Fire and Ice Under the Deep-Sea Floor:

Vast undersea deposits of gas hydrates may play a major role in climate change and the future energy economy

For the U.S. Department of Energy, they represent a potential fuel reserve that may dwarf all the fossil fuel deposits on land combined. For oil and gas companies they're a nuisance and worse, threatening pipelines and offshore drilling platforms. For ocean sedimentologists, they may be a glue that binds together deep-sea sediments or a lubricant that permits the sediments to slump periodically in huge underwater landslides – events that could have a surprising effect on global climate. Indeed, there are climatologists to whom they may provide a missing link in the mechanisms of global climate change – a factor that might have limited the severity of past ice ages and today might be contributing to greenhouse warming. And finally there are even researchers – not many, fortunately – who have proposed half seriously that they may explain why ships and planes vanish in the Bermuda Triangle.

The ubiquitous actors that seem to be something to everyone are gas hydrates: curious, ice-like solids made up of gas molecules – mostly methane – caged in a crystal lattice of water. Until recently, gas hydrates were known mostly for the trouble they can cause the gas industry. They readily form in, and clog, the high-pressure pipelines used to transport gas unless the gas is first carefully dehydrated. But gas hydrates also occur naturally in deep-sea sediments and under the Arctic permafrost, and recent research suggests that the amounts are staggering and the diversity of roles intriguing.

From seismic studies, oceanographer William Dillon of the U.S. Geological Survey (USGS) in Woods Hole, Massachusetts, estimates that the sediments of the Blake Outer Ridge – a patch of ocean floor the size of Vermont off the southeastern United States – hold about 1100 cubic kilometres of hydrates. To absorb the scale of this estimate, consider that each volume of hydrate locks up about 160 volumes of gas. This would mean that if the number Dillon presented at a meeting of the Acoustical Society of America in April is correct, the Vermont-sized undersea ridge holds about 350 times the amount of natural gas consumed by the United States in 1989. Geochemist Keith Kvenvolden of the USGS in Menlo Park, California, took an earlier, more tentative crack at the total gas content of hydrate deposits worldwide. His conclusion: They hold the equivalent of some 10 000 billion metric tons of carbon – twice the carbon in all the coal, oil, and gas reserves on land.

Such figures are getting the attention of all sorts of scientists. For those concerned about climate change, the numbers suggest that gas hydrates might be a major source of methane, a greenhouse gas. Over at the Department of Energy, there are scientists dreaming of efficient extraction processes, even though methane from hydrates may not be flowing through municipal gas lines any time soon. And among geochemists, sedimen-

tologists, and marine seismologists, a small community has grown up around a rather new research topic: the nature and role of naturally occurring gas hydrates.

"Until recently", recalls Charles Paull, a geologist at the University of North Carolina at Chapel Hill, "nobody set out to study has hydrates" in their natural setting. Typically, he says, people stumbled across them in the course of other studies; work on hydrates in nature was "absolutely unfundable". With the growing recognition of hydrates' extent and potential importance, that's starting to change.

The change had been slow in coming. The pipeline problems were originally discovered back in the 1930s, and although geophysicists suspected that hydrates might also form naturally, in undersea layers of gas-rich sediments where conditions would not be so different from those in high-pressure pipelines, they didn't get proof until the early 1970s. First, core samples extracted from seafloor sediments during the Deep Sea Drilling Project (DSDP) came up charged with gas — enough, in some cases, to blow the sediment out of the core barrels. Then, over the next decade, Soviet and U.S. drillers began glimpsing the hydrates that were responsible.

The material looked pretty ordinary, something like a grayish ice cube, says geochemist Kvenvolden, who saw some of those first natural samples. But its ordinary appearance doesn't last long. It foams at the edges, he recalls, "and after 30 minutes you have nothing but a puddle."

The first fizzy crystals of hydrate came from the floor of the Black Sea in 1974, and over the next few years drillers found nodules, veins, and even layers of the material several feet thick in the ocean floor off Mexico, Guatemala, and the southeastern United States. About the same time, oil and gas wells in the high Arctic started yielding hints that the gas-water hybrids lurked there, too, under hundreds of meters of permafrost.

Geologists had good reason to think these were not isolated deposits. "Essentially the entire ocean bottom provides thermodynamic stability for hydrates", says Jerry Holder, a chemical engineer at the University of Pittsburgh. Below a water depth of about 500 meters the temperatures are low enough and the pressures high enough to foster hydrate formation; beyond that, Holder continues, all you need is gas. And the activity of microbes in the organic-rich sediments edging the continents provides methane in abundance.

What's more, there's at least indirect evidence that the ocean does harbor extensive hydrate deposits. Before geologists began finding the natural hydrates, they had detected a puzzling boundary, located several hundred meters below the seafloor, that vividly reflects seismic waves. Hydrates, they soon realized, were a ready explanation. Because the sediments seemed to get softer at the boundary, the researchers speculated that the boundary marks the lower limit of the solid hydrate layer. Below the boundary, which is called the bottom-simulating reflector (BSR) because it follows the ups and downs of the seafloor, the heat from the deep earth would prevent hydrates from forming, giving rise to a pool of trapped gas. Even where hydrates have not been sampled directly, BSRs are generally taken as a sign of their presence – and BSRs can be traced under much of the continental slope and rise, the region where the shallow continental shelf plunges into the abyss.

Still knowing how to identify the bottom of the hydrate-ridden sediments is not the same as knowing just how rich the oceanfloor deposits really are – to say nothing of those

in the permafrost. "What we're trying to do now is work on new techniques to get at the amount of hydrates", says Dillon, who plans to continue his studies on the Blake Outer Ridge. By probing the sediments which seismic waves and sampling them directly, he and his group hope to learn what form the hydrates take — whether they tend to occur as veins, nodules or grains — how concentrated they are in the sediment they occupy, and how the temperature and chemistry of the sediments affect them.

The unknowns haven't deterred the Department of Energy (DOE) from getting interested in hydrates as a future energy resource. "It's got fantastic potential", says Rodney Malone, manager of DOE's gas hydrate project at the Morgantown Energy Technology Center in West Virginia, "but we still don't know enough to say yea or nay". In addition to funding work such as Dillon's, DOE has been looking into production technologies – ways to get the hydrate deposits to release their gas. Heating the deposits with injections of steam or hot brine is one possibility – Malone calls it the "huff and puff" approach. Drawing away the free gas thought to be trapped beneath them is another. Still, recovery costs are expected to be high, and prospects for a hydrate-fueled economy any time soon seem dim to many in the field. "Economic recovery of that gas probably won't be viable until sometime in the next century", says E. Dendy Sloan, a chemical engineer at the Colorado School of Mines.

Of more immediate concern to oil companies is the hydrates' instability. Any major change in temperature or pressure is capable of breaking down the material, releasing the methane gas, Kvenvolden says. And if that were to happen as a result of deepwater drilling operations, the roughnecks on the platform might find themselves on shaky ground indeed as the firm sediments under the supports turned to mush. "If you dissociate the hydrates", says Holder, "you've got nothing but a pile of mud".

That very instability is a big part of the fascination of hydrates for researchers outside the energy business, particularly because hydrate breakdown might have a role in climate change. Methane, which is released by the breakdown, is a greenhouse gas. It contributes to the atmosphere's ability to trap solar heat and thereby has the potential to raise global temperatures. Could hydrate breakdown contribute to the greenhouse warming most climatologists think is imminent?

Perhaps not, at least in the next few decades, most experts agree. The greenhouse warming, if it is occurring, wouldn't do much to the hydrate deposits, which are protected from temperature change by hundreds of meters of water or a blanket of permafrost. "You're not going to change the temperature of the deep ocean very quickly", says Dillon.

But processes taking place over thousands of years might do the trick. Kvenvolden points out that as the ice sheets melted and the sea level rose at the end of the last ice age about 10 000 years ago, vast areas of Arctic permafrost were flooded. Chilly as the Arctic ocean is, it is warmer, on average, than the polar air. Kvenvolden thinks that as a result, hydrates in the flooded permafrost may have been decomposing slowly for thousands of years, their methane seeping out of the sediments.

And according to a scenario developed by Chapel Hill's Paul, together with Dillon and William Ussler, a fellow geologist at UNC, hydrate decomposition may even have helped to end the last ice age. In a paper in the March Geophysical Research Letters, the researchers point out that by the time the ice age peaked about 17 000 years ago, the

growth of the ice sheets had sucked so much water from the oceans that global sea level was some 125 meters lower than today. The resulting pressure drop in the deep sediments, they argue, would have lowered the maximum temperature at which gas hydrates could remain stable. The base of the stability zone – which is set by the heat flowing out of the deep earth – would have risen by about 20 meters, he calculates, unlocking a huge volume of gas.

"Simple calculations suggest it's a big number", Paull says – several hundreds of times more methane than the atmosphere currently contains. Paul acknowledges that much of that gas would not have escaped to the atmosphere. But even a fraction of the gas might have been enough to do the trick.

And researchers analyzing bubbles of ice-age air trapped in the Antarctic ice sheet have found that methane did begin rising toward the end of the ice age. The timing, Paull cautions, makes it hard to say whether the rise was cause or consequence of the glaciers' retreat. But he has another reason to think that the rise was causative.

"We don't know what actually happens at the bottom of the [hydrate layer]" as the sea level falls, Paull says. But one possibility, he thinks, is that gas building up under the hydrate layer as it decomposes acts like a layer of grease, lubricating the overlying sediment. Where the seafloor slopes, the sediment layers will be prone to slip, producing submarine landslides that release the trapped gas in great, greenhouse-enhancing burps. And Paull notes that the methane increase recorded in ice cores is not steady; instead it comes in a series of pulses – just what you would expect, he says, if gas trapped under the hydrate layer were suddenly being released by submarine landslides.

Moreover, James Booth of the USGS in Woods Hole, collaborating with Dillon, noticed that scars left on the ridge by submarine landslides were common all along the eastern United States at water depths of between 500 and 700 meters – just where the iceage drop in sea level might have decomposed the hydrates gluing the topmost sediment layers together. According to Robert Kayen of the USGS in Menlo Park, "a pervasive belt of landslides" has also been spotted along the continental slope in the Arctic Ocean. The slip surface – the bottom of the sliding sediment mass – tends to match the base of the hydrate layer, Kayen says, although he's skeptical that hydrate-triggered landslides would release sufficient methane to the atmosphere to trigger climate changes.

Indeed, there's much that needs to be resolved about the world's hydrate deposits – a situation that may have led at least one researcher to go off the deep end. A few years back, a petroleum geologist proposed that pulses of gas released from hydrate layers might explain the loss of ships and planes in the Bermuda Triangle. An ocean roiling with gas bubbles, he said, might swallow up a ship so quickly it would have no time to send a distress signal – and the cloud of methane rising from the sea surface might choke the engines of planes.

While few researchers are buying that idea, most would agree that given all the mysteries about hydrates, there's a need for what Steve Lewis of the USGS in Menlo Park calls "a little bit of ground truthing". That won't be long in coming, Lewis hopes. He will be one of two chief scientists on leg 141 of the Ocean Drilling Project, the successor to the DSDP. On the 2-month leg, scheduled to run from mid-November of this year through mid-January of 1992 off the coast of southern Chile, researchers will for the first time drill all the way through a hydrate layer, studying its makeup and probing the

amount and pressure of the gas trapped below the BSR. What they find is likely to affect thinking about hydrates as a force in climate change, an underpinning of the seafloor, and a future energy resource.

Until recently, Lewis remarks, "the official policy of the ODP was to forbid drilling to the depths of the BSR", into what some workers saw as a potentially dangerous pool of free gas. Now the ODP researchers are laying cautious plans to do just that. They and their landlocked colleagues can't wait to see what's there.

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