

Flammable Ice

Methane-laced ice crystals in the seafloor store more energy than all the world's fossil fuel reserves combined. But these methane hydrate deposits are fragile, and the gas that escapes from them may exacerbate global warming

by Erwin Suess, Gerhard Bohrmann, Jens Greinert and Erwin Lausch





ROGER SASSEN/Texas A&M University

It was a thrilling moment when the enormous seafloor sampler opened its metallic jaws and dumped its catch onto the deck of our ship, *Sonne*. A white substance resembling effervescent snow gleamed amid the dark mud hauled up from the bottom of the North Pacific Ocean. Watching it melt before our eyes, we sensed that we had struck our own kind of gold.

As members of the Research Center for Marine Geosciences (GEOMAR) at Christian Albrechts University in Kiel, Germany, we and our colleagues were searching for methane hydrate—a white, icelike compound made up of molecules of methane gas trapped inside cages of frozen water. To that end, we had undertaken several expeditions to inspect, with the help of a video camera tethered to the ship, a submarine ridge about 100 kilometers (62 miles) off the coast of Oregon. Earlier seismic investigations and drilling had suggested that this area might hold a substantial stash of our treasure. On July 12, 1996, we noticed peculiar white spots in the mud 785 meters (2,575 feet) below our ship.

To make sure this telltale sign of hydrate was the real thing, we directed our sampler, a contraption like a backhoe with two scoops, to take a giant bite out of the seafloor. Even while retrieving the payload, we saw our expectations confirmed. As the sampler ascended, the video camera mounted inside its jaws revealed that bubbles—attesting to the rapid escape of methane gas—were beginning to emerge from the muddy heap. Stable only at near-freezing temperatures and under the high-pressure conditions generated by the weight of at least 500 meters of overlying water, methane hydrates decompose rapidly above that depth. As the sample approached the ocean's surface, the flow of bubbles gradually increased and burst through the water's sparkling surface long before the jaws of the sampler did.

We wondered how much intact hydrate would reach the deck. Moving quickly, we managed to safeguard roughly 100 pounds (45 kilograms) of the hissing chunks in containers cooled with liquid nitrogen. In the end, we even had a few pieces left over, which inspired an impromptu fireworks display. Just holding a burning match to one of the white lumps ignited the hydrate's flammable methane, which also is one of the primary hydrocarbon components of natural gas. The lump burned with a reddish flame and left only a puddle of water as evidence of its former glory.

Before 1970 no one even knew that methane hydrates existed under the sea, and our haul was by far the largest quantity ever recovered from the ocean depths. Yet hydrates are by no means a rarity. On the contrary, in recent years they have been found to occur worldwide—from Japan to New Jersey and from

BUBBLES OF METHANE escape from a decomposing gas hydrate mound surrounded by tube worms. Such icelike hydrate deposits become unstable when the surrounding temperature rises more than a few degrees above freezing or when the pressure becomes lower than that found about 500 meters (1,064 feet) below the ocean surface.



GERMAN RESEARCH VESSEL SONNE (top) has spearheaded many methane hydrate explorations off the coast of Oregon. Researchers hauled up fresh sediment from a methane hydrate field there with the aid of a video-guided sampler in the summer of 1996 (middle). The muddy chunks (bottom) consist of alternating layers of pure-white methane hydrate, sediments and limestone.

Oregon to Costa Rica—in enormous quantities. Estimates vary widely, but most experts agree that marine gas hydrates collectively harbor twice as much carbon as do all known natural gas, crude oil and coal deposits on the earth [see illustration on page 81].

The energy stored in methane hydrates could potentially fuel our energy-hungry world in the future (if practical mining techniques are devised). But the hydrates also have a worrisome aspect: methane escaping from disturbed undersea hydrates may be an ecological threat. If even a small portion of these deposits decompose through natural processes, astonishing quantities of methane will be set free to exacerbate the greenhouse effect and global warming.

Although methane remains in the atmosphere relatively briefly—10 years on average—it does not vanish without a trace. In the presence of free oxygen, a methane molecule's single atom of carbon disengages from its four hydrogen atoms to become carbon dioxide, the most infamous of all greenhouse gases because it is one of those spewed into the atmosphere during the combustion of fossil fuels.

But are decomposing methane hydrates contributing to global warming now? And are they likely to do so in the future? Our 1996 journey—along with dozens of voyages and experiments since—have revealed something about the structure and origins of a variety of these massive yet remarkably unstable deposits and have provided some answers to the climate questions, but our

understanding is far from complete. We and our colleagues at GEOMAR continue our quest to understand just what role methane hydrates play in ocean-floor stability and both past and future climatic change.

Turning Heads

It was the immense cache of energy trapped in marine methane hydrates that first turned the heads of politicians. But the challenges of tapping that resource are now making some officials look the other way. Hydrates tend to form along the lower margins of continental slopes, where the seabed drops from the relatively shallow shelf, usually about 150 meters below the surface, toward the ocean's abyss several kilometers deep. The hydrate deposits may reach beneath the ocean floor another few hundred meters—deeper than most drilling rigs can safely operate. Moreover, the roughly sloping seafloor makes it difficult to run a pipeline from such deposits to shore.

Countries that wish to rely less on foreign fossil fuels have started to overcome these technical difficulties, however. Japan was scheduled to launch an experimental hydrate drilling project off the coast of Hokkaido in October. U.S. engineers also are playing with ideas for tapping hydrate energy sources [see box on page 80]. But as long as relatively cheap gas and oil remain available, most industrial countries are unlikely to invest heavily in the technologies needed to harvest hydrates efficiently.

Methane hydrates captured the attention of petroleum geologists a bit earlier than that of politicians. When engineers first realized in the 1930s that gas-laden ice crystals were plugging their gas and oil pipelines, laboratory researchers spent time studying hydrate structure and composition. For example, they learned that one type of hydrate structure consists of icy cages that can absorb small gas molecules such as methane, carbon dioxide and hydrogen sulfide. A different type forms larger cavities that can enclose several small molecules or larger hydrocarbon molecules, such as pentane. What is more, the individual cages can differ in the kinds of gas molecules they capture.

In the 1960s scientists discovered that hydrates could also form in natural environments. They found the first natural deposits in the permafrost regions of Siberia and North America, where the

substances were known as marsh gas. In the 1970s geophysicists George Bryan and John Ewing of Lamont-Doherty Earth Observatory of Columbia University found the earliest indication that methane hydrates also lurk beneath the seafloor. The hint came from seismological studies at Blake Ridge, a 100-kilometer-long feature off the North Carolina coast.

Seismologists can distinguish layers beneath the seafloor because sound waves bounce off certain kinds of dirt and rock differently than off other kinds. Some 600 meters below the ocean floor Bryan and Ewing saw an unusual reflection that mimicked the contour of the ridge. Their conclusion: this bottom-simulating reflector was the boundary between a methane hydrate layer and a layer of free methane gas that had accumulated below. Other experts found similar features elsewhere, and soon this type of reflector was being mapped as a methane hydrate deposit in ocean basins around the globe.

We used a bottom-simulating reflector, along with underwater video cameras, to guide our 1996 search for methane hydrates along the North Pacific seafloor promontory that has since been named Hydrate Ridge. Our successful recovery of intact hydrate on that expedition made it possible to study this unusual material in detail for the first time. Being able to analyze the texture and chemistry of its microscopic structure allowed us to confirm the plausible but previously unproved notion that the methane derives from the microbial decomposition of organic matter in the sediment.

Most telling were chemical tests that showed the hydrates to be enriched in carbon 12. Inorganic methane that seeps out of volcanic ridges and vents has higher levels of carbon 13, an isotope of carbon with an additional neutron. But the bacteria that digest organic matter in oxygen-deficient conditions such as those in sediments at the bottom of the sea tend to sequester more carbon 12 in the methane they generate.

The seafloor off the coast of Oregon also proved an especially fruitful theater of operations for assessing the stability of methane hydrate deposits and their potential role in releasing carbon into the atmosphere. Combined with research from other sites, these analyses indicate that methane hydrate deposits can be disturbingly labile.

We now know that in places along

Hydrate Ridge, the seabed is virtually paved with hundreds of square meters of hydrate. These deposits form part of the packet of sediments riding piggyback on the Juan de Fuca tectonic plate, which is sliding underneath North America at a rate of 4.5 centimeters (1.7 inches) a year. As the Juan de Fuca plate is subducted, the sediments and hydrates it carries are partially sheared off by the upper plate and pressed into folds or piled several layers high like a giant stack of pancakes. This distorted material forms a wedge of mud that accumulates against the North American plate in the shape of ridges running nearly parallel to the coast.

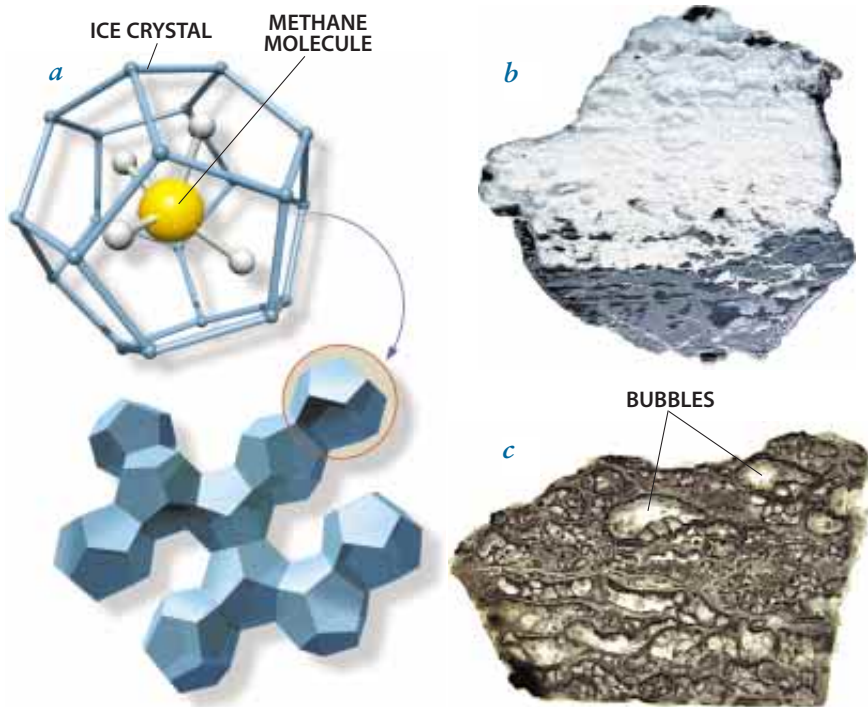
Methane Plumes

In 1984 one of us (Suess) was the first to observe these ridges and their world of cold, eternal night from *Alvin*, the research submersible operated by the Woods Hole Oceanographic Institution. Outside *Alvin*'s porthole, Suess saw a landscape of stone chimneys built by minerals precipitated from hazes of

water and gas spewing out of the earth's crust. Only later did we realize that these chimneys are partially the product of a methane hydrate deposit being squeezed as one tectonic plate scrapes past the other.

Plumes of gas and fluids also escape along faults that cut through the sediment and gas hydrates alike. Although these plumes, also called cold vents, are unlike the hot springs that form along mid-oceanic ridges (where hot lava billows out of a crack in the seafloor), they are nonetheless warm enough to further destabilize the hydrates. These melt when the surrounding temperature creeps even a few degrees above freezing. As new hydrates form near the seafloor, the lower portions melt away, with the result that the overall layer migrates upward over time.

Melting at the bottom of a hydrate layer liberates not only freshwater but also methane and small amounts of hydrogen sulfide and ammonia. Oxidation of these chemicals into carbon dioxide, sulfate and nitrate provides nourishment to rich communities of



CRYSTALLINE CAGES OF FROZEN WATER (a) sometimes snare molecules of methane gas that have been given off as microbes digest organic matter in the seafloor mud. The fresh hydrate sample shown above (b) formed a few meters beneath the seafloor off the coast of Oregon, where rising bubbles of methane gas were trapped underneath denser layers of mud. The methane reacted with the near-freezing water to form hydrates. Lens-shaped bubbles are clearly visible in another slice of the same methane hydrate sample (c), which was polished with a cold saw.

Fuel of the Future?

Given the vastness of the world's marine methane hydrate deposits—more than twice the carbon reserves of all other fossil fuels combined—it's not surprising that government agencies and the petroleum and natural gas industries have long been interested in harvesting this new energy supply. Research and development programs already exist in a number of countries, particularly Japan. But tapping into this giant energy storehouse at a reasonable cost presents enormous difficulties.

Not the least of the challenges is that marine hydrate deposits are located in ocean mud up to a kilometer (0.62 mile) below the seafloor. In addition, hydrates decompose rapidly if removed from the high pressures and low temperatures of the deep sea. Even if engineers could construct a system to bring a load of hydrate to the surface before it disappeared, extracting the methane from the matrix of mud and rock would still present a problem.

Free methane gas trapped under the hydrate layer is no easier to tap. Unlike the conditions in conventional natural gas deposits, the pressure of the overlying water and rock is too low to expel methane at a rate sufficient to make extraction worthwhile.

Methane hydrate is not completely out of reach, however. By harnessing methods similar to those used to recover dense, viscous petroleum, engineers could pump steam or hot water down a drill hole to melt the hydrate and release more methane to escape. They could then pump the escaping methane to the surface of the seafloor through another

drill hole. Ultimately, the methane would have to be brought ashore, but submarine pipelines are expensive, and on a continental slope avalanches would threaten their rigging. Mining the very hydrate that had helped stabilize the slope would exacerbate this risk.

The extent of such difficulties is reflected in the boldness of some of the mining approaches that experts in the field are discussing. For example, Timothy Collett of the U.S. Geological Survey in Denver proposes to save the cost of pipelines by liquefying the gas on ships or drilling platforms.

In Collett's setup the methane would be partly burned to form hydrogen and carbon monoxide. A catalyst would then convert the mixture into a liquid hydrocarbon, which could be readily transported by ship. The downside: a 35 percent loss of energy.

In contrast, Roger Sassen of Texas A&M University envisions a production facility on the ocean floor, where the emerging methane would be combined with water to form hydrate uncontaminated by mud and rock. Submarines would then tow the hydrate in zeppelin-shaped storage tanks to shallower destinations where engineers could



REDDISH FLAME consuming a hydrate sample is fed by methane trapped in the ice.

safely decompose it into water and fuel.

"We should see gas hydrate becoming a meaningful and environmentally friendly resource in the next century," Sassen says. Indeed, as the world's other energy reserves diminish, mining companies may find themselves compelled to invest in technologies for exploiting the world's last great reserve of carbon-based fuel.

—E.S., G.B., J.G. and E.L.

chemical-eating bacteria. These microbes in turn serve as food for such creatures as clams and colonies of tube worms. Such oases of life stand out on the otherwise sparsely inhabited seabed.

Our investigations also revealed that the gases liberated at these densely populated vents give rise to an immensely active turnover of carbon. Oxidation of the liberated methane generates bicarbonate, which combines with calcium ions in the seawater to form calcium carbonate, better known as limestone. Such limestone is what Suess saw in 1984 in the form of chimneys and vent linings along the crest of Hydrate Ridge—and what we now realize is a hint of a deeper hydrate layer.

Along the western flank of Hydrate Ridge, massive limestone blocks cover the crack created by a large fault. But

despite the limestone casing and the activities of the vent organisms, surprising quantities of methane escape into the surrounding ocean water. In fact, we measured concentrations that are roughly 1,300 times the methane content of water at equilibrium with the methane content of the air. We still do not know how much of the methane is oxidized in the water and how much actually enters the air, but it is easy to imagine that an earthquake or other dramatic tectonic event could release large amounts of this highly potent greenhouse gas into the atmosphere.

Researchers at GEOMAR have a much better idea of how much methane escapes in plumes rising up from hydrate fields in the Sea of Okhotsk off the east coast of Asia. About as big as the North Sea and the Baltic Sea com-

bined, this body of water is delineated by the Kamchatka Peninsula and the Kuril island arc. In the summer of 1998 a joint German-Russian team using fish-finder sonar documented methane plumes as tall as 500 meters billowing out of methane hydrate deposits on the seafloor. With our video camera tethered to the boat, we also saw giant chimneys reminiscent of the cold vents along Hydrate Ridge in the Pacific.

Even before we had visual evidence of the hydrate deposits, we knew that enormous quantities of methane accumulate under the blanket of ice that typically covers much of the Sea of Okhotsk for seven months a year. We measured a concentration of 6.5 milliliters of methane per liter of water just beneath the ice during a 1991 expedition. When the sea was free of ice the next summer, this

figure was only 0.13—the difference had vented into the atmosphere. No similar methane flux has yet been observed anywhere else in the world, so this event may be unique. Still, this one-time measurement of methane escape from the Sea of Okhotsk clearly demonstrates that methane hydrates below the oceans can be a significant source of atmospheric methane. To help evaluate the possible current and future climatic impact of the methane, scientists are now sampling methane concentrations in the Okhotsk seawater every two months.

Shaky Ground

Plumes caused by seafloor faulting and the natural decomposition of hydrates can release methane slowly to the atmosphere, but it turns out that this process is sometimes much more explo-

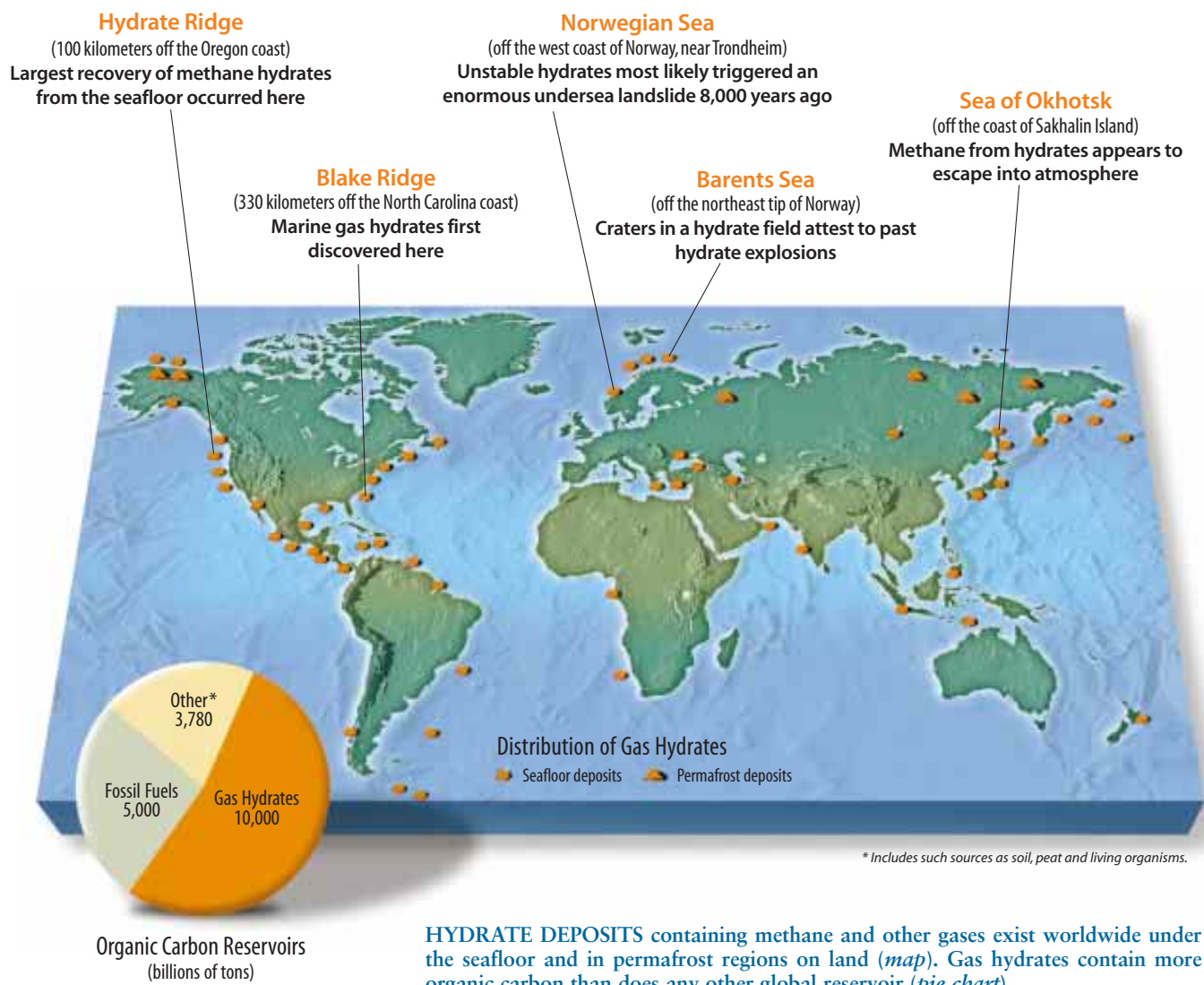
sive. In the summer of 1998 Russian researchers from the Shirshov Institute of Oceanology in Moscow found unstable hydrate fields off the west coast of Norway that they suspect are the cause of one of history's most impressive releases of trapped methane, an event known as the Storrega submarine landslide.

From previous explorations of the seafloor, scientists know that 8,000 years ago some 5,600 cubic kilometers (1,343 cubic miles) of sediments slid a distance of 800 kilometers from the upper edge of the continental slope into the basin of the Norwegian Sea, roughly at the latitude of Trondheim. The consequence of so much mud pushing water out of its path would have been devastating tsunamis—horrific swells that suddenly engulf the coastline.

The presence of methane hydrate fields in the same seafloor vicinity im-

plies that unstable hydrates triggered the slide as they rapidly decomposed because of a change in the pressure or temperature after the last ice age. As the glaciers receded, the seafloor no longer had to support the enormous weight of the ice. As the land rebounded, the overlying sea and ice both warmed and became more shallow, suddenly moving the hydrates out of their zone of stability.

Could a geologic event like this strike again? Off the coast of southern Norway the risk of new slides appears to be relatively small, because the hydrate fields have for the most part decomposed. But the issue of the stability of the continental slope is assuming a heightened importance in view of current global warming and the strong possibility of further changes in the earth's climate in the near future. Be-



LAURIE GRACE

HYDRATE DEPOSITS containing methane and other gases exist worldwide under the seafloor and in permafrost regions on land (map). Gas hydrates contain more organic carbon than does any other global reservoir (pie chart).

From the Seafloor to the Sky

HOW METHANE HYDRATES MAY ALTER THE CLIMATE

5 In the atmosphere the methane converts to another greenhouse gas, carbon dioxide. Both gases can gather into an insulating layer that heats the lower atmosphere and thereby changes climate patterns.

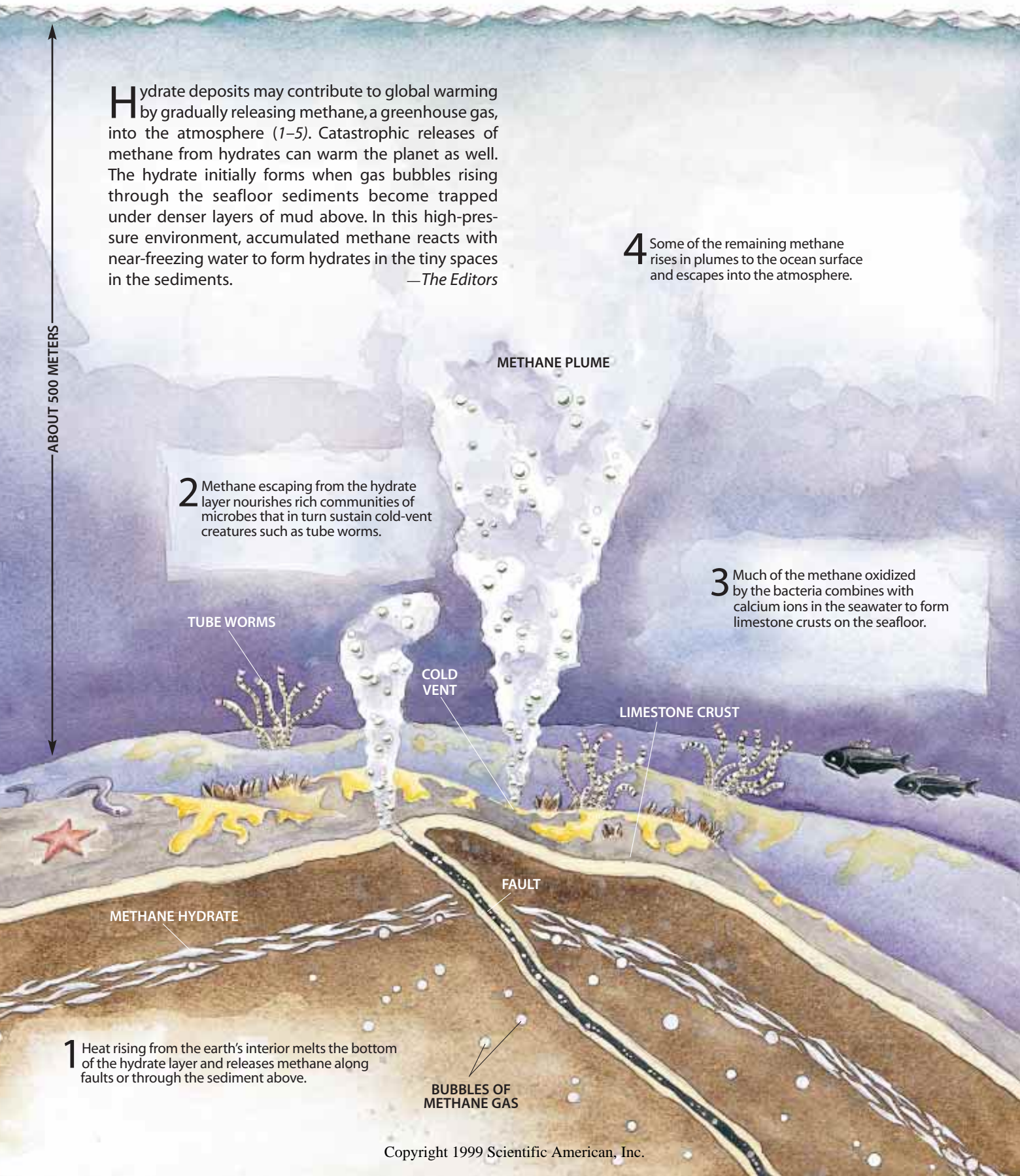
H hydrate deposits may contribute to global warming by gradually releasing methane, a greenhouse gas, into the atmosphere (1-5). Catastrophic releases of methane from hydrates can warm the planet as well. The hydrate initially forms when gas bubbles rising through the seafloor sediments become trapped under denser layers of mud above. In this high-pressure environment, accumulated methane reacts with near-freezing water to form hydrates in the tiny spaces in the sediments.

—The Editors

4 Some of the remaining methane rises in plumes to the ocean surface and escapes into the atmosphere.

2 Methane escaping from the hydrate layer nourishes rich communities of microbes that in turn sustain cold-vent creatures such as tube worms.

3 Much of the methane oxidized by the bacteria combines with calcium ions in the seawater to form limestone crusts on the seafloor.



1 Heat rising from the earth's interior melts the bottom of the hydrate layer and releases methane along faults or through the sediment above.

BUBBLES OF METHANE GAS

yond contributing to tsunamis, hydrate formations that become unstable and decompose will release methane into the oceans. In fact, melting a mere cubic meter of hydrate releases up to 164 cubic meters of methane, some of which would surely reach the atmosphere. In turn, a warming of the lower atmosphere would heat the oceans, launching a vicious circle of more dissolution of hydrates and more atmospheric warming.

Many researchers think that an explosive methane release from a single large site can create dramatic climate changes on short timescales. James P. Kennett, an oceanographer at the University of California at Santa Barbara, has hypothesized that catastrophic releases of methane could have triggered the notable increase in temperature that occurred over just a few decades during the earth's last ice age some 15,000 years ago. An international team led by former GEOMAR member Jürgen Mienert, now at Tromsø University in Norway, recently found possible evidence of this methane release on the floor of the Barents Sea, just off Norway's northeastern tip.

There, fields of giant depressions reminiscent of bomb craters pockmark the immediate vicinity of methane hydrate deposits. Mienert's team measured the biggest of these craters at 700 meters wide and 30 meters deep—a size clearly suggestive of catastrophic explosions of methane. Whether these eruptions occurred more or less simultaneously has not yet been determined, but faults and other structural evidence indicate they probably took place toward the end of the last ice age, as Kennett proposed. The explosions very likely followed a scenario like the one suggested for the cause of the Storrega landslide:

warming seas rendered the hydrates unstable, and at a critical point they erupted like a volcano.

Older Hints

Researchers have also uncovered evidence that methane liberated from gas hydrates affected the global climate in the more distant past—at the end of the Paleocene, about 55 million years ago. Fossil evidence suggests that land and sea temperatures rose sharply during this period. Many species of single-celled organisms dwelling in the seafloor sediment became extinct. A flux of some greenhouse gas into the atmosphere presumably warmed the planet, but what was the source? Carbon isotopes turned out to be the key to interpreting the cause of the rapid rise in temperature.

Scientists found a striking increase in the lighter carbon 12 isotope in the preserved shells of microscopic creatures that survived the heat spell. Methane hydrates are the likeliest source for the light carbon—and for the greenhouse gas flux—because these deposits are the only places where organic methane accumulates to levels that could influence the isotopic signature of the seawater when they melt. The carbon 12 enrichment characteristic of the hydrates disperses into the seawater with the liberated methane and persists in its oxidation product, carbon dioxide. Some of the carbon dioxide in turn becomes incorporated into the calcium carbonate shells of the sea creatures, while some of the methane makes its way to the atmosphere to help warm things up.

Gerald Dickens, now at James Cook University in Australia, used a computer simulation to test whether melting methane hydrates could have belched out enough greenhouse gases to subject

the earth to a heat shock 55 million years ago. He and his former collaborators at the University of Michigan based their simulation on the assumption that hydrates corresponding to about 8 percent of today's global reserves decomposed at that time. Because liberated methane is converted immediately (on a geologic timescale) into carbon dioxide, they tracked this compound only.

In 10,000 simulated years, 160 cubic kilometers of carbon dioxide containing carbon 12 showed up in their model atmosphere every year. Adding this carbon dioxide caused the lower atmosphere to warm by two degrees Celsius (3.6 degrees Fahrenheit). At the same time, the isotope ratio of carbon in the water and atmosphere shifted to correspond to the values observed in the fossils. Moreover, this carbon isotope ratio gradually returned to normal within 200,000 years, just as it does in actual fossil records.

Dickens's model is compelling but rare. So far the significance of methane from natural gas hydrate sources as a greenhouse gas has received only limited consideration in global climate modeling. The contribution of methane hydrates to global carbon budgets has likewise not been adequately taken into account. Trying to come up with data to correct these shortfalls is one of the greatest motivations for our work on methane hydrates at GEOMAR. We continue to focus on Hydrate Ridge off the Oregon coast—eight marine expeditions targeted the site earlier this year. We will also be looking at the seafloor off the coasts of Costa Rica, Nicaragua, Alaska's Aleutian Islands and New Zealand. Whatever happens in methane hydrate research, the future will be anything but dull. SA

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Further Reading

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