

Ice That Burns

by JOHN TOON

Although most hydrates lie buried in marine sediments, they occasionally occur at the sea floor. This image shows gas hydrate forming beneath a rock ledge above a sea floor cold seep approximately 250 miles east of Charleston, S.C.

METHANE GAS HYDRATES

COURTESY CAROLYN RUPPEL

Burning Ice.

That apparent contradiction describes methane gas hydrates, a solid form of methane and water normally found in sediment beneath the sea floor.

Methane – natural gas – is produced by the decomposition of organic material in the sediment. As the methane diffuses through the sediment, it combines with water at the low temperatures and high pressures beneath the ocean to produce an ice-like solid.

Touted as a potential energy source for a power hungry world, methane gas hydrates are really much more. Indeed, they may contribute to global warming, and could represent a potential threat to deep-sea petroleum production.

At the Georgia Institute of Technology, an interdisciplinary group of researchers studies gas hydrates from all these angles, coordinated by the Focused Research Program on Gas Hydrates. The work includes modeling, sea floor exploration, a novel chemical sensing system for continuous underwater monitoring, biological research and geo-technical studies with laboratory-grown

hydrates in sediments.

Methane gas hydrates exist along the continental margins worldwide, most in oceanic sediments hundreds of meters below the sea floor in water depths of more than 500 meters – or in permafrost areas. The U.S. Geological Survey estimates that gas hydrates off the U.S. coast or in Alaskan permafrost could contain 300 times the amount of methane available from conventional reserves. These hydrates exist as disseminated deposits, chunks several centimeters across and sometimes as concentrated layers.

But producing methane from gas hydrates faces some daunting challenges.

“If you could get these hydrates out of the sea floor, you’d have a concentrated form of natural gas,” says Carolyn Ruppel, associate professor of geophysics in Georgia Tech’s School of Earth and Atmospheric Sciences and coordinator of the gas hydrate program. “But a key question is whether it would take more energy to extract the gas hydrates than the gas may provide.”

Aside from the difficulty of deep-sea operations, mining the hydrates could destabilize the ocean floor or even trigger the runaway destabilization of the hydrates. The methane might be tapped by pumping heated liquid into the



Above: Researchers examine a core sample containing gas hydrates mixed with marine sediments. Below: a gas hydrate sample synthesized in a Georgia Tech research lab from tetrahydrofuran can sustain a flame as gas is released from the structure during heating.

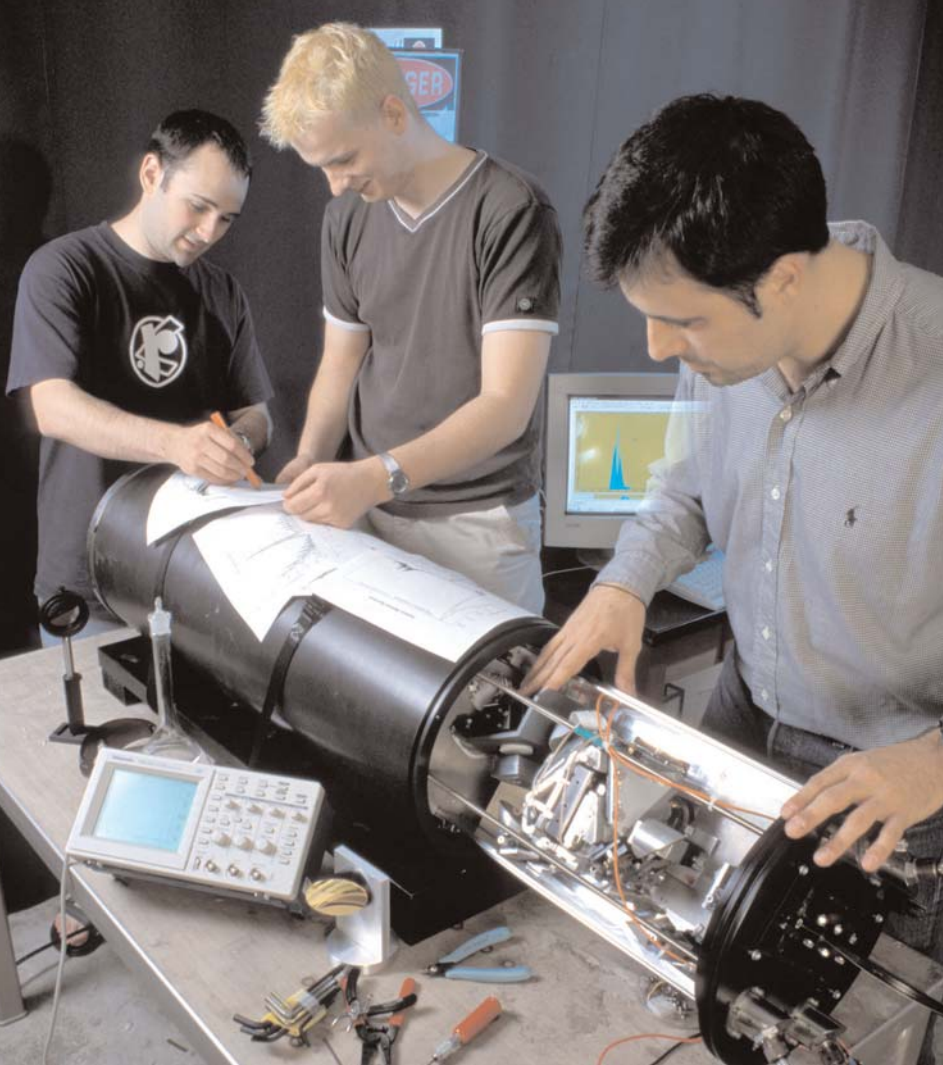


PHOTO BY GARY MEEK

Researchers (l-r) Neil Pennington, Manfred Karlowatz and Boris Mizaikoff re-align optical components and the fiber optic sensor head of the S.C.U.B.A. system. The device can operate deep in the ocean to detect and measure a wide range of hydrocarbons and chlorinated hydrocarbons.

“If you are drilling into the gas hydrate, you have to worry that the hydrate could suddenly dissociate, leading to the collapse of the sediment supporting the drill stem.”

hydrate deposits to dissociate and recover the gas, but this would be an energy-intensive operation. Another alternative would be to drill through the hydrate layers into pools of free gas below – a potential hazard.

And methane production presumes the ability to identify large hydrate deposits – something scientists are only now discovering. As part of a National Oceanic and Atmospheric Administration (NOAA)-sponsored multi-university research team aboard the RV Atlantis last autumn, Ruppel helped explore an area off the South Carolina coast known as the Blake Ridge. There, researchers found hydrates just above the ocean floor and filmed the formation of a hydrate cluster from a methane bubble. Through such explorations, scientists hope to learn more about where to find deposits of gas hydrates – without widespread drilling.

Later this year, Ruppel – along with Assistant Professor Daniel Lizarralde from the School of Earth and Atmospheric Sciences and colleagues from Rice University and Scripps Institute of Oceanography – will explore hydrates in the Gulf of Mexico as part of a project sponsored by the National Science Foundation.

“We will be trying to measure heat, the volume of methane coming out, and the rate that fluid is flowing from the sea floor,” she explains.

“This information may give us a good handle on what’s going on deeper in the sediments and how to predict the location of the gas hydrates.”

Continuous Chemical Monitoring Underwater

Boris Mizaikoff specializes in underwater optical sensing. An assistant professor in the School of Chemistry and Biochemistry, he and his colleagues have developed a compact sensing system able to continuously measure organic compounds deep beneath the ocean surface.

Known as Spectroscopy using Chemical sensors for Undersea Based Applications (S.C.U.B.A.), the system uses a chemically modified fiber-optic sensor connected to a Fourier transform infrared (FTIR) spectrometer – operating within a cylindrical pressure vessel less than a meter long. The special polymer coating on the optical fiber reversibly absorbs organic compounds from the water. An infrared light source excites the absorbed molecules via the evanescent field guided outside the fiber, whose absorptions are analyzed by the FTIR. This produces qualitative and quantitative measures of compounds present.

“Rather than taking a sample, bringing it to the lab and putting it into a spectrometer, we want to bring the measurement device to the sample so we can do in-situ analysis,” Mizaikoff explains. “That allows us to do these measurements continuously and under fairly harsh conditions.”

S.C.U.B.A. has already shown its ability to measure a range of organic compounds, including hydrocarbons and chlorinated hydrocarbons. With support from the U.S. Department of Energy through the University of Mississippi, Mizaikoff and his colleagues are developing an optical sensor system that will allow accurate methane measurement.

Growing and Studying Hydrates in the Lab

Scientists lack a clear understanding of how gas hydrates form in sediments – and how their formation affects the stability of the ocean floor. Carlos Santamarina, a professor in the School of Civil and Environmental Engineering, hopes to provide answers by growing gas hydrates in “dirty systems,” that is, at mineral surfaces and within different types of soils.

In a process he compares to medical diagnosis, Santamarina and his colleagues use electromagnetic and elastic waves to monitor hydrate growth, studying the formation process to learn about its effects on sediment response. Instead of

methane – which forms hydrates in sediments very slowly – they grow the icy structures from tetrahydrofuran (THF) so they can reproduce the very lengthy natural hydrate formation in shorter laboratory time. In addition, they study the formation of hydrate monolayers on minerals using atomic force microscopy.

Hydrate deposits in sea floor sediments may form “lenses,” like water forms ice layers in the soil during the winter months in northern states. In spring, if the ice melts faster than the water can dissipate, the soil becomes unstable and can cause extensive damage to highways. “If methane hydrates form these lenses under the sea floor and become destabilized for whatever reason – petroleum production or climatic change – we could have massive landslides on the sea floor,” he says.

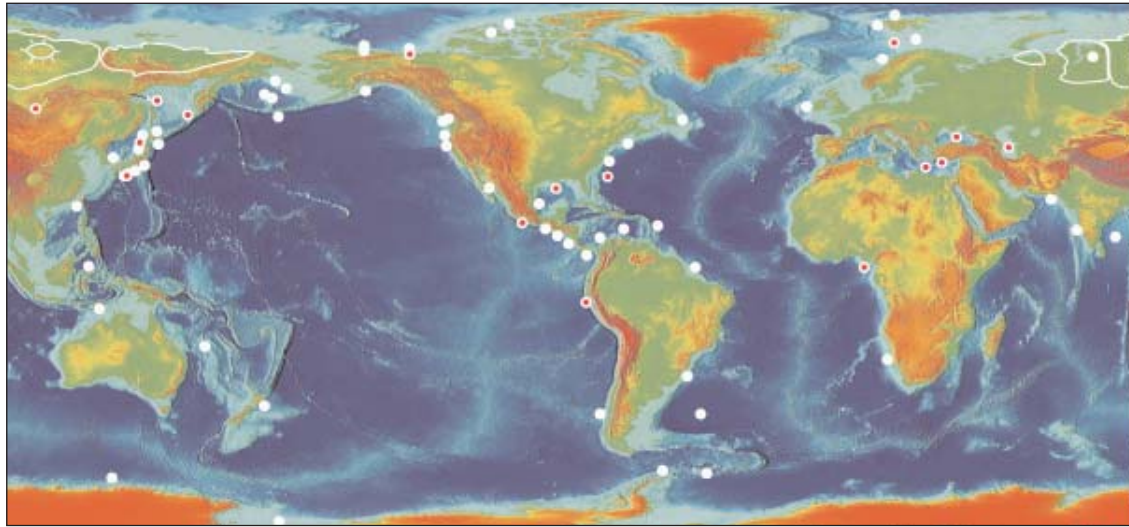
A Concern for Drilling, Climate Change

While the value of gas hydrates as a future energy source remains uncertain, the hazards they pose to production of conventional energy are clear. Oil companies are running out of reserves in shallow waters, forcing them to operate in areas where they may drill through hydrate formations. While they may eventually be able to produce energy from these hydrates, the more immediate concern is the potential hazards that gas hydrates may pose for oil drilling.

“If you are drilling into the gas hydrate, you have to worry that the hydrate could suddenly dissociate, leading to collapse of the sediment supporting the drill stem,” Ruppel says.

Perturbations of the sea floor can produce still bigger problems. Major sea floor slides can cause tsunamis, large oceanic waves that bring catastrophic damage to low-lying coastal areas. Beyond energy interests, methane gas hydrates may also play a role in global warming. Even slight warming could free significant amounts of methane, a potent greenhouse gas.

“You’d have to warm the deep ocean waters by just a few degrees,” Ruppel notes. “There is a time delay built into the system, so it would take quite a while for the sediments to heat up. But if even a portion of the methane released from hydrates gets out of the oceans and into the atmosphere, it could exacerbate global warming and lead to a synergy between destruction of hydrates, release of



methane and climate change.”

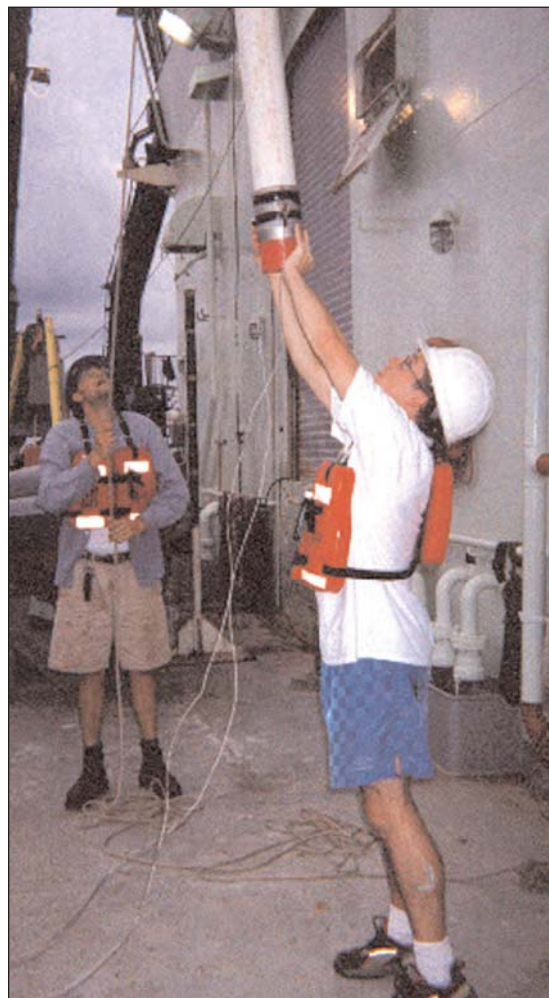
As an alternative source of energy, a hazard to conventional energy production and a global warming concern, “burning ice” is indeed a contradiction. **RH**

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Above: This map, modified from one published by the U.S. Geological Survey, shows the distribution of known gas hydrate deposits.

Below: An artificially-colored gas hydrate crystal synthesized in the lab of Carlos Santamarina shows its crystalline structure. Left: Researchers retrieve a core sample containing gas hydrates taken from a site off the South Carolina coast.



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