EC PHARMACOLOGY AND TOXICOLOGY
Review Article

Formation and Harvesting of Methane Hydrates

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Abstract

Most of the Earth's methane is biogenic and is produced by methanogenesis, a form of anaerobic respiration known only to some members of the domain, Archaea.

Keywords: *Methane Hydrates; Archaea*

Introduction

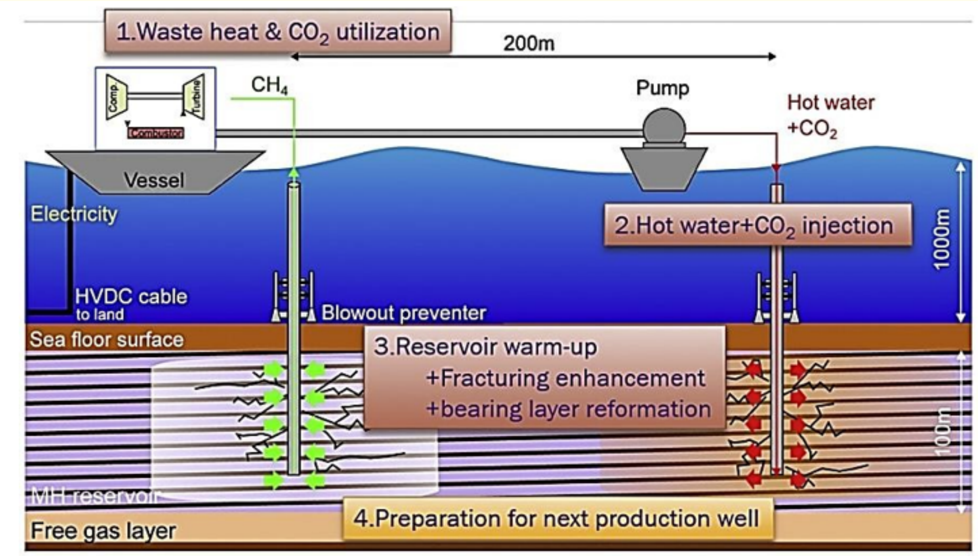


Figure 1: *Schematic figure of utilization system by strategic heating up process.*

Strategy for oceanic methane hydrate extraction and power generation with Carbon Capture and Storage (CCS) [1-3].

Gas hydrates difficult to extract but estimated abundance makes mining attractive.

Methanogens occupy land and other landfills, ants (e.g., cows or cattle), termite intestines and anoxic sediment beneath the seabed and lake bottom. Ricefields also produce large amounts of methane during plant growth. These microorganisms use this long, multistep endothermic cascade of reactions for energy. The net response of methanogenesis is:

$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$ $\Delta H = -165 KJ/Mol$ (Sabatier)

H_2 is rarely detectable in its nature and under absolute anaerobic conditions in the absence of sulfate with the conversion of CO_2 to methane (CH_4) and water (H_2O). By removing electrons from the system through inorganic hydrogen transfer reactions to generate CH_4 by reducing CO_2, the methanogenic bacteria affect the overall anaerobic metabolism of organic compounds towards complete stripping of water and carbon dioxide [4]. The removal of hydrogen allows thermodynamic negative reactions to occur in a different way. The final step in the process catalyzes the enzyme methyl coenzyme M reductase (MCR).

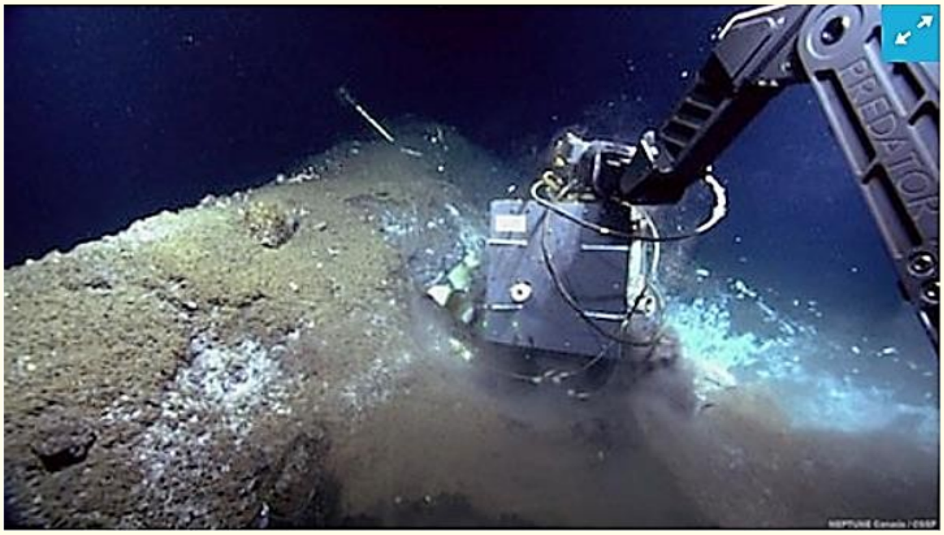


Figure 2: *A remote-controlled vehicle, known as an 'osmosampler', retrieves samples from a gas hydrates mound in Barkley Canyon, May 18th, 2010. Source: Neptune Canada.*

Chinese strategic extraction and production planning

The new proposed system is focused on extraction production. A strategy that considers thermal balance during the long-term manufacturing process is much different than before Designs. The necessary steps of a methane gas production system are as well Shown in figure above, The first well utilizes the underlying depression planning for methane gas production then used for electricity generation in a boat through a gas turbine. Then the waste is brown Thermal recovery and management of the system is performed during Generation, and hot water (with CO_2 pressure) are injected Sister wells nearby (with some distance) to heat the reservoir Regions. This process may take 12 months or more, as well as Heat the surrounding area until ready for production.

This design is as crucial to the thermal balance as it provides Logical heat corresponds to the reservoir during the endothermic Detachment reaction when methane hydrate becomes methane gas And water inside the porous reservoir. After that, the production The boat will move to the next production pit and will warm up nearby Sister wells until methane hydrate reservoirs are finished For life. In detail, consists mainly of the extraction design Well production and well injection molding and control system. In case the initial fluid flow of the reservoir is not in sound, hydraulic condition A fractional system can be used. As shown in figure. The explosion voucher is also set up in production to prevent Geological failures during heating and production process. When the gas produced goes into the vessel, it will be used To generating electricity. Also, the electricity produced will be Transmitted to the country (client-side) via high voltage directly Electric Power Transmission System (HVDC).

Until 10 years ago, almost no one had heard of methane hydrants. But now these seabed chemical compounds are destined to be an energy source for the future.

The formation of the solid "methane hydrate" in the ocean floor

In general, methanogens share the properties of strict anaerobiosis and the ability to reduce carbon dioxide with molecular hydrogen to produce methane [5].

Conversion of CO_2 to methane [6]

Biogas contains such a portion of CO2 that is provided by a number of electrons available in the organic matter molecule in the substrate (equivalent to an average number of oxygen per carbon atom) so that it cannot be avoided in anaerobic fermentation. Converting CO_2 to methane with hydrogen is possible to obtain gas of more energetic value, since the volumetric energy content of hydrogen is low (10.88 MJ/m^3) compared to methane (36 MJ/m^3). If we want to convert CO_2 into biogas into CH_4 chemically, hydrogen supply is needed, under proper conditions of pressure, temperature, catalyst and relatively expensive equipment. The advantage is the output that is already compressed. A biochemical reaction requires additional hydrogen reduction parallels, can be applied directly to the hydrogen in the system or to provide electrons directly to the system. Reducing the parallelism can also come from the gases from the thermal treatment of organic waste and biomass (gasification and pyrolysis).

The amount of hydrate associated with u far exceeds the reserves in conventional deposits. However, methane hydrates are not just a potential source of energy; They also pose a significant climate risk.

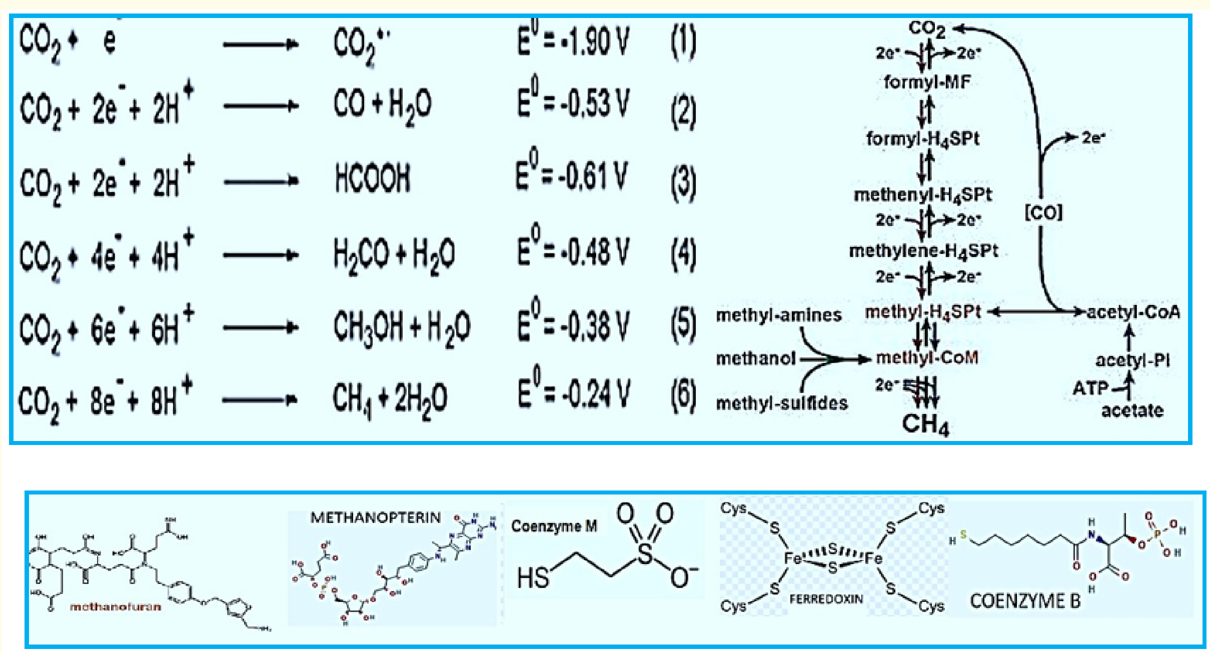


Figure 3: *The stepwise conversion of CO_2 into CH_4 in methane-bacterium (credit ref. [7]).*

MF: Methanofuran; MP: Methanopterin; CoM: Coenzyme M; Fd: Ferredoxin; CoB: Coenzyme B.

Methane bacteria possess the enzymatic cascade that enables the reduction of carbon dioxide CO_2 to the energy rich methane CH_4. In this process the carbon-based molecule gains energy. The work of Paul Sabatier (Nobel Laureate in Chemistry):

$$CO_2 + 4H_2 \xrightarrow[\text{pressure}]{400\ °C} CH_4 + 2H_2O \quad \Delta H = -165.0 \text{ kJ/mol}$$

The methane – bacterium is of the archaea class and are abundant not only in the intestinal system of the ruminant. Also, the human gut has such bacteria in its microbiome and the ocean floor is rich in these archaea. The methane in the atmosphere is in part only the result of grass digestion by the ruminants.

Methane molecules are enclosed in tiny cages made up of water molecules. Methane gas [8,9] is mainly formed by microorganisms living in the deep sediment layers [10] and slowly converts organic materials into methane [11]. These organic materials. Archaea are the only confirmed biological sources of methane in nature and *Methane-brevibacter smithii* is the predominant methanogen in the human intestine are plankton [12] remnants that lived in the ocean long ago, sunk to the bottom of the ocean and were finally incorporated into the sediment. Methane moisture is stable only at pressures exceeding 35 bar and at low temperatures. The seafloor is therefore an ideal location for their formation: the bottom waters of the oceans and the deep seafloor are almost uniformly cold, with temperatures of 0 to 4°C. In addition, under a water depth of about 350 meters, the pressure is sufficient to stabilize the hydrates. But as the depth of the seabed thickens, the temperatures begin to rise again because of the proximity to the Earth's surface. At depths greater than one kilometer, temperatures rise above 30°C, so no methane hydrates can be deposited. However, this is where methane formation is particularly vigorous. First, slightly methane gas bubbles are formed deep within the sediment. These rises and becomes methane hydrate in the calmer waters near the seafloor. So, methane is formed in the deep warm precipitation horizons and converted and crystallized like methane hydrates in the cold upper sediment layers. Methane hydrates were not found in the sea and shelf areas because the pressure at the seabed is insufficient to stabilize the hydrates. At the bottom of the broad ocean basins, however, where the pressure is high enough, almost no hydrates are present because there is insufficient organic matter embedded in the deep-sea sediments. This is because open water is relatively weak in the diet, producing little biomass to sink into the seabed. Thus, methane hydrates occur mainly near the terrestrial margin at water depths between 350 and 5000 meters. For one reason, enough organic matter is deposited in the sediment there, and for another reason, the temperature and pressure conditions are favorable for converting methane into methane.

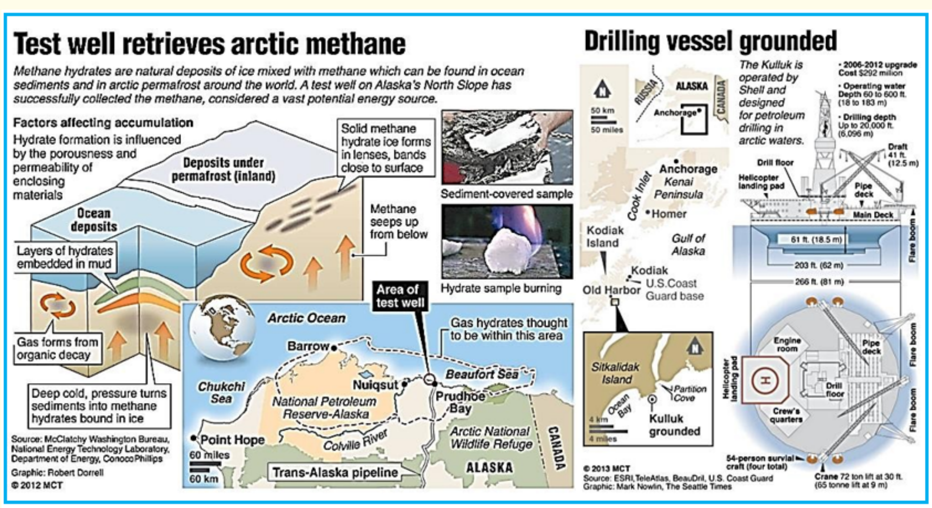


***Figure 4**: Test successfully pulls natural gas from Alaskan ice (credit ref. [4]).*

Methanobacterium

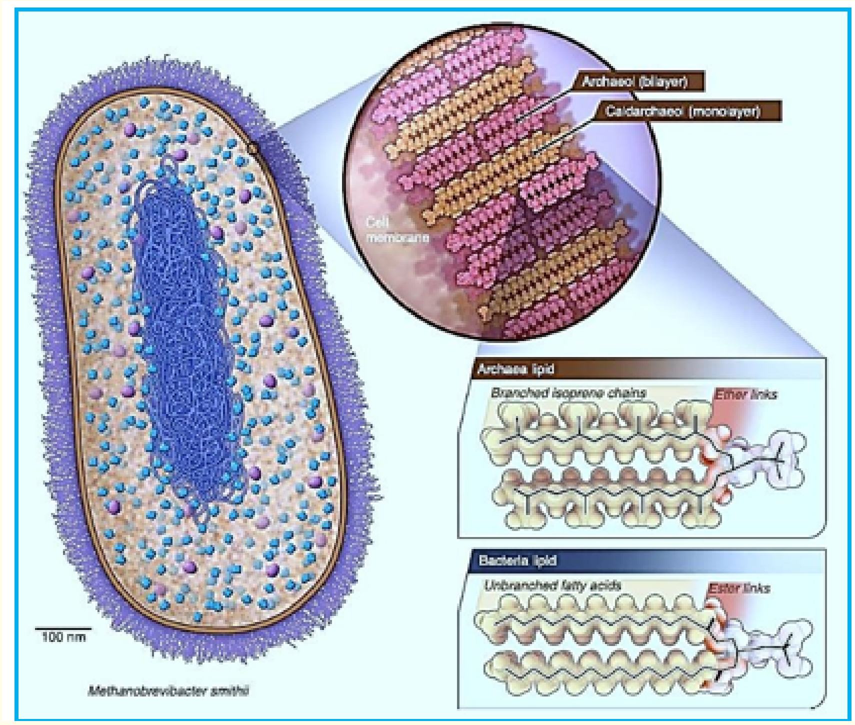


Figure | *Methanobrevibacter smithii* **cell wall and cell membrane determine susceptibility to antibiotics and statins.** The cell wall (violet) is composed of pseudomurein (and not murein as in bacteria) which makes archaea resistant to lysozyme and many antibiotics that interfere with cell wall synthesis. The cell membrane (ochre) consists of a lipid bilayer or monolayer the backbone of which composed of *isoprene* units that are linked to glycerol by *ether* bonds. In contrast, the lipid bilayer of bacteria consists of a *fatty acid* backbone that is linked to glycerol by an *ester* bond. The presence of statin-sensitive isoprene units in the cell membrane of archaea allows statins to selectively interfere with the growth of archaea while leaving the cell membrane of bacteria unaffected. While bacteria do not use isoprene units in their cell membrane they are still required elsewhere. These bacterial isoprene units are, however, synthesised by a pathway (MEP) that is not inhibited by statins. See also Figure 3.

Figure 5

Methanogens perceive a unique ecological niche, and serve as the ultimate recipients of anaerobic electrons, and their genome presents a significant change towards energy conservation. Genome is enabled Recombinant metabolism reported here has a meaning for diverse anaerobic communities and has led to this The use of the proposed substrate has not previously been reported in isolation, such as metabolism in MSPH. cuniculi The bedding they have recently offered is vital as a basis for deciphering the behavior of methanogens in native communities, such as CO_2 and as a preparation Electron carriers are common in bacterial colonies.

In taxonomy, *Methane-bacterium* is a genus of the *Methane-bacteriaceae* [13] Contrary to their name, they are not precisely a bacterial species as they belong to the archaea and have the different biopolymer, peptidoglycan, missing from their cell membranes [14]. *Methane-bacterium* are nonmotile and live without oxygen. Some members of this genus can use formate to reduce methane; others live exclusively through the reduction of carbon dioxide with hydrogen. They are ubiquitous in some hot, low-oxygen environments, such as anaerobic digestors, their wastewater, and hot springs [15].

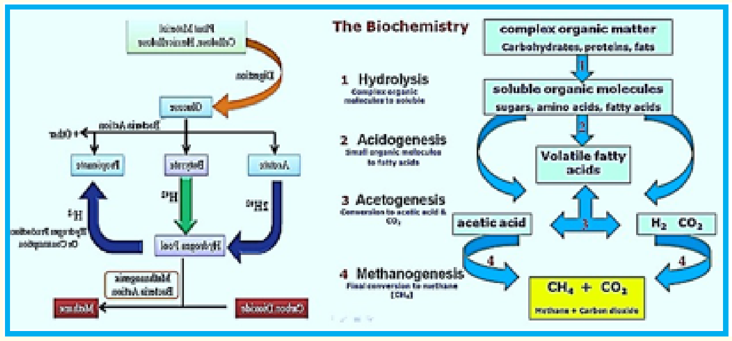
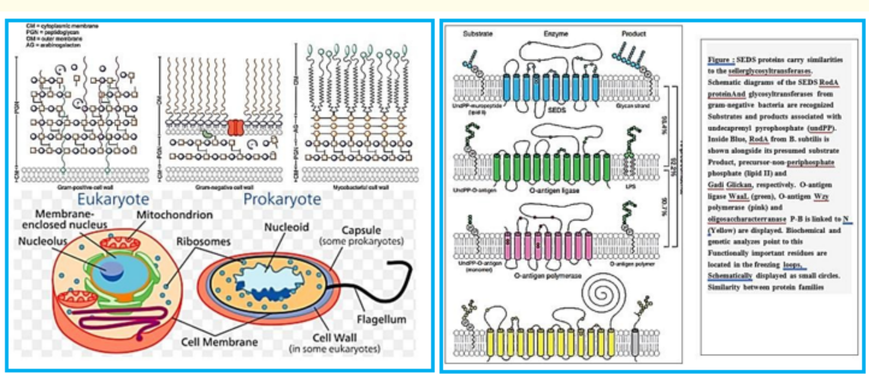


Figure 6: *Digestion of Grass and biosynthesis of methane by methane bacteria in ruminants.*

Today there is an increasingly important flow in the sense of using microorganisms, especially bacteria, algae and fungi, to purify and help recover from natural environments and to treat urban or industrial wastewater. people estimate that the best microorganisms for detoxification existing in place are initially isolated in their area, where they are naturally selected, although the second genetic prevention of these can significantly strengthen the ability of culture collections of microorganisms and isolates. In order to know the details of these mechanisms, water purification, such as the use of bacteria capable of capturing heavy metals on their cell walls, can be exploited [16].

Background

Methanogenic archaea [17] are critical players in anaerobic communities and as such contribute significantly to the global warming and energy production, with exciting potential Roles in Human and Animal Health [18,19]. Goddess Exceptional bacteria perform a type of anaerobic Breathing known as methanogenesis by either reduction Decomposition of carbon dioxide, or methyl compounds Acetate for methane or methane and carbon dioxide Several ecosystems and consortia [20]. Methanogenesis is operating at a shallow reduction potential compared to Other forms of aerobic and anaerobic breathing [21]. As Such as, can be found in diverse environments like the deep ocean, rice pads, wet areas, Landfills, and digestive tracts of termites, ants, And humans, where the electron is more positive Accept as oxygen or organic ions are not available [1]. Because they are a significant source of the atmosphere Methane, was the drive to increase Understanding their metabolism and interactions with other organisms [22]. Thisunderstanding of Metabolic metabolism is essential for optimal planning of biochemical processes aimed at producing either Removal of methane [23,24].



Sorts of bacteria (credit ref. [25])

SEDS cell wall proteins (shape, elongation, division and sporulation) (credit ref. [2])

Figure 7

The elongation of rod-shaped bacteria [26] is mediated by a dynamic peptidoglycan synthetic machine called Rod compound. Here, we report that in *Bacillus subtilis*, this compound is functional in the absence of all known peptidoglycan polymers. These enzyme-free cells survive by causing an envelope stress response that amplifies the expression of Roda, a widely preserved core component of the Rhode compound. Roda is of the SEDS family (form, elongation, division, and computation), which have vital functions but are not defined in the biogenesis of the cell wall during growth, division, and computation. There genetic and biochemical analyses indicate that SEDs are a family of peptidoglycan polymers. Thus, *B. subtilis* and probably most bacteria use two different polymerase groups to synthesize their gas skeletons. Our findings indicate that SEDS family proteins are core cell wall syntheses of elongation and cell division machines and represent attractive targets for the development of antibiotics.

Archie's cell wall, like any other prokaryote, surrounds the cell outside the cytoplasmic membrane and mediates interaction with the environment. In this regard, it can be involved in the maintenance of cell form, protection from viruses, heat, acidity or alkalinity. Along with the formation of porous-like structures it can resemble a micro sieve and thus enable or disable transport processes. In some cases, cell wall components can account for more than 10% of all cellular proteins. To date, a large variety of structures and compounds of different cell envelopes have been found and described in detail. The most common structure of the cell is the Slayer. Other structures of the old cell walls are pseudomorin, monocondorotin, glutamine, glycogen, glycoprotein, and protein. They are sometimes associated with proteins and other protein complexes such as the stable or the bronze protease. Recent advances in electron microscopy have also demonstrated the presence of an extracellular membrane (most) within several archival groups, similar to the negative cell wall Gram in bacteria. Each structure of a new cell wall that can be explored in detail and assigned a specific function helps us to understand what the earliest cells on earth looked like [27].

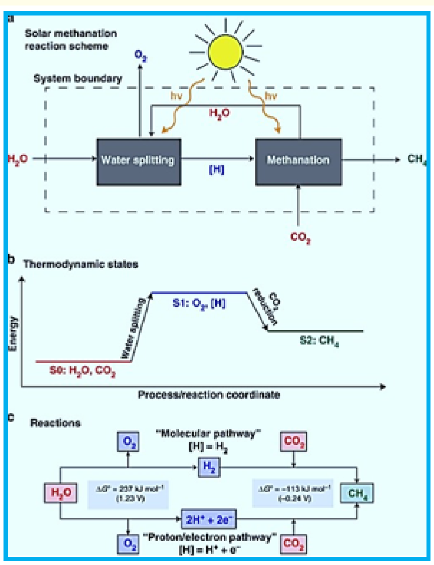


Fig. Graphical representation of solar methanation reaction schemes and energetics. **a** In a first reaction step, water is split into reducing equivalents [H] and O_2. [H] can be molecular H_2 or a H^+/e^- pair. If [H] is molecular H_2, then CO_2 is reduced to CH_4 via the "molecular pathway". If [H] is a H^+/e^- pair, then CO_2 is reduced to CH_4 via the "proton/electron pathway". **b** Graphical representation of the thermodynamic states of the solar methanation reaction. The energy level of the system is elevated from S0 to S1 during the water splitting step. Energy is released during CO_2 reduction, reaching the energy level of the products, S2. **c** Reactions occurring during the solar methanation pathways shown in **a**. The "molecular" pathway represents the state-of-the-art of industrial methanation, where H_2 is produced during water electrolysis, as discussed in the "State-of-the-art industrial CO_2 methanation" section credit ref [28]

Figure 8

Extraction and burning of fossil natural gas, mainly composed of methane, produces Huge amounts of greenhouse gases contributing to climate change. However, approximately the result of recent research efforts, “solar methane” can be produced using the photo-catalytic Conversion of carbon dioxide and water to methane and oxygen.

$$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2 \quad \text{AG= -124 kJ/mol}$$

This approach can play an integral role in realizing a sustainable energy economy by closing down carbon Recycle and enables efficient storage and transport of intermittent solar energy The chemical bonds of methane molecules [28].

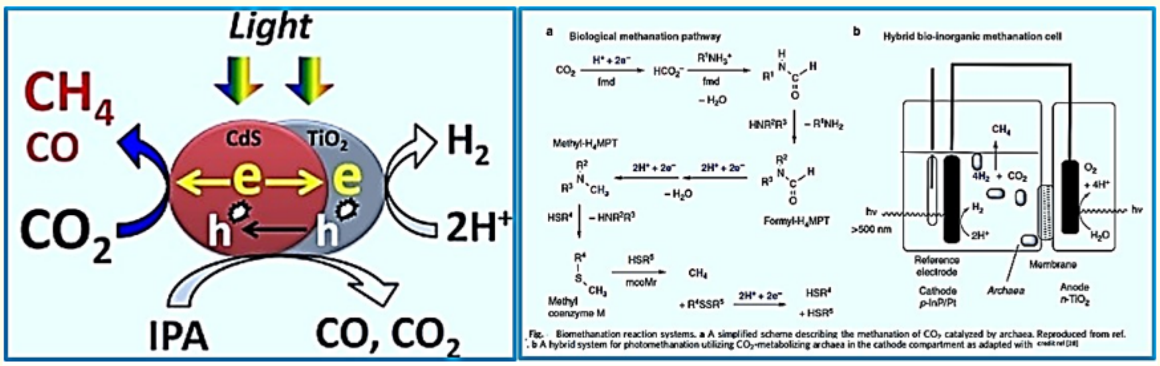


Figure 9

Climate change impacts on methane hydrate

Huge amounts of methane are stored worldwide on the seabed in the form of solid dies. These hydrates represent a great energy reserve for humanity. However, climate warming can cause water to stabilize. Methane, a strong greenhouse gas, will escape without the use of the atmosphere and can even accelerate.

rate climate change [29]. The Huge amounts of methane hydrate are buried in sediment deposits on the continental slopes. The total global amount of methane carbon accumulated in these hydrates is in the order of 1000 to 5000 Gt – i.e. 100 to 500 times more carbon than is released each year into the air by burning fossil fuels (coal, oil and gas). At low temperatures, methane dries on the sea. Formation of Carbon Dioxide (CO_2) by reaction with the oxygen (O_2) that is soluble in the water, is considerable. Another problem is that oxygen in seawater is used up through the formation of carbon dioxide.

There is no methane “ice” in the deepest oceanic regions, the areas with the highest pressures, because there is little methane there. The reason is that methane in the ocean is produced by seabed bacteria that dissolve organic matter that sinks from the sunlit area near the surface. Organic matter consists of, for example, the remains of dead seaweed and animals, as well as their feces. The most profound areas of the ocean are weak in living creatures, below about 2000 to 3000 meters, only a minimal amount of organisms reach the bottom because other organisms break most of them on their way through the water. As a rule of thumb, it due to only about 1 percent of the organic matter produced on the surface, in fact, ends in the deep sea. The deeper the seabed, the less organic matter settles on the bottom. Thus, methane hydrates die down inland, the same areas where continental plates meet deep-sea areas. Here there is enough organic matter that accumulates at the bottom and the combination of temperature and pressure is positive. In the coldest areas such as the Arctic, damp evenings occur on the shallow continental shelf (less than 200 meters from the depth of water) or on the frosted soil, the deep-frozen arctic soil that does not thaw even in summer.

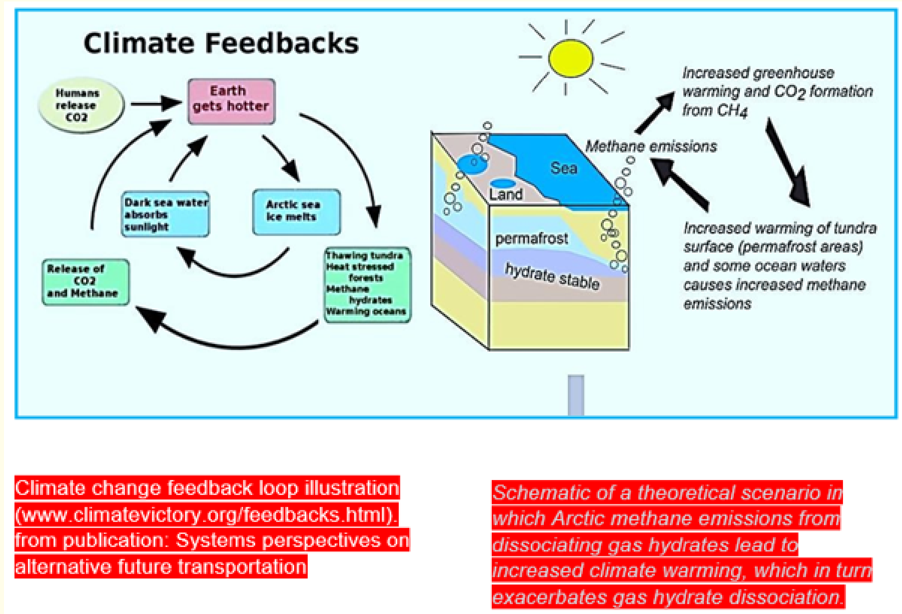


Figure 10

Estimates point out that there may be more potential fossil fuel in methane. hydrates than the classic coal, oil, and natural gas reservoirs. According to the mathematical model used, calculations of their abundance ranged from 100 to 530,000 gigatons of carbon. Looks like, values between 1000 and 5000 gigatonnes. That is about 100 to 500 times more carbon-like, which is released into the atmosphere each year by burning coal, oil and gas. Their possible future excavation is likely to produce only part of it as actual useful fuel, as many deposits are inaccessible, or production will be too expensive or will require too much effort.

However, India, Japan, Korea, and other countries are currently engaged in mining development.

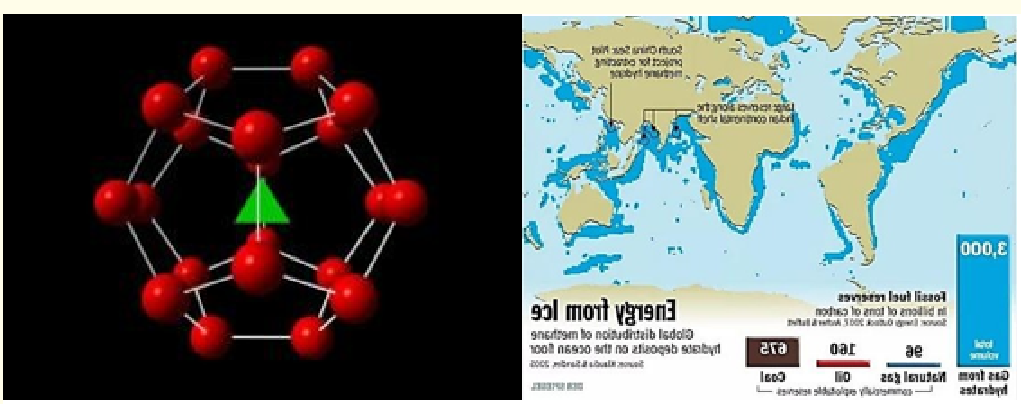


Figure 11: *Methane hydrate deposits around the world: Graphic Der Spiegel.*

Techniques to be able to use methane hydrants as a future energy source.

During the limited operating period in the first winter of 2007, we placed the electric submersible pump below the puncture interval and depressed us by lowering the water level down the cistern by injecting production water into the injection layer below. As a result, gas production at the pressure of the bottom hole of about 8 MPa was confirmed, which was higher than expected (initial formation pressure was about 11.4 MPa) and then the production of 830m^3 of gas during the depression period was observed for about 12.5 hours after being pressurized to 7.2 MPa.

However, because a large volume of stream sand to the bottom hole was much earlier than expected and the pump did not malfunction, we had no other choice to stop the test 60 hours after it started [30].

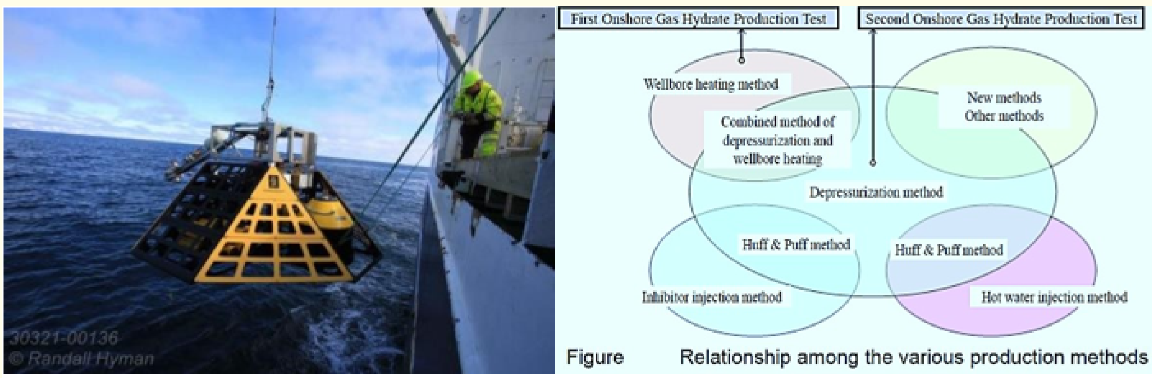


Figure 12

Landing of the seabed

Scientists and others were already on deck with hard hats and life jackets gently rocking the 1.6-ton unit with a cargo lever. After years of preparation, the pyramidal lander rocked over the Cobalt Sea, connected to a detachable launch module equipped with a video cameras. The on-land high-tech instrument roster read like a Christmas toy list for oceanographers, with half a ton of lithium batteries included to run the package for a full year. In addition to three separate sensors for measuring methane, carbon dioxide and pH (acidity), the carrier also carries a gas bubble monitor and sonar, a fluorescence meter for detecting algal blooms and a Doppler instrument for monitoring ocean currents.

Within minutes, the group lowered the landing to the sea. As the cable began to twist, Linke hung up his safety gear and rushed to the instrument room to flip the video feed from the landfill removable launch frame. Inside an array of computer screens, a grainy blue scene appeared as the craft descended 240 feet (787 feet) toward the seabed.

Scientists and engineers were anxiously gathering in the dark room to watch, with only silent murmurs and beats of the ship's engines filling the silence. It felt like the Apollo moon landing. Suddenly the seabed appeared and the cable seemed to stop completely. As the ship turned slowly toward the pre-designated landing site, rocks occasionally appeared and a shark swayed by.

Then the moment of truth: bubbles. As expected, methane seepage was abundant here, but the challenge was to place the lander between them, not on them, where best observations could be made. The CAGE sailing leader sat nervously beside Linke. When the critical moment came he gave her the honor of releasing the lander. At the touch of a button on the computer key, the video image was handled wildly as remote explosives fired the launcher over its freight charge and allowed the lander to sit down.

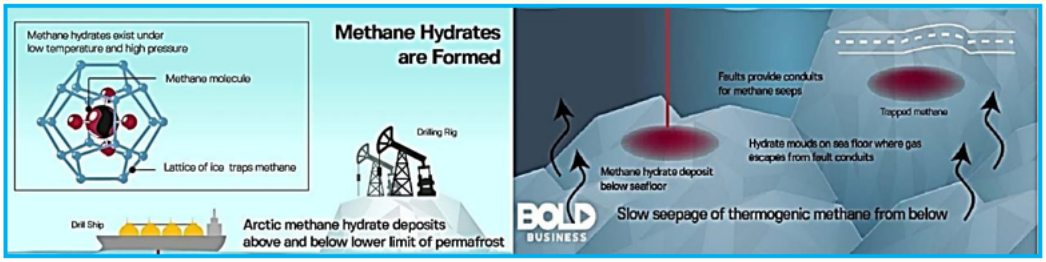


Figure 13: *The natural environment for water is a combination of low temperatures and high pressure. The hydrates are melted by raising the temperature or lowering the pressure. However, extraction by heating water is more expensive than the last option. In turn, the MH21 project opted for pressurized pressure using a submersible pump to drain sediment-separating*

Applause and handshakes filled the room, but the celebration was brief. The lander will be returned a year later for data download and analysis. For now, the team has turned its attention to a few days of water sampling using a cluster of containers affixed to a round steel carousel known as a rosette. At each measuring station on our map, the crew lowered the rosette slightly above the seafloor and then began paving it back in, snatching open ants on consecutive containers to fill them at specific depths.

Over the next 96 hours, with a brief hiatus for launching the second lander, scientists gathered around the roses every hour after being aboard 65 separate stations, draining containers for dozens of glass vials for each experiment. They worked continuously on rotating shifts, catching the sleep they could.

Over the weekend, exhausted and bleary-eyed. Scientists documented some clear examples of the carbon dioxide levels that mysteriously fell over methane seepage, just as he had the year before. Whether or not methane permeates proves to be greenhouse gas-soaked, the bigger issue remains in their cousins, methane hydrates. If the warmer days cause the water to start to decompose and release gas, then what? Towards the end of the cruise, other researchers mentioned new research into this "GEOMAR" has a project we call SUGAR because, like CAGE's name, sugar is similar to the structure of the gas hydrate molecule," Linke told me. "The idea is to replace methane with hydrogen dioxide to harvest methane as energy, and on the other hand get rid of carbon dioxide, which is also a threat".

Not only does the "SUGAR" process restore harmful carbon dioxide and methane diameters to energy, it also leaves a compound that is more stable and more heat- tolerant than methane hydrate. GEOMAR's patented process is a scientific hand-held operation at specific pressure and temperature, magically substituting carbon dioxide for methane in its "tiny" hydrate cage. The project is currently being tested in the Black Sea, where large quantities of methane are present. If "SUGAR" works there, hydrates could sweeten lives for countries around the world.

On our last day, the crew treated a bit of tourism in the Russian ghost town, which lies deep within the fjord. It was a perfect conclusion to our trip. Abandoned coal mining village and a reminder that although there is plenty of coal, gas and oil in the Arctic, one of them is difficult to harvest.

Conclusion

The Clathrates of methane hydrate is one of the most abundant materials that may support the growing demands for carbon-based energy sources for decades and centuries. Since they are located on the ocean floor, current technology for mining and exploitation of these vast deposits is minimal. However, technology for underwater mining is in its advent. The vast amounts of methane are stored worldwide on the seabed in the form of solid deposits. These hydrates represent a great energy reserve for humanity. However, climate warming can cause water to destabilize. Methane, a powerful greenhouse gas, will escape without the use of the atmosphere and may even accelerate climate change.

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