MAN-MADE NUGGET
of frozen methane hydrate
burns readily in air.
Methane hydrates could solve the world’s energy challenge— or make global warming worse

By Lisa Margonelli
One morning last August, the Monterey Bay Aquarium Research Institute’s deep-sea robot, named Doc Ricketts, was snooping around the ocean floor in 1,812 meters of very cold water off the coast of northern California. It was gliding over an oblong mound 2,000 meters long and 60 meters thick, draped in places with a thin layer of khaki-colored sediment. Video from the robot’s underwater camera suddenly revealed what looked like a dirty yet nonetheless luminously white snowbank—the kind found at the edge of a plowed parking lot, except for the clams and fish around it. This glowing ledge showed that the mound contained methane hydrate, a lattice of frozen water that traps methane gas molecules within its icy cages. If you grabbed a snowball of the stuff, you could light it on fire.

Outcrops like this one are the proverbial tips of icebergs. Most methane hydrate deposits are trapped in sediments just below the seafloor, at the bottom of deep, cold oceans. Together the deposits are enormous, and scientists are finding them lurking everywhere, off the edge of every continent. The latest estimates indicate that, worldwide, methane hydrates under the sea hold at least as much carbon as all the coal, oil and natural gas reserves on the planet. Yet few have been studied in detail.

The goal of this 11-day expedition was to probe the large mound of hydrate and sediment, a tricky operation. The remotely operated robot, kitted out with mechanical arms, was tethered to the research ship Western Flyer. The institute’s senior scientist, marine geologist Charlie Paull, clucked happily when the images appeared on the 20 video screens in the ship’s small control room. More than a dozen scientists from the institute and the U.S. Geological Survey were jammed in the room with Paull, me and others, perched on old airplane seats and overturned plastic buckets. All these minds and equipment would bear down on the mound’s secrets: How was it formed? Where did its methane come from? And did it start emerging from the seafloor 10 years ago, or had it been growing for a million years?

The team was seeking basic information that might help address larger issues. A recent geologic survey suggests that the hydrates off the coasts of the lower 48 states alone hold

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**IN BRIEF**

**Methane hydrates** are massive deposits of gas trapped in vast, icy structures underneath the coastal seafloor. They may hold more energy than all known reserves of oil, coal and natural gas worldwide.

**Scientists are probing** hydrate outcappings to determine how easily the gas can be tapped for energy. They are also examining how readily the methane can escape on its own when heated by warming seawater. Deposits could potentially release enormous quantities of greenhouse gases.

**In another hazard,** deposits can expand rapidly when disturbed by earthquakes, setting off tsunamis.
equivalent of 2,000 years of natural gas supply at the country’s current rate of consumption. If companies could harvest even a small percentage of that fuel, hydrates could be very useful; in March 2013 the Japanese research ship Chikyu became the first to extract natural gas from hydrate in the sea. But if warming oceans destabilize the hydrates so they release methane up through the water and into the atmosphere, the gas could hasten a climate catastrophe. Over a century methane has 20 times the global warming power of carbon dioxide. Are methane hydrates the next big thing in energy or the next big environmental worry? Scientists like Paull are trying to find answers.

AN ICY BLACK BOX
Paull, a tall man with a broad white moustache and a flat Rhode Island accent, began studying hydrates in the 1970s, when they were mainly known as a nuisance to the oil industry because their ice crystals clogged pipes in deepwater wells. If you ask him a question about hydrates, he nearly always starts, emphatically, with a burst of facts, only to end with a pained grimace when he gets to the things he does not know. During his career, hydrates have gone from esoteric curiosities to potentially massive players in the earth’s carbon system, making them even more mysterious. Once upon a time, each sighting of a methane hydrate was exciting, but “now the question is: Where aren’t they?” Paull says.

About 1 percent of methane hydrate is actually on land, sandwiched in layers of permafrost near the planet’s poles. Most of the rest exists in what is called the hydrate stability zone, at low temperature and high pressure underneath at least 300 meters of seawater. There vast networks of crystals saturate layers of sediment up to 1,000 meters thick. Beyond 1,000 meters of sediment, methane simply exists as gas, warmed by the earth’s deeper interior. Hydrates form constantly but not predictably, becoming solids in some pore spaces between sand grains while remaining a flowing gas in others. Scientists are not sure why a given state prevails in a particular location.

Pinning down the devilish details of hydrates—why they fluctuate between gaseous and solid states or how long they hold their methane in one place—is crucial for anyone trying to harvest their energy. These questions have become more urgent with successful tests. The Chikyu drilled into hydrate-rich sediments, then pumped out water from the surrounding area. Removing the water lowered the local pressure, which caused...
Methane hydrates exist in the seabed along coastlines around the world (blue regions on map). Researchers have taken samples (red dots) mostly under shallow seas, but they think greater deposits lie below deeper water. Hydrates form in sediments on the seafloor (bottom left), as methane gas gets trapped inside ice crystals there (bottom right). The gas can originate from deep in the earth or from microbes that digest organic matter in the sediment. In certain spots, pieces of hydrate may rise through the water, giving off methane gas bubbles as they exit the stability zone (dotted lines). Hydrates can also form in permafrost on land.

Japan leads the small but significant international race to develop hydrates for energy, spending $120 million on research last year. In 2010 the U.S. invested about $20 million, but by 2013 that had fallen to just $5 million. Germany, Taiwan, Korea, China and India have small research programs, as do oil companies Shell and Statoil. Although these expenditures are significant, they pale against the billions of dollars that the global oil industry spent on research and development in 2011 alone.

For a country that struggles with importing energy and is still cleaning up the Fukushima nuclear disaster, the sheer quantity of methane lying off Japan’s coast makes harvesting it attractive. Americans are less motivated to explore hydrates as an energy source because the U.S. is already awash in inexpensive shale gas, which makes hydrates seem very costly by compari-
son. Canada is rich in hydrates, too, but dropped its research program in 2013 for similar reasons.

If there were a “killer app” for mining methane hydrates, it would be a system that stabilizes their structures, sequesters greenhouse gases that the mining would release and provides fuel. In 2012 a team of researchers from the USGS, the U.S. Department of Energy, ConocoPhillips, Japan and Norway tried to do just that. They pumped a mixture of carbon dioxide and nitrogen (to prevent icing) into a hydrate that was capped by permafrost on Alaska’s North Slope. The hope was that the CO₂ would push out methane and take its place, becoming trapped in the icy lattice to keep the hydrate structure intact.

Methane flowed from a test well for a month, but researchers could not be sure if the CO₂ had replaced methane. “The concept is straightforward, but nature is more complicated,” says Ray Boswell, technology manager for hydrates at the DOE’s National Energy Technology Laboratory. Boswell says data from the tests revealed “a messy black box underground.”

Deep-sea hydrates bordering the lower 48 states could hold the equivalent of 2,000 years of natural gas supply at the country’s current consumption rates.

Despite the relative success, ConocoPhillips has reassigned the employees who were involved. The DOE is looking for a new industry partner to continue the experiments.

To Paull, the experiment reflects our limited understanding of hydrate behavior. In 2010 he led a National Academy of Sciences committee that reviewed the DOE’s work on methane hydrates as an energy resource. The panel concluded that engineers can probably surmount the technical challenges of producing fuel from hydrates but that many scientific, environmental and engineering questions remained to be answered before informed decisions could be made about whether to proceed. Unlike oil deposits, hydrates are inherently unstable and hard to map, and their effects on surrounding ecosystems are poorly understood. “I don’t think we know enough about what it would mean to harvest them in an environmentally sound manner,” Paull says.

STUCK IN A FROZEN AIRPORT LOUNGE

Understanding the shifty, unpredictable nature of hydrates is fundamental to determining whether they can be reliably mined and whether they might amplify heating of the planet.

Simply touching hydrates, for instance, can cause them to shift from solid to gas, ruining an experiment. For that reason, Paull told the Western Flyer crew to avoid poking the icy outcrop until the very end of the dive. As the robot glided over the murky, greenish seafloor, the mound rose up like a mammoth blister, with small pockmarks in places, as though tiny meteorites had hit it. Paull suspects that the pockmarks are where pieces of hydrate broke off, from so little as a nudge from a fish. Wherever deposits are found in the sea, snowy pieces of fragile hydrate are seen drifting upward, led by gas bubbles—like comets being pulled toward the sea’s surface by their tails.

Hydrates are constantly disassociating and forming throughout the stability zone. On one dive, sonar on Doc Ricketts located a stream of gas bubbles emerging from the mound. Paull wanted to know whether this gas was formed in a hot kitchen deep in the earth’s crust, similar to where natural gas and oil are generated, or if it was made biologically in sediments by consortiums of microbes that process bits of organic material that drift in with sediments. Virtually all deposits contain gas from biogenic sources, and some contain gas from thermogenic sources; understanding the mix can help determine how a mound formed and what lies under it. Paull had the pilot lower the robot to the source of the bubbles, a dingy crevice surrounded by clams that consume bacteria that live using chemosynthesis—turning the methane into energy.

The crew landed Doc Ricketts on the outcrop, and the cameras immediately revealed a crab perched near the gas bubbles, furiously trying to wave them into its mouth with its claws. Because the water was only two degrees Celsius, and the pressure was immense, the gas formed small hydrate crystals quickly, crustling the crab’s mouthparts with a ridiculous white beard, foiling its attempts to eat them. A biologist onboard said that crabs are often found attempting to gobble up methane bubbles, even though the critters do not appear to gain any nutrition from them.

To avoid having the same problem as the crab, the institute’s engineers connected a heating unit to a funnel that leads into sampling bottles, all of which the robot can manipulate. Even so, the crew needed several dives over the next few days to get enough of a sample to determine the mix of thermogenic and biogenic gases in it.

Paull also wanted to find out how old the mound was to understand how quickly it had formed. The crew landed Doc Ricketts on one edge of a mound and manipulated its arms to take core samples by pushing specially designed tubes down into it. In some places, the robot easily drove the tubes into the icy, mucky sediments. In others, the tubes jammed against ledges of what may have been ice or another hard substance, such as calcium carbonate.

In the midst of the work, eerie bright-blue bubbles appeared in the robot’s LED lights. In the control room, USGS geologist Thomas Lorenson suggested that the bubbles might be petroleum. Seeps from undersea oil and gas reservoirs are an ongoing

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natural oil spill on seafloors. A 2003 National Academy of Sciences publication estimated that 680 million liters of oil seep up into the world’s oceans yearly. The seeps, which support large communities of clams, worms and other organisms, demonstrate just how difficult it would be to determine what constitutes a healthy environment if hydrates were harvested for energy.

Once the core samples, two meters long, were stowed on Doc Ricketts, it took the crew an hour to draw the robot and its cache back to the ship. When the vehicle entered through a sliding air lock in the hull, it brought an overwhelming smell of petroleum and rotten eggs. Researchers put some of the samples into freezers for later analysis and processed others on the boat. The muddy cores resembled brownie batter, fizzing with the presence of so much dissolved gas.

Paull and his team began to quickly process the smaller cores, spilling them out into trays to measure each centimeter of sediment and determine when it was deposited. The muck in front of me was the scene of a wild microbial party: the cold sediments contain many different microbes that create methane, consume it, and swap molecules of sulfur and oxygen. Hydrate formations, big as they may be, are just way stations between methane in the sediment below the ocean floor and the seawater above. Lorenson compares the space to a “transit lounge at the airport,” where everyone is waiting for his or her chance to take off.

Gerald Dickens, an earth scientist at Rice University, describes hydrates worldwide as a giant storage capacitor for methane that rises into, or is created within, sediments—holding the gas, then gradually releasing it into ocean water and, potentially, the atmosphere. What we do not know is how fast this capacitor is acting—how long hydrates wait in the lounge before emerging. The gas may wait as long as seven million years, or it may be released relatively quickly, which could exacerbate global warming.

Adding to the uncertainty is the fact that researchers are not sure about how much hydrate is really on standby in the capacitors down there. In 2011 Dickens referenced a variety of papers to arrive at an estimate of 170 to 12,700 gigatons of carbon, a wide range that speaks to the great uncertainty. The upper end of that estimate implies that methane hydrates could hold more than three times as much carbon as all other quantified reserves of fossil fuels, which is commonly estimated at 4,000 gigatons of carbon.

**METHANE TSUNAMIS**

As capacitors, hydrates also can release large amounts of energy at once, which concerns both energy and climate researchers. Because hydrates are powerfully buoyant, they can be dangerous when disturbed. A cubic meter of hydrate brought to ambient temperature and pressure expands to 164 cubic meters of methane gas and 0.8 cubic meter of water. When earthquakes rattle hydrates, the expansion can trigger landslides, which can cause tsunamis. Such a domino effect is blamed for the Storegga slides, which created a wave that hit what is now Great Britain 8,100 years ago, as well as the Sissano tsunami, which killed more than 2,000 people in Papua New Guinea in 1998.

Preventing such geohazards will be a challenge for anyone trying to mine hydrates for energy. Conventional oil and gas are produced by drilling through rocks to sealed underground reservoirs. But the methane in a hydrate is in a solid that must change phase to a gas for extraction, putting the entire structure in motion.

A broader planetary concern is where the methane goes when it dissociates. If it gets into the atmosphere instead of being absorbed by seawater, it could have a dramatic impact on the climate. I had the opportunity to watch a chunk of hydrate rise through the water column. On one dive, the robot removed a melon-size chunk of hydrate ice from the outcropping at 1,800 meters and struggled to put the buoyant lump into a mesh bag in a frustrating dance one observer described as “antigravity
Underwater dives could settle a vigorous debate: whether warming oceans could release massive quantities of methane.

basketball.” As I watched from the control room, the ball stayed mostly intact in deep water. But as the robot rose above the stability zone, more gas dissociated, and the bag became obscured by a lacy haze of bubbles. When the robot finally reached the surface, the volume of hydrate was just a few tablespoons.

On deck, Lorenson quickly plunged the disappearing sample into liquid nitrogen for later testing. He also lit a small piece of it on fire and offered me another shard to eat. It fizzed in my mouth and was about as unappetizing as you would expect a hydrocarbon sorbet to be, except for an aromatic aftertaste that was almost minty.

That wild upward ride could provide clues to how much methane might escape into the air. Ocean chemist Peter Brewer of the Monterey Bay Institute has used x-ray tomography to examine rising hydrate. He has found that hydrate dissociates from both the outside and the inside. Another experiment showed that the bubbles formed thin hydrate “skins” like Ping-Pong balls that fizzed and popped eccentrically as they rose. Unraveling the physics and chemistry of dissociation, Brewer says, will help researchers determine where it occurs in the water column, how it is consumed by ocean microorganisms, how much, if any, typically makes it to the surface and how much can be expected to enter the atmosphere.

SMOKING GUN

Those insights could help settle a vigorous debate that scientists have held for more than a decade: whether warming seas could trigger a massive release of methane and whether that discharge would overwhelm the oceans’ ability to absorb it. An early theory called the Clathrate Gun hypothesis suggested that hydrates build up and then catastrophically release methane in cycles that repeat over many thousands of years. This cyclical scenario is not borne out by the fossil record, but the possibility remains that a large, one-time release of methane from hydrates could have contributed to the rapid warming of the earth during its peak heating—the “thermal maximum” 55 million years ago.

In contrast, modeling by David Archer of the University of Chicago suggests that, over millennia, hydrates could continuously release methane, leading to a big change in global warming, in which rising temperatures would cause some hydrates to oxidize to CO₂ in the ocean, prolonging the warming trend.

Hydrates that are trapped under permafrost on land in the Arctic, along with those submerged under shallow seas just offshore, could be a more imminent threat. In November 2013 a team led by Natalia Shakhova of the University of Alaska Fairbanks estimated that the East Siberian Arctic Shelf is venting 17 million metric tons of methane into the atmosphere every year—twice previous estimates. Shakhova found significant methane bubbles rising from permafrost-covered hydrate deposits in just 50 meters of seawater. During the area’s frequent storms, these bubbles appear to get mixed directly with the atmosphere. Until more research is done, no one can tell whether this dynamic is occurring across the Arctic or even whether the methane is coming primarily from the hydrates or the permafrost. It is yet another “black box” in our understanding.

Work on the ship brought more mystery. During my last day onboard, Paull had been poking at the small core samples in the Western Flyer’s large wet lab, ahead of results that would come later from the USGS analysis of the long, frozen cores. Paull thought that the sediment we saw on top of the mound was probably relatively recent—something he may be able to pinpoint by scanning for traces of DDT, which appear only after 1945. The fact that the sediments had pushed up and blistered the seafloor, however, suggested they had built up over perhaps 10,000 years—still relatively new on geologic time scales.

Analysis of the frozen hydrate shards, which Lorenson sent to the Colorado School of Mines, later revealed that the mound not only contained its own methane but was also capping a system of storehouses under it. The Colorado researchers discovered multiple carbon isotopes, suggesting that the hydrate was formed from two different deep, hot reservoirs and two kinds of gases from microbes.

That pattern meant that gas had flowed upward from a previously unknown kitchen deep in the earth’s crust, picked up another gas from a shallower kitchen and then wiggled up through the sediments to pick up biogenic gases, including one formed by microbes that had processed light petroleum into methane. Lorenson was surprised: “It points out the complexity of the migration [of oil and gas]. We don’t understand what all the principal actors are doing down there.”

In trying to measure one mound, the robot had stumbled on a much larger world underneath. Our mound was a relatively small cork holding back a massive stash of methane and oil. Methane hydrate turns out to defy simple questions about whether it is an energy blessing or a climate curse, posing much larger puzzles about how global systems work and what their time frames are. Scientists need to answer those questions—with much greater investment in basic earth science—to understand how this mysterious substance connects the carbon from past life on earth to the future of the planet. 

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A blog about the methane expedition described in this article: www.mbari.org/expeditions/Northern13/Leg1/index_L1.htm

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October 2014, ScientificAmerican.com