# The Mother Lode of Natural Gas

## Methane hydrates stir tales of hope and hazard

By RICHARD MONASTERSKY

For kicks, oceanographer William P. Dillon likes to surprise visitors to his lab by taking ordinary-looking ice balls and setting them on fire.

"They're easy to light. You just put a match to them and they will go," says Dillon, a researcher with the U.S. Geological Survey (USGS) in Woods Hole, Mass.

If the truth be told, this is not typical ice. The prop in Dillon's show is a curious and poorly known structure called methane hydrate. Unlike ordinary water ice, methane hydrate consists of single molecules of natural gas trapped within crystalline cages formed by frozen water molecules. Although chemists first discovered gas hydrates in the early part of the 19th century, geoscientists have only recently started documenting their existence in underground deposits and exploring their importance as a potential fuel.

Late last year, a team of oceanographers conducted the most in-depth investigation of methane hydrates to date by drilling into an extensive accumulation beneath the seabed off the coast of the southeastern United States. The results of this research, which are now beginning to appear in the scientific literature, seem to bolster extremely sketchy estimates made years ago about the vastness of the hydrate resource.

"It turns out there is a tremendous amount of gas down there," says Charles Paull, a marine geologist at the University of North Carolina at Chapel Hill and a leader of the recent drilling expedition. "It shores up the fact that these are large reserves and makes it increasingly important that they get assessed in terms of whether they are energy-producing deposits or not."

At the same time, scientists wonder whether this resource also has a dark side. "There have been extremely rapid changes in climate in the past. Some think that these were caused by methane released from methane hydrates," says Dillon.

Despite their potential importance, methane hydrates have evaded scientific scrutiny until now, largely because they are extremely difficult to study. They exist only where high pressures and low temperatures squeeze water and methane into a solid form.

Most known deposits of methane hydrate lie below the seafloor in regions that slope from the continents to the deep ocean basins thousands of meters underwater. Marine geologists have tentatively identified deposits off the coasts of Costa Rica, New Jersey, Oregon, Japan, India, and hundreds of other sites around the globe. Petroleum companies have also encountered hydrates while drilling through Arctic permafrost in Siberia, Alaska, and Canada.

Like vampires, hydrates disintegrate quickly if pulled from their dark lair. When researchers on the recent drilling expedition hauled up cores of sediment from the ocean floor, the drastic reduction in pressure caused much of the hydrate to melt before it even reached the ship. Without unusual precautions, any remaining hydrate fizzed away when the scientists cut open the core.

"Gas hydrates have largely escaped traditional geologic observation because gas hydrates and humans are sort of incompatible. The gas hydrates decompose under the conditions [in which] people traditionally analyze cores. Conversely, humans have no experience in operating in the conditions where gas hydrates are stable. We die under the conditions of gas hydrate stability," says Paull.

Oceanographers first drilled through methane hydrates unintentionally, on an expedition in 1970. Although that encounter was uneventful, research drilling cruises purposely avoided suspected hydrate deposits for 2 decades afterward, fearing they might hit an overpressurized pocket of gas, which could blast away the drilling equipment. Concerns over pressurized gas gradually diminished, and mounting scientific curiosity emboldened researchers to try boring through more hydrate fields. Starting in 1992, the international Ocean Drilling Program (ODP) intentionally breached hydrate deposits several times without incident.

On the recent expedition, Paull and his colleagues drilled at three sites along the Blake Ridge, a large, submerged promontory 330 kilometers off the southeast coast of the United States. Working in water depths of 2,800 meters, the researchers penetrated 700 meters below the seafloor with a hollow drill bit that cuts away a core of sediment the diameter of a soda can.

The investigators had to take special precautions to prevent losing methane hydrate during the 10 minutes it took to haul fresh sections of core up from the ocean bottom. At various depths, they sealed small bits of core in pressurized barrels, thereby containing the gas until the core reached shipboard laboratories. These samples provided the first direct measurements of how much methane hydrate exists at different depths beneath the seafloor.

"The amount of hydrate down there is much higher than had previously been estimated," says Paull. "It was not uncommon to get from 10 liters up to 30 liters of gas per liter of sediment."

The researchers also measured, for the first time, large amounts of free gas trapped beneath the frozen hydrate deposits. The volume of gas was far more than expected, exceeding even the amount within the frozen layer, says Paull.

Although the exact origin of hydrates remains unknown, Paull and others suspect that bacteria within the sediments consume rich organic material and generate methane gas. At a certain depth beneath the seafloor, the low temperatures and high pressures ensnare the gas within the frozen hydrate structure. Methane below the hydrate layer remains in gaseous form because the temperatures there are too high to support freezing.

Conventional deposits of methane, or natural gas, form through a different process, when seafloor sediments get buried far deeper. Exposed to much higher temperatures, the organic material in the sediments simmers until it transforms into petroleum and eventually methane.

Nearly a decade ago, several researchers independently tried to estimate how much methane exists in hydrate deposits. Because of the scarcity of direct hydrate measurements at the time, the estimates rested on indirect seismic studies, which probe the ocean bottom sediments with blasts of sound that reflect off hidden layers.

These studies suggested that global hydrate deposits contain approximately 10,000 gigatons, or $10^{13}$ tons, of carbon. That number represents double the combined amount in all reserves of coal, oil, and conventional natural gas.

The newly emerging evidence supports these rough approximations, says Gordon J. MacDonald, one of the scientists who made the calculations in the 1980s. "All these estimates are quite uncertain. But it remains abundantly clear that methane hydrates contain the largest store of carbon that we know about that is underground," says MacDonald, who now directs the International Institute for Applied Systems Analysis in Laxenburg, Austria.

In fact, hydrates may be more widespread than previously thought. The recent ODP expedition found hydrates in regions that lack the seismically reflective layers usually used to identify potential deposits, the team reports in the Sept. 27 SCIENCE.

"Given their worldwide distribution and their very large quantities, they make a very attractive energy source, provided that one can bring the gas up at somewhere near market price," MacDonald says. The cost of accessing hydrates has served as a barrier in the past, but some energy-hungry nations lacking conventional fossil fuels are extremely interested in future use of hydrates.

Japan plans to drill exploratory wells in the next few years, first on land in Alaska and then in Japanese waters. The Japanese National Oil Company is currently negotiating with the U.S. and Canadian governments to conduct experimental drilling of hydrate deposits near Prudhoe Bay, Alaska, in early 1998. They hope to have more success than the nations and commercial companies that tried to extract frozen methane in Canada, Alaska, and Siberia during the 1970s and 1980s.

In nature, methane hydrates are fickle molecules, liable to melt whenever the pressure drops slightly or the temperature creeps upward. Evidence of this instability pockmarks the ocean floor along the Blake Ridge. Marine geologists have identified numerous craters there that apparently formed when hydrates melted, releasing methane gas.

"The Blake Ridge is a pressure cooker, over geological time. The gas and fluids come up and blow through the sediments. We can see depressions 500 to 700 meters wide and 20 to 30 meters deep," says Dillon.

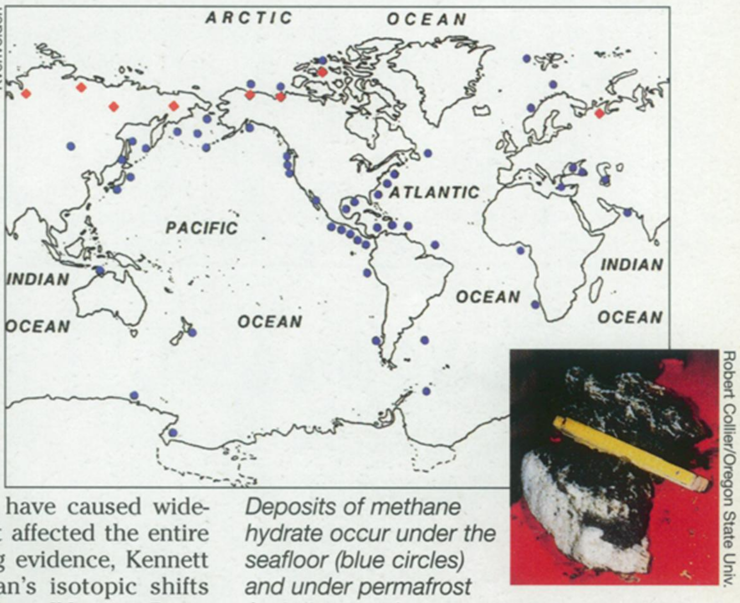
In other cases, melting at the base of the hydrate layer has destabilized seafloor slopes, leading to massive submarine landslides. Researchers have suggested hydrate weakness as a factor behind landslides off Alaska, the U.S. Atlantic coast, British Columbia, Norway, and Africa, says Keith A. Kvenvolden of the USGS in Menlo Park, Calif.

Such inherent instability could spell problems for future drilling platforms resting on top of hydrate-rich deposits. If the collapses are large enough, they could also produce the destructive waves called tsunamis that race across ocean basins.

Hydrates may exert their greatest impact through their indirect links to climate. Because methane is a powerful greenhouse gas—about 10 times as strong as carbon dioxide—massive melting of hydrates and the ensuing release of methane gas could raise Earth's surface temperature.

James P. Kennett of the University of California, Santa Barbara has recently discovered intriguing evidence implicating methane hydrates as an instigator of climate change. Sediments off the California coast show signs that carbon isotopic ratios in the ocean shifted quite dramatically and quickly at several times during the last 70,000 years. Because methane has a distinctive isotopic fingerprint that matches the shifts, Kennett suggests that large volumes of methane must have poured into the ocean at these times.

In his theory, the methane came from hydrates that melted when ocean waters warmed slightly. The liberation of so much methane over a few decades would have caused widespread warming that affected the entire globe. As supporting evidence, Kennett notes that the ocean's isotopic shifts indeed coincide with well-known Dansgaard-Oeschger episodes when Earth's ice age climate went suddenly warm.



Kvenvolden

Robert Collier/Oregon State Univ.

*Deposits of methane hydrate occur under the seafloor (blue circles) and under permafrost (red diamonds). Inset shows a chunk of gas hydrate collected off the coast of Oregon.*

"Until now, [hydrates] haven't really entered into discussions of climate change. They have been almost completely ignored. Until the beginning of this year, I had not even considered them. But I'm now convinced that they are of great importance to the global environment and have been for billions of years," says Kennett. He presented his findings in September at a gas hydrate conference in Ghent, Belgium.

Kvenvolden has proposed a different mechanism that might have released hydrates at the end of the last ice age. As the great blanket of continental ice melted at that time, global sea levels swelled by more than 90 meters, submerging many Arctic regions where hydrate layers exist. The relatively warm ocean water would have melted the hydrates, unleashing tremendous amounts of methane into the atmosphere, Kvenvolden believes.

The same rationale could apply to the modern world. Sea levels are currently rising slowly, at a rate of a few centimeters per decade. Projections suggest that they will rise even faster in the future because of the climatic warming caused by greenhouse gas pollution. At the same time, ocean temperatures are expected to creep upward.

"If you reason that hydrates were important in climate change in the past, there is no reason they wouldn't be important in the future," says Kvenvolden. Indeed, some scientists speculate that melting methane hydrates could greatly exacerbate global warming.

For now, though, Kvenvolden and others remain unsure exactly what role hydrates have played in past climate changes. Lacking this knowledge, they say it is impossible to predict how hydrates will behave in the future.

A greater understanding of hydrates and their importance will come as oceanographers tap deposits in other areas of the world, testing whether the lessons learned on the Blake Ridge apply elsewhere. Scientists are also creating synthetic hydrates in the laboratory (SN: 10/19/96, p. 252). By squeezing methane and water in a pressurized apparatus, Dillon and his colleagues can not only gauge how hydrates weaken seafloor sediments but also improve seismic methods for detecting hydrates.

When the experiments are over, the remaining synthetic hydrates could have other uses. "I hadn't really thought of it before, but you could try cooking with them," says Dillon. "I wouldn't want to plan a major meal, but you could probably scramble an egg on it." □