

# Fire in Ice

Trapped beneath the permafrost, and under the deep ocean floor that surrounds continents, is enough natural gas to power humankind for thousands of years.

This natural gas, mostly methane, is frozen in water in a form we call *methane hydrates*. The methane came from decaying organic matter or migrated up from deeper natural gas deposits, and was then trapped in very high concentrations in frozen layers of sediment at high pressures.

When brought to the surface, the hydrates melt, releasing around 160 times their volume in natural gas.

This sounds like a very promising energy source, and companies and countries, especially those with limited resources like Japan, are trying to recover the gas.

But test plants have produced very little. This is partly because processing methane hydrates is a new and difficult engineering challenge. And partly because we know very little about them.

To study methane hydrates, scientists have built special highpressure, low-temperature labs, where they can be kept in their frozen state.

One innovative project in Alaska is trying to pump in liquid  $CO_2$  under high pressure to liberate the gas. If successful, this new process could make methane hydrate deposits not just an energy source but a place to sequester carbon.

Eventually, engineers will probably figure out cost-effective, low-impact ways to produce methane from methane hydrates—one more reason that natural gas will likely play a larger role in our energy future.



Gas hydrates are ice that burns.

Credit: J. Pinkston and L. Stern (USGS), public domain

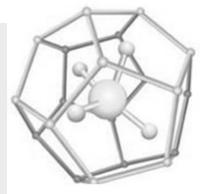


### **Background: Fire in Ice**

Synopsis: Methane hydrates are ice...that burns! Naturally occurring deposits buried below permafrost and throughout continental slope environments are thought to hold vast quantities of gas—enough for centuries of power generation. But hydrate deposits are unstable at Earth's surface, making them difficult to access and produce. If we could safely and efficiently develop these resources, methane hydrate could become an energy game changer for the world.

- Methane hydrate deposits are believed to be an immense future hydrocarbon resource, possibly twice as large as all of the world's fossil-fuel resources combined.
  - The USGS estimates that between 106.000 and 876,000 trillion cubic feet (TCF) of resources exist globally. With limited direct data available, these resource estimates carry a large range of uncertainty.
  - The U.S. Bureau of Ocean Energy Management estimates that somewhere between 15,000 and 100,000 TCF of gas hydrates may exist "in place" off the Atlantic, Pacific, and Gulf of Mexico coasts in federal waters of the lower 48 United
  - In 2016, the U.S. used nearly 27.5 TCF, and the globe used about 125 TCF, of natural gas.
  - Today, methane hydrate production technology is in its infancy. We don't know how long production can be sustained, over what areas, at what rates, and with what percentage of recovery, so we can't yet determine whether deposits will be commercial.
  - In some parts of the world where hydrocarbon reserves are lacking, like Japan, large methane hydrate deposits near high-population areas might ultimately decrease or end dependency on gas imports.
- What is methane hydrate and where is it found?
  - Microbial consumption of carbon buried along with sediments produces methane into the pore systems of sedimentary deposits. Methane may also migrate into pore water in the hydrate stability field from nearby conventional natural gas traps.

A ball-andstick model of methane hydrate shows the central methane molecule surrounded by a "cage" of water molecules. Other hydrocarbon molecules such as



pentane and ethane, as well as carbon dioxide and hydrogen sulfide, can occupy the central position in the hydrate lattice.

Credit: U.S. Department of Energy (public domain)

- Under the right pressure and temperature conditions, water molecules form icy cages that trap individual natural gas molecules in a highly concentrated form.
  - When they melt, these methane hydrates produce about 163 times their original volume as gas at atmospheric pressure.
- Four environments on Earth have the right conditions for the formation of methane hydrates.
  - Sediments along continental margins
  - Sediments in deep inland lakes and seas (usually within several hundred meters of the floor)
  - Sedimentary deposits below Arctic permafrost
  - Sediments under Antarctic ice



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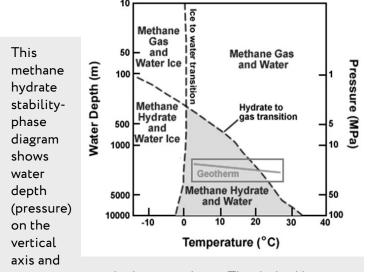
Gas Hydrate in Nature I USGS Proven under Pressure: Methane Hydrate Lab I USGS Methane Hydrate I Geology.com Unlocking the Potential of Methane Hydrate I UT Austin JSG News U.S. and Japan Methane Hydrate Production Technologies I energy.gov



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- Naturally occurring methane hydrate is stable at temperatures and pressures that occur in ocean sediments at water depths of more than 1000-1500 ft, or beneath permafrost.
- Hydrates occur as layers, nodules, and cements between grains in the sediments, often becoming so dense that they trap fluids moving up from below them.
- The difference in the mechanical strength of hydrates compared to that of weaker materials may cause slope instability in some situations.
- Given their huge potential, scientists have been drilling and studying gas hydrates all over the world, from the Gulf of Mexico to the northwestern United States, Canada, India, Japan, South Korea, China, Norway, and New Zealand.
  - Once removed from their native high-pressure environment, hydrates become unstable, so they are very difficult to study.
  - Scientists have developed methods of creating hydrates of different sorts in special highpressure labs. Other such labs are equipped for research and storage of naturally formed methane hydrates that were cored using state-of-the-art technologies.
- Typically, gas is produced from methane hydrates by depressurizing the sediments, which causes the gas hydrate to dissociate into gas and large volumes of water that must be managed.
  - Methane hydrates are still not produced anywhere in commercial quantities—all production has been small-scale or experimental. Both Japan and China have tested production from hydrates for a few weeks, but little information has been published about their results.
  - The methane production process may create instability in the subsurface as the crystalline ice structure turns to liquid, possibly leading to slope failure in some settings.
    - The thermodynamics of this reaction are limited, sometimes requiring additional heat to keep it going, so runaway reactions aren't a concern.



temperature on the horizontal axis. The dashed lines separate stability fields of water, water ice, gas, and gas hydrate. Conditions for the formation of methane hydrate occur below the dashed line labeled "Hydrate to gas transition." Above this line, methane hydrate will not form. The red line traces a geotherm (the change of temperature with depth at a specific location). Note how, as depth increases, the geotherm crosses the hydrateto-gas transition line. This means that gas hydrate in sediments usually overlies free gas.

Credit: Graph modified after NOAA

- In 2012, the U.S. Department of Energy partnered with ConocoPhillips and the Japan Oil, Gas and Metals National Corporation to try a different approach, developed under laboratory conditions by the University of Bergen (Norway) and ConocoPhillips.
  - They asked: What if you could swap molecules of the greenhouse gas CO<sub>2</sub> for molecules of the cleanest-burning fossil fuel, methane (CH<sub>4</sub>), in the hydrate lattice without causing dissociation, melting, and possible slope instability?
  - Test well Ignik Sikumi ("fire in the ice" in the local dialect) No. 1 was drilled on the North Slope of Alaska in early 2012, safely producing a steady stream of natural gas.



### References: Fire in Ice

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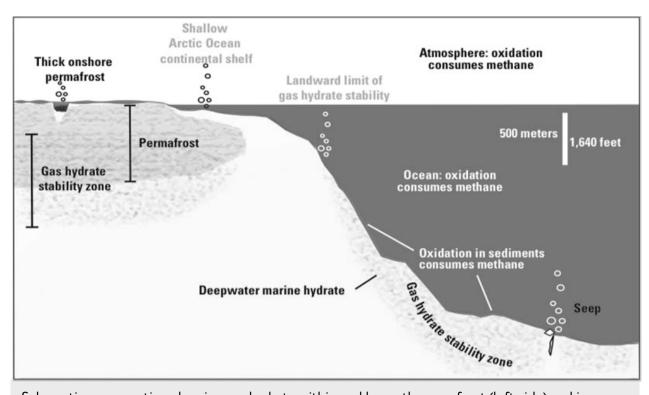


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- Liquid nitrogen and liquid carbon dioxide were heated together to make gas, then pressurized for injection into the methane hydrate zones exposed in the well, where the CO<sub>2</sub> replaced and liberated the CH, but left the solid ice hydrate structures intact.
- The trial worked but was only sustained for 30
- More work is necessary to access the bounty of methane hydrates.
  - Scientists need to develop a basic exploration model for these environments:
    - How does hydrate form in nature?
    - What is the gas source and migration history?

- Engineers need to understand fundamental properties to guide production:
  - Permeability of hydrate sediments before and after dissociation
  - Seal properties
  - Geotechnical properties
  - Diffusion of heat and salt through the system
- Improved inventories and additional safe and economical methods for production are needed.



Schematic cross section showing gas hydrate within and beneath permafrost (left side) and in deepwater marine sediments (right side). The locations described in orange are the most susceptible to climate processes that can affect the stability of methane hydrate deposits. Oxidation shown in red can destroy methane in sediments, in the water column, and in the atmosphere.

Credit: Gas Hydrate in Nature I USGS



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