone. The rig will collect a 3.45-inch (9-centimeter) core, with casing placed downhole and blowout prevention equipment installed at the surface. Highly chilled drilling fluid will be used to keep the hydrates from dissociating before the samples get to the surface and to the onsite core lab for analysis.

The partners are nearing completion of the project's first phase, a one-year intensive effort to finalize operational plans and logistics for the well. Experts in gas hydrates from the U.S. Geological Survey, Lawrence Berkeley Lab, the University of Oklahoma, University of Alaska at Anchorage and Schlumberger provided assistance and input during the planning stages.

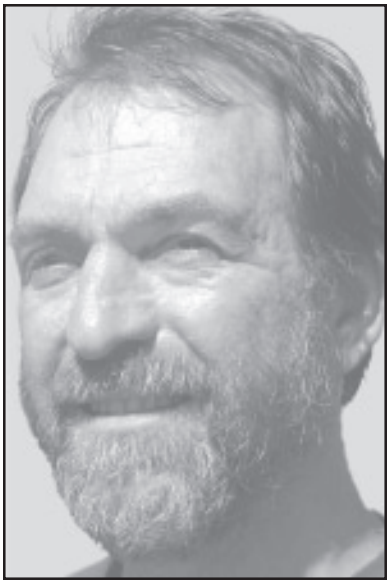
Hydrates have been identified in many wells in the North Slope, mainly from geophysical logging in conventional oil and gas wells. The total recoverable gas resource locked in Arctic hydrates is estimated at 11,000 to 24,000 trillion cubic feet (Tcf). However, details on its concentration, mode of occurrence and physical and chemical properties are lacking. This well should help to better define the resource and possible production scenarios. Tom Williams, Maurer's Vice President for Marketing and Business Development, said, "Routinely producing gas from Arctic hydrates is still a long way off, but this project will give the industry a good start in getting there."

For more information, contact Tom Williams at t.williams@maurertechnology.com, (713) 683-8227; or Frances Toro at frances.toro@netl.doe.gov, (304) 285-4107.



Location Map of the Drill Site

Interior of the Mobile Core Characterization System



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WHAT ARE THESE STRANGE MOUNDS WITH STREAMS OF BUBBLES FIZZING OFF THEIR TOPS?

That's the question Ian MacDonald and his coworkers kept asking themselves in the early 1990s while working with Texas A&M University's Geochemical and Environmental Research Group (GERG). Ian notes it was obvious what they were, but he had completely missed the interpretation. He finally understood what they were seeing when Harry Roberts of Louisiana State University sent back some video from a cruise in 1993. The video was of seafloor deposits of gas hydrates. Since then, Ian and his coworkers have developed sampling and observation experiments. And hydrates have been an important component of Ian's research ever since.

Ian feels that he has been fortunate to be in on the "marvelous process of discovery" using submarines and steadily better imaging and geophysical data. He has been involved in major breakthroughs simply by looking out of the submarine window at the right time. He is proud of his work showing that gas hydrates decompose in response to changing water temperatures, especially since the work was done on a shoestring budget using simple equipment that he tested in his bathtub. The equipment has since been replicated and remains accepted.

During the same time, he got the idea of looking at photographs taken from the space shuttle of his area of interest in the Gulf of Mexico. He discovered that oil slicks from natural seeps over 100 miles (161 kilometers) offshore can be reliably and accurately mapped using remote sensing data. This has also become an accepted tool in basin exploration.

He credits Jim Brooks, founder of GERG and one of his graduate advisors, with giving him and all graduate students who worked for him the freedom and scope to take responsibility for important research while throwing tremendous challenges at them. He also notes that Keith Kvenvolden has been wonderfully encouraging to his younger colleagues.

Ian responds strongly to the visual aspects of his research. He loves creating images that capture the essence of a problem—graphics or photographs. It's not surprising that photography is one of his hobbies. His wife, high-school English teacher Ann Blake, and their children, son Colin and daughter Basil, have been unbelievably supportive through his many absences at sea or meetings. Ian notes that Colin wants to be a computer game designer, and Basil is determined to be a geologist.

What does Ian see as the future of methane hydrates and hydrate research? He says, "Well obviously, we need to consider whether hydrates are a potential fuel source. But beyond that, we need to refine the theory of how hydrate deposits form, persist and sometimes fail catastrophically." He believes that the discovery of just how vast the hydrate carbon pool is will turn out to be one of the paradigm shifts in earth science. Our current estimates of the magnitude of gas hydrates are double the amount of organic carbon in the carbon cycle than was known even 15 years ago.

He concludes "I hope to produce accurate estimates of the total carbon input to the oceans from gas seeps."