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



### Features

# Interagency Group "Zooms In" on Methane Hydrate Pore Structures

One of the challenges of investigating gas hydrates is being able to examine the grain and pore structures, which are guides to the physics and chemistry of hydrate growth and the effects of changes in environmental conditions. Some of the technical hurdles of gas hydrate imaging involve (1) avoiding condensation on samples during cold transfer, (2) coating the samples without introducing heat or damage to the sample surface, (3) maintaining the sample material at conditions that avoid spontaneous decomposition or significant sublimation under vacuum, and (4) avoiding electron beam damage of the imaging area.

Yuri Makogan of Texas A&M and Dendy Sloan at the Colorado School of Mines have been the leaders in using pressurized optical-cell technology to investigate the growth of gas hydrates in the laboratory. Now, the scanning electron microscope (SEM), with its ultra-high resolution and large depth of focus, shows promise in allowing scientists to observe laboratory-made methane hydrates. These new investigations have expanded the work of Werner Kuhs and his colleagues, who pioneered cryo-SEM techniques to image and identify hydrate grain structures.

USGS scientists Laura Stern, Sue Circone, and Steve Kirby are using a Gatan Alto 2100 cryo-system to image a suite of gas hydrate samples made in their laboratory for physical property testing. The Gatan attachment circumvents the problems of hydrate imaging by creating a sample preparation chamber for (1) cold transfer of samples to the vacuum system, (2) maintaining cold temperatures while samples are cleaved to reveal fresh surface material, and (3) cold coating to prevent electrical discharge under the beam. Samples are then vacuum transferred to an auxiliary cold stage installed in the SEM chamber.

Preliminary SEM images clearly reveal the fundamental grain and pore characteristics of hydrate samples after synthesis, compaction, pressuretemperature processing, and deformation. Distinguishing hydrates from ice remains challenging, although using sublimation, surface decomposition, or both can help in identification. Extreme care must be taken to avoid producing sample surface artifacts, and to distinguish them from intrinsic sample surface morphology. The initial success with this tool suggests that it will be an extremely useful in resolving the surface morphology of both lab-made and natural gas hydrates. Such comparisons will help scientists determine how closely lab-made gas hydrates emulate gas hydrates in nature, and should also aid in interpreting physical property measurements.

This work was supported by the U.S. Geological Survey's Gas Hydrate Project and NETL's National Methane Hydrate R&D Program through a grant to Lawrence Livermore National Laboratory. For more information on this project, contact Sue Circone at scircone@usgs.gov, Steve Kirby at skirby@usgs.gov, or Laura Stern at lstern@usgs.gov.



Four SEM micrographs of lab-synthesized gas hydrates show fairly uniform sample textures of well-crystallized hydrate material with crystal-face development exposed along pore walls.

A. Low magnification. Granular but cohesive texture is quite different from the simple spherical grain shapes and geometrically simple pore shapes of the granular ice from which it was made. B. Higher magnification. Considerable recrystallization and more complex pore geometry than in the granular ice reactant. The "bumpy" surface texture of the pore walls is also different. C. Features imaged along pore walls vary from sample to sample, but many of the "bumps" on the pore walls are small hydrate crystals with characteristic cubic-crystal faceting. D. Highest magnification. Tiny dome-shaped structures on these crystal facets may be hydrate crystal growth structures.

#### 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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# Monitoring Station for Deep-Water Methane Hydrates Coming Soon

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The Center for Marine Resources and Environmental Technology at the University of Mississippi is developing a remote, multi-sensor monitoring station for naturally occurring deep-water methane hydrates. Design and development have been ongoing since 1999, and the observatory should begin operation by 2004 at a selected site in 800 to 1,000 meters of water.

Under the direction of Robert Woolsey, the monitoring station will be used for long-term investigation and research of the near-sea floor hydrocarbon system within the hydrate stability zone of the northern Gulf of Mexico. The station will monitor physical and chemical parameters of the sea water and sea floor sediments continuously over an extended period of time

The heart of the station will be a network of vertical arrays of sensors. Each array will occupy the lower portion of the water column and a hole bored into the sea floor. Sensors will include hydrophones to record compression waves, thermistors to measure temperature within the water column and the sediment, and eventually, optic fibers connected to an optical spectrometer to identify pore fluids and hydrocarbon gases in the sediment section. The lowermost sensor of each array will be a three-component accelerometer embedded in the sediments at the bottom of the hole to record compression and shear waves.

Peripheral sensors will include a sea floor positioning system and acoustic Doppler current profilers. If sufficient electrical power is available, several video systems with pan-and-tilt capability will be installed. The video images would be posted on a website in real time for education and public outreach.

Retrieving the huge volume of data that the station will produce is not a trivial problem. The most likely scenario is that, at first, the data will be recorded on the sea floor and will be periodically downloaded by an underwater vehicle.



Multi-sensor monitoring station, developed by the University of Mississippi, will continuously monitor ocean environments over an extended period of time. Eventually, the station will be connected by optic fiber to a surface structure, such as an oil platform, and the data will be relayed to a shore facility at the Stennis Space Center, Mississippi.

Prototypes of the sensor systems are being tested on research cruises this summer. The prototypes include hydrophones fabricated in vertical line arrays (VLAs) and a sea floor probe (SFP), which functions as a sub-sea floor extension to the VLAs. In late 2003, three VLAs/SFPs will be installed in the Gulf on Mexico, and initial operation of the monitoring station will begin.

Data collection will begin in 2004. The observatory will first collect data and then researchers will develop a database to establish baseline conditions and models. Research will focus on physical and chemical information about sea floor stability and the accretion/dissociation of gas hydrates. Modeling, appropriate for exploration and eventual production of hydrates and associated free gas, will be pursued from both technical and environmental perspectives. If, as expected, the data elicits responses from chemosynthetic communities residing nearby, the station's capabilities could be expanded to include biologic monitoring. This should provide an excellent means to explore the interactions between life forms and physical/chemical stimuli as well as how biologic agents produce or modify geologic materials and processes.

Technology transfer to industry and government agencies is a primary responsibility. An effort will be made to broadcast scientific activities and results available for use in classrooms. The access will be real time and, as much as possible, interactive.

# **Current Activities**

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#### ChevronTexaco Makes Gulf Exploration Safer

Researchers are investigating how naturally occurring gas hydrates affect seafloor stability. Seafloor instability may cause problems with drilling and production for oil and gas and in building and operating pipelines.

ChevronTexaco is involved in this quest to better understand naturally occurring gas hydrates in the marine environment. The location is the deep-water environment of the Gulf of Mexico. Scientists will gather additional data to study climate change. They will determine how the results of this project can be used to assess if and how gas hydrates act as a trapping mechanism for shallow oil or gas reservoirs.

ChevronTexaco organized a Joint Industry Project (JIP) to plan and conduct this research. Original members of the JIP were ChevronTexaco, Schlumberger, Phillips, Conoco, and Halliburton. The Minerals Management Service (MMS), TotalFinaElf, and Japan National Oil Company recently agreed to participate in the JIP.

Four workshops have been held to initiate and plan Phase I of the project. JIP scientists identified 12 tasks and four technical teams at a **technical team organizational workshop**. The objective of a **data collection workshop** was to obtain feedback on the quantity and quality of existing public and private data. The purpose of the **geoscience/reservoir modeling workshop** was to find out what data the geoscience and engineering communities need to run any type of model. A **drilling and coring workshop** was designed to discuss the state-of-the-art in drilling, coring, and testing wellbores that encounter natural gas hydrates in deep water.

The JIP is currently reassessing the 12 Phase I tasks in terms of cost, time, and resources (CTR) required. The CTRs will be used to write requests for proposals (RFPs). In Phase II, three data collection wells will be drilled to help improve the technologies required to characterize gas hydrate deposits in the deep water Gulf of Mexico using seismic, core, and logging data.

Drilling and coring in Phase II is expected to be conducted in the last quarter of 2003 or the first quarter of 2004. Depending on the contracted drill ship, there may be scope for additional scientific personnel and research projects to be conducted while the JIP collects the data that it needs to meet its goals.

#### First Methane Hydrates Interagency R&D Conference

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The first Methane Hydrates Interagency R&D Conference was held in Washington in March 2002. The purpose of the conference was to present results and future plans for methane hydrate research by participating federal agencies.

Scientists from each of the participating federal agencies presented new findings and discoveries and reported technological advances in hydrate research. Topics included (1) a review of resource assessments, (2) the interaction of hydrates, global climate change, the world's oceans and newly discovered chemosynthetic life forms, and (3) the potential of producing methane from hydrates. The presentations and papers have been compiled on a compact disc. To order a CD, please visit www.netl.doe.gov and click on publications.



Over 100 participants from collaborative agencies, government organizations, industry, academia, professional organizations, and research institutions attended the conference.

# Announcements

### **Cruisin' for Hydrates**

## 2002 Methane Hydrate Research Cruises

Fourteen projects utilizing six marine research vessels are scheduled during the spring, summer, and fall of this year. Details can be found through the National Methane Hydrate website at http://www.netl.doe.gov/scng/hydrate/events/calendar.htm

Dates 2002	Institution	Chief Scientist	Cruise Name	Research Vessel	Research Area
5/19-6/5	LSU	H. Roberts	L128400	Seward Johnson II	Gulf of Mexico
6/6-6/14	TAMU	I. MacDonald	DE-AP26-02- NT20372	Seward Johnson II	Gulf of Mexico
6/15-6/26	Penn State	C. Fisher	OCE0117050	Seward Johnson II	Gulf of Mexico
6/17-7/15	NSF	J. Gettrust	OCE617795	?	North Carolina shelf
6/28-8/21	OMEGA	Suess	OTEGA I	Sonne	Hydrate Ridge
7/1-7/31	NOAA (WHOI)			Atlantis	Western Gulf of Alaska
7/1-7/10	USGS	W. Dillon, P.Coffin	PRE Cruise 02018	Marion Dufresne	Gulf of Mexico
7/1-7/14	USGS	D. Hutchinson	PRE Cruise 02001	Gyre	Gulf of Mexico
7/5-7/22	Georgia Tech	P. Sobecky	OCE0085549	Seward Johnson	Gulf of Mexico
7/7-7/20	INGGAS	Fluh		Jan Mayen	Storrega Slide
7/8-9/6	ODP	G. Bohrmann, A. Trehu	Leg 204: Gas Hydrates 3	Joides Resolution	Hydrate Ridge
7/22-7/27	SIO	M. Kastner	OCE0096415	Atlantis	Juan de Fuca
10/18-11/1	Georgia Tech/NSF	C. Ruppel	OCE0118071	Seward Johnson	Gulf of Mexico
11/30-12/22	UCSB	J. Childress	OCE0002426	Atlantis	EPR



Methane hydrate research shifts into high gear during the summer.

# Spotlight on Research: Timothy S. Collett, USGS



#### THE FIRST TIME TIM HEARD THE TERM GAS HYDRATES WAS IN 1982.

His adviser at the University of Alaska told him that he knew of an interesting problem that Tim might be able to work into a Masters thesis topic. Now, some 20 years later, Tim reports that he is still working on his original thesis topic until he gets it right. In 1983, Tim's Masters thesis evolved into a research position with the Geologic Division of the U.S. Geological Survey (USGS). From his original research focus on gas hydrates in northern Alaska, Tim has studied numerous gas hydrate accumulations throughout the world, including those of the Messoyakha field in West Siberia and the marine gas hydrate occurrences on the Blake Ridge.

Tim was also the Principal Investigator responsible for organizing and conducting the 1995 USGS national oil and gas assessment of naturally occurring gas hydrates. This assessment included, for the first time, a systematic, geology-based, appraisal of the volume of gas in the gas hydrate accumulations of the United States. Most recently, Tim was co-chief scientist of an international, cooperative, gas hydrate research project to drill several dedicated gas hydrate research wells in the Mackenzie Delta of Canada. Tim also sailed as a logging scientist on the Ocean Drilling Program, Leg 164 gas hydrate research cruise to the Blake Ridge. He plans to again sail as a logging scientist on Leg 204 to Hydrate Ridge off the coast of Oregon this summer.

Since 1997, Tim has been working with the DOE to rekindle interest in a national gas hydrate research program. This initiative has provided several opportunities for Tim to serve as an expert witness before both House and Senate subcommittees. Tim is the co-founder and co-chair of the Gas Hydrate Research Committee in the Energy Minerals Division of the American Association of Petroleum Geologists. Tim holds a B.S. in geology from Michigan State University, an M.S. in geology from the University of Alaska, and a Ph.D. from the Colorado School of Mines. While at the Colorado School of Mines, Tim had the opportunity to study under Dr. E. Dendy Sloan, one of the pioneers in gas hydrate research.

Tim sees the recent explosion of interest in gas hydrates as an unparalleled opportunity to advance our understanding of gas hydrates in nature. As Tim explains, individual researchers often focus on specific issues, such as gas hydrates as a potential energy resource, a potential geologic hazard, or a possible agent of global climate change. However, all of these efforts are fundamentally linked under our need to understand the geologic controls on the formation, occurrence, and evolution of gas hydrate accumulations in nature.

Over the years, the gas hydrate research community has become very familiar with Tim's family, particularly his twin boys Michael and Gabriel. Tim explains that many of his colleagues have generously helped with the needs of his twin boys and young daughter when their father often spends several months of the year in the Arctic or at sea.

## Endnote

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#### Hydrates Make the Best Seller List

Methane hydrates are no longer confined to the realm of the scientist. With the publication of Clive Cussler's newest book, *Fire Ice,* international intrigue, geologic disasters, and methane hydrates are combined for a thrilling tale of impending doom.

We have reprinted an editorial review of Cussler's book, compliments of *Publishers Weekly*, Copyright 2002, Cahners Business Information, Inc.:

his newest addition to the Kurt Austin series (after Blue Gold) has the men from NUMA ([National] Underwater & Marine Agency) team up with former KGB spies to face down a Russian mobster with czarist aspirations and a zealot's hatred for the "corruption and materialism" of the Western lifestyle.

The NUMA research vessel Argo is in the Black Sea for a PR jaunt when Austin spots the overdue TV crew being chased down an island beach by mounted Cossacks. Austin learns from his old KGB Cold War adversary Vladimir Petrov that the island is a mothballed submarine base commandeered by paranoid mobster Mikhail Razov (employer of the Cossacks), a billionaire who built Ataman Industries by taking over utilities and mines sold by the state. Razov claims descent from the Romanovs and is plotting to assume the throne.



Cover photo from Amazon.com website

Meanwhile, when a U.S. Navy sub goes missing and a mysterious tidal wave swamps a Maine coastal town, the NUMA team figures out that Ataman is mining "fire ice"—unstable and explosive solid methane in the high-pressure deep-sea bottom.

Austin and his oceanographic team join forces with Petrov and set out to foil Razov's plot. Cussler is in top form here, working in a role for Old Ironsides and Czar Nicholas II's crown while throwing in enough derring-do and eco-lore to leave his fans breathless. Coauthor Kemprecos (Blue Gold, with Cussler) adds his oceanographic expertise to the mix.